

# リグニン討論会

第1回—第57回

発表題名、著者、キーワード、要約

## Lignin Symposium

1st (1956) – 57th (2012)

Title, author, and keywords or abstract

2013.02.07 改訂版

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## はじめに

リグニン討論会は1956年に発足しました。事務局も会長もなく、毎年世話人が交替しながら、この討論会が半世紀以上も続いて開催されてきたのは実に希有なことです。これはリグニンが、人々の科学的探究心を常に奮い立たせる魅力的な未踏峰の如き物質であるからでしょう。曾て世界のリグニン研究をリードしてきた欧米諸国の拠点の多くでは、近年の「すぐ目に見える研究成果」を求める風潮のなか、次第にその活動は寂れてきています。一方、日本では、毎年若い優秀な研究者がこの分野に参入し、厚い研究者層を形成して、樹木・木材科学分野で世界の研究をリードしつつあります。半世紀以上にわたるリグニン討論会の活動が、このことに大きく貢献していることは疑いのないことです。

高等植物は、リグニンの形成によってその大型化が可能となり、多様な進化を遂げました。そのため、リグニンおよびリグニン由来の腐植物質等は地球上最多の有機物となり、炭素循環の大きなプールとして、生態系の変遷に深く関わっています。したがって、リグニンに関する知見は、樹木や作物の生産・利用のみならず、人類生存圏の理解にとっても重要であります。しかしその化学構造さえも、天然有機化合物中最も複雑・多様であるため、未だ完全には解明されていません。いろいろな意味で未踏峰の連なる山脈のような未解明物質リグニンは、種々の異なる視点から異なる手法で見た断面の知見を総合することで、始めてその全貌を捉え得るものでしょう。そのため、リグニン討論会は、紙パルプ技術協会、高分子学会、繊維学会、日本化学会、日本農芸化学会、日本木材学会の共催となっており、異なる分野の研究者たちが、自由な討論を通してリグニンの全貌への理解を深めることを目指しています。このため、たとえ未完成の研究であっても、新しい着想や手法・技術、実験結果についての自由な討論が歓迎され、特定の学会の年次大会とは異なる性格を持っています。

リグニン討論会の講演要旨集には、その研究の最初の着想やデータが載ります。その後論文として発表されないものもあるので、貴重な文献です。審査済みの論文でなくとも、あるいは古い着想やデータでも、それがヒントになって優れた研究が触発されることは多々あります。この分野に新しく参入される研究者には、過去の講演要旨集を通覧することによって、リグニン研究の内容や手法の進歩・変遷を知り、巨大なリグニン山脈に立ち向かうための新しい戦略的発想の手掛りを得る「温故知新」の効果が期待できるかも知れません。しかしリグニン討論会には公式の記録を残す事務局もなく、半世紀余の間には研究者の世代交代も進んで、古い講演要旨集は散逸しようとしています。そこで第1回討論会以来の全講演要旨集の原本を整備し、下記の研究拠点で保存公開することになりました。

★紙パルプ技術協会

★東京大学大学院農学生命科学研究科木材化学研究室(問合せ先、松本雄二)

★名古屋大学大学院生命農学研究科森林化学研究室(問合せ先、福島和彦)

★京都大学生存圏研究所(問合せ先、梅沢俊明)

そして約2000件を超える研究発表内容の検索を容易にするため、和文と英文とで発表題目、研究者名と所属を記録し、キーワードを本文内容から選定し、デジタル記録として整理しました。第35回討論会以降の要旨についてはキーワードの代わりに Abstract を記載しました。ただし重要なキーワードでも表題中に含まれる場合は、二重記録を避けるため省略してあります。各発表番号の最初の4桁は発表年次を、次の3桁は要旨集記載の発表番号を示しています。またリグニン討論会発足の経緯と変遷を知るための参考資料として、討論会発足の頃から深く関与して来られた3名の方々の特別寄稿を載せました。今後のリグニン研究のための参考資料として利用されることを期待しています。

この記録を整理するに当たっては、なるべく原著者を含む多くの方々にお願ひし、点検・修正をして頂きました。貴重な時間を割いてご協力下さいました皆様に厚くお礼を申し上げます。なお、英文の表題、氏名、所属の誤訳・誤読、キーワードの選定などの責任はすべて編集世話人にあります。これらの記録は、原講演要旨集の検索の目的以外には、転用なさらぬ様にお願ひします。さらに、誤字、脱字、その他修正を要する点などお気付きのときは、世話人宛お知らせ下さい。適時に修正版を下記の URL よりお配りして、正しい記録を皆様と共有したいと思います。

[http://www.agr.nagoya-u.ac.jp/~lignin/Lignin\\_Symposium\\_1-57.pdf](http://www.agr.nagoya-u.ac.jp/~lignin/Lignin_Symposium_1-57.pdf)

編集世話人、名古屋大学名誉教授 寺島 典二  
(Tel/Fax: 052-782-0981, e-mail: norteras@quartz.ocn.ne.jp)

| リグニン(化学)討論会 開催記録 |                  |                   |      |          |      |                  |
|------------------|------------------|-------------------|------|----------|------|------------------|
| 回                | 日時               | 開催地               | 講演   | ポスター     | 特別講演 | 備考               |
| 1                | 1956.11.12       | 大阪、府立教育会館         | 16   |          | 0    |                  |
| 2                | 1957.11.15       | 東京、紙パルプ会館         | 20   |          | 0    |                  |
| 3                | 1958.11.04       | 福岡、九州大学農学部        | 15   |          | 0    |                  |
| 4                | 1959.11.13-14    | 京都、楽友会館           | 29   |          | 0    | 会期が2日間となる。       |
| 5                | 1960.11.19-20    | 名古屋、商工会議所         | 21   |          | 0    |                  |
| 6                | 1961.11.18-19    | 大阪、府立農林会館         | 18   |          | 0    |                  |
| 7                | 1962.10.04-05    | 札幌、北海道大学クラーク会館    | 22   |          | 0    |                  |
| 8                | 1963.11.05-06    | 松江、自治会館           | 20   |          | 0    |                  |
| 9                | 1964.11.11-12    | 東京、紙パルプ会館         | 21   |          | 0    |                  |
| 10               | 1965.11.08-09    | 大阪、科学技術センター       | 31   |          | 0    |                  |
| 11               | 1966.10.31-11.01 | 広島、広島学会館          | 38   |          | 0    |                  |
| 12               | 1967.11.01-02    | 福岡、九州大学農学部        | 26   |          | 0    |                  |
| 13               | 1968.10.26-27    | 名古屋、名古屋大学農学部      | 27   |          | 0    |                  |
| 14               | 1969.10.28-29    | 東京、日本化学会講堂        | 20   |          | 0    |                  |
| 15               | 1970.10.08-09    | 札幌、市民会館           | 25   |          | 0    |                  |
| 16               | 1971.11.04-05    | 高松、電気ビル           | 34   |          | 0    |                  |
| 17               | 1972.11.04-05    | 京都、京都大学農学部        | 19   |          | 1    |                  |
| 18               | 1973.11.03-04    | 福岡、九州大学農学部        | 35   |          | 0    |                  |
| 19               | 1974.10.19-20    | 秋田、秋他大学教育学部       | 30   |          | 1    |                  |
| 20               | 1975.10.20-21    | 名古屋、名古屋大学農学部      | 34   |          | 2    |                  |
| 21               | 1976.10.18-19    | 東京、東京大学農学部        | 28   | 1+総合討論   |      |                  |
| 22               | 1977.10.08-09    | 札幌、北海道大学農学部       | 28   | 1+総合討論 2 |      |                  |
| 23               | 1978.11.01-02    | 松山、愛媛大学農学部        | 34   |          | 1    |                  |
| 24               | 1979.11.01-02    | 京都、生産開発科学研究所      | 30   |          | 2    |                  |
| 25               | 1980.10.17-18    | 福岡、九州大学農学部        | 32   | 1+総合討論   |      |                  |
| 26               | 1981.10.29-30    | つくば、工業技術院筑波研究センター | 32   |          | 2    |                  |
| 27               | 1982.10.21-22    | 名古屋、名古屋大学農学部      | 33   |          | 2    |                  |
| 28               | 1983.10.07-08    | 札幌、北海道大学農学部       | 30   |          | 1    |                  |
| 29               | 1984.10.15-16    | 東京、東京大学農学部        | 30   |          | 2    | リグニン討論会に改称。      |
| 30               | 1985.11.06-07    | 高知、高知会館           | 34   |          | 2    |                  |
| 31               | 1986.10.21-22    | 京都、京大会館           | 35   |          | 2    |                  |
| 32               | 1987.10.20-21    | 福岡、福岡リーセントホテル     | 36   |          | 2    |                  |
| 33               | 1988.11.08-09    | つくば、ホテルサンルート筑波    | 36   |          | 1    |                  |
| 34               | 1989.10.16-17    | 名古屋、名古屋大学農学部      | 37   |          | 2    |                  |
| 35               | 1990.10.15-16    | 東京、東京大学山上会館       | 36   |          | 1    | 英文 Abstract を記載。 |
| 36               | 1991.10.14-15    | 札幌、北海道大学学術交流会館    | 42   |          | 2    |                  |
| 37               | 1992.10.19-20    | 京都、京大会館           | 41   |          | 0    |                  |
| 38               | 1993.11.15-16    | 高松、四国電力 KK 総合研究所  | 39   |          | 2    |                  |
| 39               | 1994.10.12-13    | 福岡、福岡リーセントホテル     | 25   | 23       | 1    | ポスター発表を開始。       |
| 40               | 1995.10.12-13    | つくば、研究交流センター      | 26   | 18       | 1    |                  |
| 41               | 1996.10.03-04    | 名古屋、名古屋大学農学部      | 32   | 17       | 1    |                  |
| 42               | 1997.10.27-28    | 札幌、北海道大学学術交流会館    | 33   | 23       | 1    |                  |
| 43               | 1998.10.26-27    | 府中、府中グリーンプラザ      | 25   | 17       | 2    |                  |
| 44               | 1999.10.07-08    | 岐阜、岐阜大学農学部        | 29   | 19       | 2    |                  |
| 45               | 2000.10.26-27    | 松山、愛媛大学農学部        | 34   | 20       | 2    |                  |
| 46               | 2001.11.01-02    | 宇治、京都大学木質科学研究所    | 41   | 24       | 3    |                  |
| 47               | 2002.10.31-11.01 | 福岡、アクロス福岡国際会議場    | 34   | 17       | 2    |                  |
| 48               | 2003.10.30-31    | 福井、福井工業大学芦原学舎     | 35   | 27       | 2    |                  |
| 49               | 2004.11.18-19    | つくば、筑波大学          | 27   | 17       | 1    |                  |
| 50               | 2005.10.19-20    | 名古屋、名古屋大学野依学術交流館  | 20   | 13       | 1    |                  |
| 小計               |                  |                   | 1475 | 235      | 50   | 総計 1760          |

| リグニン(化学)討論会 開催記録 |               |                        |      |      |      |         |
|------------------|---------------|------------------------|------|------|------|---------|
| 回                | 日時            | 開催地                    | 講演   | ポスター | 特別講演 | 備考      |
| 51               | 2006.10.26-27 | 北海道大学、学術交流館            | 27   | 30   | 2    |         |
| 52               | 2007.11.14-15 | 宇都宮大学、大学会館             | 33   | 22   | 2    |         |
| 53               | 2008.10.30-31 | 東京大学、弥生講堂              | 28   | 19   | 1    |         |
| 54               | 2009.10.29-30 | 静岡県男女共同参画センター「あざれあ」    | 28   | 24   | 1    |         |
| 55               | 2010.10.20-21 | 京都大学、百周年時計台記念館 国際交流ホール | 30   | 20   | 1    |         |
| 56               | 2011.09.15-16 | 山形大学農学部                | 28   | 19   | 1    |         |
| 57               | 2012.10.17-18 | 福岡、アクロス福岡国際会議場         | 24   | 12   | 1    |         |
| 総計               |               |                        | 1673 | 381  | 59   | 総計 2113 |

「リグニン討論会の発足の頃」

九州大学名誉教授 千手諒一

リグニン討論会も今年で39回を迎えると言う。「10年ひと昔」と言います。40年も前のことを思い出すのは、82歳の翁には難儀なことです。かすかな記憶を頼りにペンをとってはみましたが、思い違いはお許し願います。

リグニン討論会の第一回目(昭和31年)は阪大工学部の八浜義和先生(故人)のお声がかかりで聞かれました。当時は日本も、経済発展の真只中でありました。大東亜戦争で、エネルギーの総てを使い果たした日本も、ようやく復興の波に乗り、朝鮮事変も重なって、復興景気に湧き立っておりました。3P景気、3白景気(紙、砂糖、硫安)と騒がれた時代です。製紙工場も増設また増設、勿論SP法ですから、蒸解廃液は垂れ流しです。公害問題は、早速田子の浦の汚染で始まりました。紙パルプ産業は四面楚歌で、私どもは肩身の狭い思いをしたものです。当時私は、九大の木材研究所で、キチン、キトサンの研究からSP廃液中のリグニンスルホン酸のコロイド滴定を始めておりました。それがご縁で、八浜先生に親しくして頂きましたが、先生は木材化学工業に深い関心を持っておられました。ある時私に、「紙パルプ工業も木材の大半を流失するようでは、真の化学工業とは言えせんね」と言われました。農学部の子学生時代から、工学部の応化にコンプレックスを感じていた私には、胸に突き刺さるひと言でした。私は廃液リグニンの利用を中心とした研究を進めて、木材の完全利用と共に、SP廃液による公害を防止せねばと思いました。早速、八浜先生を初め東大の右田信彦先生(故人)、国策パルプの三川礼氏(後に阪大工学部教授)や佐藤孝一郎氏、九大木研の北浦貞夫先生(故人)、にお願いして、初回は阪大工学部で開くことになりました。初めの頃は、発表件数も少ないので、リグニンに関する事なら何んでもよいと言うことで、パルプ蒸解のことまで発表されましたが、それでも数件で寂しいものでした。しかし回を重ねるにつれて参加者も段々増えて来ました。大学関係のみならず、工試(東京、大阪)の方々まで参加され、討論会も一段と活発になってきました。私なんか、わざわざあるマイクも使わずに口角泡を飛ばしたものです。中野さん(東大)、越島さん(大阪工試から京大木研)、林さん(立命館大)、猪狩さん(東京工書式)などなど、懐かしいご仁が大勢でした。この討論会の魅力はなんと言ってもその会の雰囲気でした。参加者全員が、恰も一家族のように、心おきなく語りあえる。その喜びは他の学会では到底味あうことのできない大きな魅力でした。メンバーの各人は、年一回のこの討論会を楽しみに、日々研究に励んでいたように思います。リグニン討論会が、39回を数える今日もなお、旧に倍して盛大であるのも、一因がその辺にあるのかもしれませんが。しかし時は流れて、パルプの製造法もKP法に変わりました。廃液リグニンは、公害の元になる廃物ではありません。燃料として立派に利用されておりますから、パルプ工業も真の化学工業と言える時代になりました。リグニンの利用研究も、そろそろ看板を下してもよい頃かと思っておりましたが、今回のプログラムを拝見して安堵致しました。これからはリグニンの生化学を中心に、リグニンの本質を明らかにしたいものです。リグニンのない木材などは無理だとしても、丸太の木材をそのままシートに変えることができれば最高ですね。ナインティ(90)、ナインティ(90)、ナイン(9)の収量、白色度、強度を目標とするリグニンのメカノケミカルの研究も進められている由、私は大きな期待を寄せております。リグニン討論会の進路も、時の流れと共に、大きく変わりつつあることをこの上なく嬉しく思います。皆さんの御研鏡を祈ります。

「リグニン討論会の黎明」

京都大学名誉教授 越島哲夫

寺島先生の、本当に先生らしい純粋なご提案に賛同しながら、この討論会はそもそも誰が、どんな経緯で始めたのかを、先ず知りたいと思って、私なりに努力してみました。当時私は、京大木材研究所の助手をしており、大凡のことは解っているつもりでしたが、調べてみると、かなり誤っていたようです。

第1回の討論会は、皆さんもご承知の様に、阪大、八浜義和先生のところでした。八浜先生が日本化学会に要望書を出して“リグニン化学討論会”が発足したのには千手諒一先生(当時九大生産科学研究所助教授)と八浜先生の出会いが一つのきっかけになった(坂田功氏)ようです。もう一人、設立に当って外せない人は、当時、国策パルプ(株)農林科学研究所の三川礼先生(のちに阪大教授)です。三川先生もその頃、八浜先生に討論会をつくることを強く要望されていたのではないかというのが私や林アキラさん(のちに立命館大教授)の推測です。その結果、八浜(阪大)、西田(九大)、右田(東大)、館(京大)先生が発起人となり、リグニン化学討論会がスタートしたようです。第1回討論会の開催には当時阪大助教授だった京極先生が奔走され、16件の発表がありました。この時、企業からは国策パルプのみで、3件の発表があったのも、三川先生のリグニン化学への情熱が現れていたようにおもえます。第1回では、当時、大御所といわれた、八浜、右田、館、北浦、大野(一月)各先生のほか、近藤(民)、千手、三川、軒原、佐藤(孝)、石川、中野、榊原、本田(真)、京極など錚々たる名前がならんでいます。第2回は東大において右田-中野先生で、第3回は九大、第4回は京大で行われました。九大では、北浦-千手先生で実施され、千手先生が世話人として大変努力された(坂田功氏)と聞いています。京大では、林アキラさんが世話人を任せられ、この時始めて企業からの参加を呼びかけ、寄付も募った結果、発表数が増えたので会期を二日間とした(林アキラ氏)ようです。同時に懇親会も加え学生は無料としたのも第4回からでした。第2回の、東大での討論会には私、欠席したので詳しい情報は私の所になく、寺島先生から補足して頂ければ幸いです。何れにしろ創世期のころは大学を代表する大先生のほかに、実際の運営に当った世話人各位の情熱と努力がこの討論会の維持と発展の大いなる原動力となったことは記録されるべきでありましょう。

ここで私は、あまり知られていないと思われるので、もう一度三川先生について触れておきたい。先生は国策パルプ時代、昭和26-31年にかけて、当時有名であった三川理論を展開された。それは、X基、Z基、B基となづけられた、リグニンの反応性の異なる官能基がサルファイト蒸解やクラフト蒸解でどのように挙動するか、そして脱リグニンが進行するかを示したもので、当時としては理路整然として真に興味深いものでした。私は後になってリグニンの話を直接お聞きするため三川先生を阪大にお訪ねしたことがあります。その頃“基礎木材工学”なる学生向け冊子を当時近畿大学で講義をもっていた5名の共著として執筆中であって、初版は昭和48年に出版されました。従って三川先生にお会いしたのが45-47年の間だと思います。既にその時、八浜先生の後任として阪大にきておられ、リグニン研究から離れて半導体をご研究中ということでしたが、実に懐かしそうにリグニンの話をされました。自らを誇るでなく、また惜しむ様子もなく一人の研究者として淡々と話された雰囲気がとても印象的でした。ただ繰り返し話された言葉は“リグニンは別れた女房のようなものだ。懐かしくもあり忘れ難い”と。東大理学部化学科卒の、いかにも秀才らしい、しかもえらぶった所のない紳士の面影が、育ちの良さともいえるのでしょうか、その柔和さと共に私にとって忘れられないリグニン化学者の一人です。

黎明期を便宜上昭和30年代と位置づけると、私自身にとっても一つの転換期でした。恩師のお勧めを無げに断って大学を去り、通産省(当時)の工業試験所(いまの産総研)へ移ったのが昭和37年で、その主たる理由が十分な研究費を使って研究室をもちたいということでした。若気の至りとい

う所でしたが、さて試験所で何をしたかということになると、これがリグニンのグラフト重合でした。時、恰も高分子全盛時代であって京大、阪大、阪市大などの工学系では物凄いブームで、高分子化学が跋扈した世の中でした。その時、工業技術院でも放射線の平和利用のための予算がつき、高分子センターになっていた大工試にガンマ線照射室が設けられることになった訳です。予算がついたから成果を出せという話になって、リグニンを基体とするグラフト重合を行うことを決めた訳です。今にして思えば、よくまあ、やったものだという感じがします。しかし、ガンマ線を使ったリグニンのグラフト重合は一つのアイデアだったかもしれないと今ではおもうのです。何故なら、リグニンは放射線に比較的強いからです。ただし、グラフトポリマーの物性に関する知識に乏しかったのが世に出なかった最大の理由だったと思います。放射線照射研究の場合、そのものが持つ $G_R$  値、すなわち吸収エネルギー100e.V.当り生成するラジカル数が大きい意味をもちます。例えばメタクリル酸メチルはこの値が6.3、スチレンが0.66、つまり芳香核など共鳴構造を多く持つものは放射線に強いこととなります。この点から類推するとリグニンはかなり放射線に強くすぐに崩壊するセルロースとは対照的です。この特性を利用しリグニン-スチレングラフトポリマーをつくり、特性を調べると耐磨耗性は高く、半導体的性質も併せ持つことがわかりました。用いたリグニンは淡黄色の塩酸リグニンで研究用としては木粉から容易に製造できましたが、企業用原料としては当時適当とは言えず、また、放射線を使うことは設備、その他で制限を受けることとなります。それでリグニン原料としては後述するようにパルプ廃液から得られるリグノスルホン酸がよく、レドックス開始グラフト重合が有望であることがわかりました。塩酸リグニンを用いるグラフト研究は昭和37-39年に行ったもので、リグノスルホン酸をベースにしたメタクリル酸メチルのグラフト研究は私が京大に移った為中断したのがいささか残念ではありました。昭和39-41年初頭まではシラキユウスのニューヨーク州立大学で働き、帰国後はリグニンとヘミセルロースの結合体、所謂LCCの研究に移りましたので、リグニンへのグラフト研究は終了しました。リグノスルホン酸にメタクリル酸メチルあるいはアクリロニトリルをレドックス系、例えば過酸化水素-第1鉄塩を開始剤としてグラフト重合させる反応は、前者は室温付近で、後者は零度でも進行する大変面白い反応なのでグラフトポリマーの物性を含めて、関心のある方は是非試してみる価値があると思っています。リグニン化学討論会は、後に化学系だけでなく生物系の研究者も加わってもらうため、東大での幹事会の際中野先生らと話しあって“化学”を取り去り今のようにしたことを覚えています。このサロニックな集いが今後とも発展の原動力として存続することを願っています。

「第50回リグニン討論会を迎えて」

京都大学名誉教授(京都大学木質科学研究所)樋口隆昌

第50回リグニン討論会を迎えるにあたり、これまで、私達のグループが岐阜大学、京都大学で進めてきた、リグニンの生合成と微生物分解研究の流れと将来への展望に就いて簡単にまとめてみました。

私は1950年4月、岐阜大学農学部林学科木材化学講座(川村一次教授)の助手に採用されてから一貫してリグニンの生化学的研究を続けてきました。当時、欧米(Heidelberg, Prof. K. Freudenberg; Göteborg, Prof. E. Adler; Stockholm, Prof. H. Erdtman, Prof. E. Hägglund; Wien, Prof. K. Kratzl; Wisconsin, Prof. F.E. Brauns; New York, Prof. F.F. Nord; Toronto, Prof. H. Hibbert 等)では理学部、工学部関係の研究者が、主としてリグニンの化学構造、木材のパルプ蒸解と関連したリグニンの化学反応機構、リグニンの化学分解反応(ニトロベンゼン酸化、過マンガン酸酸化、エタノリシス、アシドリシス等)が研究されていました。更に1956年、A. Björkman によって milled wood lignin が調製され、リグニンの IR, UV スペクトル、分子量、上記した分解反応と分解生成物の解明が急速に進展しました。

しかし、リグニンは、タンパク質、セルロース、デンプンなど加水分解によって定量的に構成モノマーに分解される生体高分子と異なり、上記代表的な分解法でも分解生成物の収量は 10-40%で、分解法によるリグニン化学構造の解明は不可能な特異な高分子である事が次第に明らかになってきました。

当時、我が国では、主としてリグニン研究に携わっておられた右田伸彦教授(東大農学部)、西田屹二教授(九大農学部)、館勇教授(京大農学部)、八浜義和教授(阪大工学部)の諸先生による協議の結果、第1回リグニン化学討論会が発足しました。その後、次第にリグニン研究の内要と分野が広くなり、現在のリグニン討論会に至っている。

私のリグニン研究は、そのような時期に始まりました。私は名大理学部生物学科(植物)の出身で、有機化合物の合成、反応解明、構造決定などの経験に乏しく、植物生化学の手法でリグニンの生化学的研究ができればと思っていましたので、リグニンの生合成に就いて研究を始める事にしました。その頃、八浜義和、岡部次郎:リグニン化学の最近の進歩(I), (II). 化学の領域、南江堂、11, 1-12(1956), 12, 15-31 (1956)が出版され、Freudenberg の研究室で、マッシュルーム酵素によるコニフェリルアルコールの脱水素重合で生成した、オリゴリグノール(グアイアシルグリセロール- $\beta$ -コニフェリルエーテル、*d,l*-ピロレジノール、デヒドロジコニフェリルアルコール)と DHP の構造研究が詳細に紹介されました。

そこで手始めに Freudenberg の方法でマッシュルームのフェノールオキシダーゼを調製して酵素的性質を調べ、コニフェリルアルコールを脱水素重合させる酵素は CO 阻害を受けないラッカーゼ(*p*-ジフェノールオキシダーゼ)である事を突き止め、漆ラッカーゼとも比較した結果、樹木の木化(モノリグノールの脱水素重合)に関与する酵素は、ラッカーゼより、植物に一般的に分布しているペロキシダーゼである事を明らかにする事が出来ました。この結果(Biochemical studies of lignin formation (1), (2), (3). *Physiol. Plantarum* 10, 356, 621, 633 (1957); Further studies on phenol oxidase related to the lignin biosynthesis. *J. Biochem.* 45, 515 (1958) が Wien 大学の Prof. Kratzl の目にとまり、第4回国際生化学会(1958, Wien)で講演する機会を与えられたわけです。(T. Higuchi: Studies on the Biosynthesis of Lignin. pp161-188. Proc. 4<sup>th</sup> International Congress of Biochemistry 1958)

この学会で Prof. Freudenberg, Adler, Erdtman, Nord, Neish 等、それぞれの分野の代表的な研究者の研究発表と真剣な討論に接し、強い感銘を受けました。さらに学会後、ドイツ、スウェーデンで各先生の研究室を訪問し、研究の実体を知る事が出来たのが、私の将来の研究方向を決定したように思

います。

Dr. A.C. Neish (Prairie Regional Laboratory, Saskatoon, Canada) から同研究所の Dr. S. A. Brown がリグニンの生合成の研究を始めたので、一緒に研究をしませんかとお誘いをうけたのもこの学会でした。当時、岐阜大学ではアイソトープによるトレーサー実験は出来ませんでしたので、1960-62の2年間、Saskatoonの平原地方研究所に滞在し、 $^{14}\text{C}$ -ラベルしたリグニン前駆物質(グルコース、シキミ酸、フェニルアラニン、ケイヒ酸、 $\rho$ -クマール酸、カフェー酸、フェルラ酸、シナピン酸など)を小麦植物体に投与して24時間代謝させてから、ニトロベンゼン酸化生成物(バニリン、シリンガアルデヒド)、エタノリス生成物(ジケトン)の $^{14}\text{C}$ 活性を測定する方法で、モノリグノール生合成経路を解明していきました。その結果をとりまとめたのが、Dr. Brown と私によるモノリグノール生合成経路で、その後、内外の研究者によりモノリグノール生合成経路の基礎として引用されて来ています。

1968年、京都大学木材研究所に新設されたリグニン化学研究部門に招待され、島田幹夫(現京都大学名誉教授)、中坪文明(現京都大学教授)等の協力を得てリグニン生合成に関与する酵素(OMT等)の解明、オリゴリグノールの合成、リグニンの微生物分解反応機構の解明等に力を入れてきました。

最近の研究法、分析法の進歩、関与する酵素の細胞内分布などが解明され、上記のモノリグノール生合成経路にバイパスや、一部改定が加えられていますが、我々のモノリグノール生合成経路の基本は、保たれていると思っています。

私の定年退職の頃からモノリグノール形成に関与する酵素の遺伝子解明が進み、最近ではポプラ、テーダ松、*Zinnia*、*Arabidopsis* などによる細胞壁合成に関する遺伝子と、その発現機構の解明(T. Higuchi, Pathways for monolignol biosynthesis via metabolic grids: coniferyl aldehyde 5-hydroxylase, a possible key enzyme in angiosperm syringyl lignin biosynthesis. Proc. Jpn. Acad., 79, 227-236. Ser B (2003) が進みつつあり、将来は利用目的と生態系に適した樹木の生産が可能になるものと考えられ、私達の研究がここまで発展してきている事を大変嬉しく思っています。

さらに私等はリグニンの微生物分解機構に就いても研究を進め、白色腐朽菌が分泌するリグニンペロキシダーゼ、ラッカーゼによって、リグニン側鎖ばかりで無く芳香環も分解される機構を $^{13}\text{C}$ , D,  $^{18}\text{O}$ で標識したオリゴリグノール、DHPを基質として $\text{D}_2\text{O}$ ,  $^{18}\text{O}_2$ の存在下でリグニンペロキシダーゼ分解し、分解生成物の分析によってそれらの分解機構を明らかにする事が出来ました。この研究分野も現在遺伝子レベルの研究に移行していますので、将来、バイオパルピングや生態環境浄化に繋がっていくものと期待しています(T. Higuchi, Microbial degradation of lignin : Role of lignin peroxidase, manganese peroxidase, and laccase. Proc. Jpn. Acad., 80, 204-214. Ser B(2004).

以上、私達がこれまでやってきたリグニンの生化学的研究についての経過と感想を思い出すままに記述しました。第50回リグニン討論会に出席され、現在第一線でリグニンの研究に携わっておられる方々に少しでも参考になれば幸いです。今後、リグニン討論会のますますの発展を祈念しております。

## 第1回 (1956.11.12) 大阪、府立教育会館

1956-001

亜硫酸蒸解の速度を支配する因子について

坂田 功、千手諒一

九州大学大生産研究所

Factors controlling sulfite cooking rate.

Isao Sakata, Ryoichi Senju

Institute of Industrial Science, Kyusyu University

Keywords: lignin sulfonic acid, delignification, sulfonation, successive reaction

1956-002

亜硫酸蒸解におけるフェノール成分の挙動

中野準三

東京大学農学部

Behavior of phenolic components during sulfite cooking.

Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: Japanese red pine, *Pinus densiflora*, larch, *Larix Kaempferi*, pinosylvin, taxifolin, vanillyl alcohol, quercetin

1956-003

落葉樹のサルファイト蒸解について

軒原栄三

国策パルプ株式会社

Sulfite cooking of larch.

Eizo Nokihara

Kokusaku Pulp Co., Ltd.

Keywords: heartwood, sapwood, taxifolin,  $\epsilon$ -galactan

1956-004

クラフト蒸解機構

三川 礼

国策パルプ株式会社

Mechanism of kraft cooking.

Rei Mikawa

Kokusaku Pulp Co., Ltd.

Keywords: lignin, sodium sulfide, mercaptan, monosulfide, disulfide, X-group, Z-group, B-group

1956-005

リグノスルホン酸中の酸性基について(第一報)

佐藤孝一郎

国策パルプ株式会社

Acidic groups in lignosulfonic acid. I.

Koichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: sulfonic acid group, carboxylic acid group, guaiacyl-type, phenolic hydroxyl group, condensed phenolic hydroxyl group, X-group, Z-group, B-group

1956-006

リグノスルホン酸の鞣皮性と多分子性

京極与寿郎、八浜義和

大阪大学工学部

Tannability and multimolecularity of lignosulfonic acid.

Yojuro Kyogoku, Yoshikazu Hachihama

Faculty of Engineering, Osaka University

Keywords: degree of sulfonation, tannability, multimolecularity

1956-007

幼植物のリグニン形成について

石川久雄、高市克美、喜多川重樹、沖 妙

愛媛大学農学部

Formation of lignin in juvenile plant.

Hisao Ishikawa, Katumi Takaiti, Sigeki Kitagawa, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: shikimic acid, phenylalanine, tyrosine, coniferin, syringin, coniferyl alcohol, peroxidase, mung bean, *Robinia pseudoacacia*,

1956-008

植物体中におけるリグニンの形成機構

樋口隆昌、川村一次

岐阜大学農学部

Formation mechanism of lignin in plant.

Takayoshi Higuchi, Ichiji Kawamura

Faculty of Agriculture, Gifu University

Keywords: phenylalanine, coniferin,  $\beta$ -glucosidase, coniferyl alcohol, peroxidase, laccase

1956-009

リグニンの呈色機構に関する研究

右田伸彦、中野準三、平川公夫

東京大学農学部

On the mechanism of color reaction of lignin.

Nobuhiko Migita, Junzo Nakano, Kimio Hirakawa

Faculty of Agriculture, the University of Tokyo

Keywords: Mäule color reaction, Cross-Bevan color reaction, phloroglucinol-hydrochloric acid color reaction

1956-010

リグニンの呈色について

中村徳郎\*<sup>1</sup>、北浦貞男\*<sup>2</sup>

\*<sup>1</sup>興国人絹パルプ株式会社、\*<sup>2</sup>九州大学生産研究所

On the color reaction of lignin.

Tokurou Nakamura\*<sup>1</sup>, Sadao Kitaura\*<sup>2</sup>

\*<sup>1</sup>Koukoku Jinken Pulp Co. Ltd. \*<sup>2</sup> Institute of Industrial Science, Kyusyu University

Keywords: chromopholic group, coniferaldehyde, Schiff's reagent

1956-011

リグニンの水添分解に関する研究

榊原 彰、荒木 正

林業試験場

Hydrogenolysis of lignin.

Akira Sakakibara, Tadasu Araki

Forestry and Forest Product Research Institute

Keywords: hydrogenolysis, residual lignin from wood saccharification, sulfite spent liquor

1956-012

リグニンに関する研究(第3報)低スルホン化木紛のエタノリシスについて

石原達夫、近藤民雄

林業試験場

Studies on lignin. III. Ethanolysis of sulfonated wood meal.

Tatsuo Ishihara, Tamio Kondo

Forestry and Forest Product Research Institute

Keywords: ethanolysis, Hibbert's ketones, guaiacylglycerol, structure moiety A by Erdtman

1956-013

リグニンの分解に関する研究(第1報)ニトロベンゼン酸化生成物について

田中次郎、近藤民雄

林業試験場

Studies on degradation of lignin. I. Nitrobenzene oxidation products.

Jiro Tanaka, Tamio Kondo

Forestry and Forest Product Research Institute

Keywords: vanillin, paperchromatography, quantitative determination by UV absorption

1956-014

木材糖化リグニンの性状(続)

岡部次郎、八浜義和

大阪大学工学部

Properties of residual lignin from wood saccharification.

Jiro Okabe, Yoshikazu Hachihama

Department of Engineering, Osaka University

Keywords: nitrobenzene oxidation, Klason lignin, vanillin

1956-015

竹リグニンの研究

大野一月、三浦克己

大阪府立大学工学部

Studies on bamboo lignin.

Kazuki Ono, Katsumi Miura

Department of Engineering, Osaka Prefectural University

Keywords: nitrobenzene oxidation, paper chromatography, kraft cooking

1956-016

リグニン多糖類複合体とパルプ原木の近似組成の関係

本田真一

浜松商科短期大学

Similarity in composition between pulp wood and lignin-carbohydrate complex.

Shinichi Honda

Hamamatsu Commercial College

Keywords: hardwood, conifer, furfural, pentose

## 第 2 回 (1957.11.15) 東京、紙パルプ会館

1957-001

幼植物のリグニン形成について(第 8 報)

石川久雄、高市克美、沖 妙

愛媛大学農学部

Formation of lignin in juvenile plant. VIII.

Hisao Ishikawa, Katsumi Takaichi, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: aromatic amino acid, tannin, shikimic acid, phenylalanine, tyrosine

1957-002

コニフェリールアルコール重合に関与するフェノールオキシダーゼについて

樋口隆昌、川村一次、井藤佳美

岐阜大学農学部

On the phenol oxidase responsible for polymerization of coniferyl alcohol.

Takayoshi Higuchi, Ichiji Kawamura, Yosimi Ito

Faculty of Agriculture, Gifu University

Keywords: laccase, peroxidase, tyrosinase, dehydrogenative polymerization

1957-003

リグニンと炭水化物との化学結合に関する研究(第 5 報)小麦藁中におけるフェノールグルコサイド結合の存在について

林 暁、館 勇

京都大学農学部

Studies on the chemical linkages between lignin and carbohydrates. V. Presence of phenylglucoside bonds in wheat straw.

Akira Hayashi, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: acetylated xylolignin, dioxane lignin, UV spectra

1957-004

樹皮のリグニンについて

幡 克美、十河村男

香川大学農学部

On lignin in bark.

Katsumi Hata, Murao Sogo

Faculty of Agriculture, Kagawa University

Keywords: dioxane lignin, Willstätter lignin, nitrobenzene oxidation, *Pinus densiflora*,

1957-005

消石灰による S.P.廃液中の L.S.の沈澱について

北浦貞男、上野雄造

九州大学農学部

On the precipitation of liginosulfonic acid by calcium hydroxide from sulfite spent liquor.

Sadao Kitaura, Yuzo Ueno

Faculty of Agriculture, Kyusyu University

Keywords: carbohydrates, glucose, mannose, galactose, arabinose, xylose

1957-006

リグニンスルホン酸の沈降恒数の測定

京極与寿郎、八浜義和

大阪大学工学部

Determination of sedimentation coefficient of liginosulfonic acid.

Yoshiro Kyogoku, Yoshikazu Hachihama

Faculty of Engineering, Osaka university

Keywords: molecular weight, diffusion coefficient, sulfite spent liquor

1957-007

赤外線吸収スペクトルによるリグニンの研究

祖父江寛、福原節雄

東京大学工学部

Studies on lignin by infrared spectroscopy.

Hiroshi Sobue, Setsuo Fukuhara

Faculty of Engineering, the University of Tokyo

Keywords: Brauns' s native lignin, beech, *Picea jezoensis*, spruce, *Cryptomeria japonica*, holocellulose

1957-008

リグニンのベンジルアルコール性 OH 基の新反応と考えられるチオ尿素とリグニンとの反応について

三川 礼

国策パルプ株式会社

Reaction of lignin with thiourea - A new reaction of benzyl alcoholic hydroxyl group in lignin.

Rei Mikawa

Kokusaku Pulp Co., Ltd.

Keywords: lignin, thiourea, benzyl alcoholic hydroxyl group, X-group, Z-group

1957-009

リグニンモデル化合物の硫化に関する研究

石原達夫、近藤民雄

林業試験場

Studies on the reaction of lignin model compounds with hydrogen sulfide.

Tatsuo Ishihara, Tamio Kondo

Forestry and Forest Product Research Institute

Keywords: hydrogen sulfide, benzyl alcohol, benzyl ether, thioxane

1957-010

ベンジルグループの hydrogenolysis

右田伸彦、中野準三、石津 敦

東京大学農学部

Hydrogenolysis of benzyl group.

Nobuhiko Migita, Junzo Nakano, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: benzyl alcohol, benzyl ether, aromatic hydroxyl group, methanol lignin

1957-011

リグニンの臭素化について

北浦貞男、中村徳郎

九州大学農学部

On the bromination of lignin.

Sadao Kitaura, Tokurou Nakamura

Faculty of Agriculture, Kyusyu University

Keywords: *Abies sachaliensis*, substitution reaction, lignin model compounds, native lignin

1957-012

パルプ漂白の際のリグニンの挙動について

佐藤孝一郎、海老沢きよ

国策パルプ株式会社

Behavior of lignin during bleaching of pulp.

Koichiro Sato, Kiyo Ebisawa

Kokusaku Pulp Co., Ltd.

Keywords: bleaching, chlorination, liginosulfonic acid, hydrochloric acid lignin, thiolignin, carbonyl group

1957-013

ハドロトロピック塩による脱リグニン

右田伸彦、中野準三

東京大学農学部

Delignification by hydrotropic salt.

Nobuhiko Migita, Junzo Nakano, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: beech, sodium xylenesulfonate, semichemical pulp, dissolving kraft pulp, kraft pulp

1957-014

ハドロトロピックリグニンの酸化

万木 正、鈴木英吉

繊維工業試験所

Oxidation of hydrotropic lignin.

Tadashi Yurugi, Eikichi Suzuki

Institute of Fiber Science and Technology

Keywords: beech, nitrobenzene oxidation, guaiacyl group, syringyl group.

1957-015

広葉樹リグニンのニトロベンゼン酸化生成物

田中次郎、近藤民雄

林業試験場

Nitrobenzene oxidation products from hardwood lignin.

Jiro Tanaka, Tamio Kondo

Forestry and Forest Product Research Institute

Keywords: beech, condensed structure, dehydrodivanillin

1957-016

リグニンの水素添加分解物の硝酸酸化

岡部次郎<sup>\*1</sup>, 八浜義和<sup>\*2</sup>

<sup>\*1</sup> 山陽パルプ, <sup>\*2</sup> 阪大工

Nitric acid oxidation of hydrocracking products of lignin.

Jiro Okabe<sup>\*1</sup>, Yoshikazu Hachihama<sup>\*2</sup>

<sup>\*1</sup>Sanyo Pulp Co., Ltd., <sup>\*2</sup> Faculty of Engineering, Osaka University

Keywords: lignin, hydrogenolysis, Nitric acid oxidation, adipic acid

1957-017

鞣剤としてのリグニンスルホン酸

千手諒一

九州大学農学部

Lignin sulfonic acid as a tanning agent.

Ryoichi Senju

Faculty of Agriculture, Kyusyu University

Keywords: plant tannin, adsorption of tanning agent, diffusion of tanning agent

1957-018

リグニンスルホン酸の酸化

祖父江寛、齊藤吉民

東京大学工学部

Oxidation of lignosulfonic acid.

Hiroshi Sobue, Yoshitami Saito

Faculty of Engineering, the University of Tokyo

Keywords: sulfite spent liquor, oxidation by sodium hydroxide, vanillin

1957-019

バニリンより高分子化合物の合成に関する研究

舘 勇、村上浩二

京都大学農学部

Studies on the synthesis of macromolecular compounds from vanillin.

Isamu Tachi, Koji Murakami

Faculty of Agriculture, Kyoto University

Keywords: polyurethane, polyamide urethane, polyester

1957-020

6(及び7-)-カルボキシ-2-ヒドロキシメチル-1,4-ベンゾジオキサンより生成するポリエステル繊維の製造研究

万木 正、長谷川正木

繊維工業試験場

Production of polyester fiber from 6-(or 7-)-carboxy-2-hydroxymethyl-1,4-benzodioxane.

Tadashi Yurugi, Masaki Hasegawa

Institute of Fiber Science and Technology

Keywords: protocatechuic acid, epichlorohydrin

### 第3回 (1958.11.04) 九州大学農学部

1958-001

プロトリグニンの臭素化について

中村徳郎、北浦貞男

九州大学農学部

On the bromination of protolignin.

Tokurou Nakamura, Sadao Kitaura

Faculty of Agriculture, Kyusyu University

Keywords: *Abies sachaliensis*, lignin model compound, dehydrogenative polymer, urushi laccase

1958-002

リグニンの生成母体の生成に関する研究

石川久雄、沖 妙

愛媛大学農学部

Studies on the biosyntheses of lignin precursors.

Hisao Ishikawa, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: biosynthesis, shikimic acid, phenylalanine, tyrosine, gallotannin

1958-003

幼植物のリグニンについて

川村一次

岐阜大学農学部

On the lignin in juvenile plant.

Ichiji Kawamura

Faculty of Agriculture, Gifu University

Keywords: *Pinus Thunbergii*, *Robinia pseudoacacia*, guaiacyl nucleus, syringyl nucleus, methoxyl content

1958-004

リグニンと炭水化物との化学結合に関する研究(第6報)小麦藁のジメチルホルムアミド抽出物について

林 暁、館 勇  
京都大学農学部

Studies on the chemical bond between lignin and carbohydrates. VI. Dimethylformamide extracts from wheat straw.

Akira Hayashi, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: lignin-carbohydrate complex, milled wood lignin,

1958-005

針葉樹及び広葉樹に生育した寄生木(やどりぎ)のリグニンについて

中島浩二、八浜義和、F.E. Brauns

大阪大学工学部

On the lignin of mistletoe grown on coniferous trees and broad-leaved trees.

Koji Nakajima, Yoshikazu Hachihama, F.E. Brauns

Faculty of Engineering, Osaka University

Keywords: *Quercus* sp., *Pinus ponderosa*, *Mistletoe pholadendron flavescens*, Mäule color reaction, thioglycolic acid lignin, ethanolysis

1958-006

Lignum Vitae 中のリグニンについて

中島浩二、八浜義和、F.E. Brauns

大阪大学工学部

On the lignin in lignum vitae.

Koji Nakajima, Yoshikazu Hachihama, F.E. Brauns

Faculty of Engineering, Osaka University

Keywords: *Guaiacum officinale*, methoxyl content, Mäule color reaction

1958-007

リグニンスルホン酸の高分子化学的性状について

京極与寿郎、八浜義和

大阪大学工学部

Macromolecular properties of lignin sulfonic acid.

Yoshiro Kyougoku, Yoshikazu Hachihama

Faculty of Engineering, Osaka University

Keywords: polymolecularity, ion-exchange resin chromatography

1958-008

リグニンのエステルグループ

中野準三、石津 敦、右田伸彦

東京大学農学部

Ester group in lignin.

Junzo Nakano, Atsushi Ishizu, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: *p*-hydroxybenzoic acid, vanillic acid, syringic acid, *p*-coumaric acid, ferulic acid, *Populus Sieboldii*, *Populus Maximowiczii*

1958-009

リグニンとメルカプタンの反応

石原達夫、近藤民雄

林業試験場

Reaction of mercaptan with lignin.

Tatsuo Ishihara, Tamio Kondo

Forestry and Forest Product Research Institute

Keywords: hydrogen sulfide, ethyl mercaptan, vanillyl alcohol, mercaptolysis

1958-010

広葉樹リグニンのアルカリ分解

田中次郎、近藤民雄

林業試験場

Degradation of hardwood lignin by sodium hydroxide.

Jiro Tanaka, Tamio Kondo

Forestry and Forest Product Research Institute

Keywords: beech, sodium hydroxide, 4,4'-dihydroxy-3,3'-dimethoxystilben

1958-011

S.P.廃液のアルカリ溶液に於ける酸化について

舘 勇、浦野信清、赤嶋晋一郎、山本昭

京都大学農学部

Oxidation of sulfite spent liquor in alkaline medium.

Isamu Tachi, Nobukiyo Urano, Sinichiro Akashima, Akira Yamamoto

Faculty of Agriculture, Kyoto University

Keywords: vanillin, vanillic acid, yield of vanillin

1958-012

バニリンより高分子化合物の合成に関する研究-  $\beta$ -ヒドロキシエトキシ-バニリン酸のポリエステル  
の性状について

舘 勇、村上浩二

京都大学農学部

Studies on the synthesis of macromolecular compounds from vanillin- On the properties of polyester prepared from  $\beta$ -hydroxyethoxy-vanillic acid.

Isamu Tachi, Koji Murakami

Faculty of Agriculture, Kyoto University

Keywords: transesterification, catalyst, infrared spectrum

1958-013

バニリン酸誘導体の合成とその高分子物質への応用

長谷川正木

繊維工業試験場

Synthesis of vanillin derivatives and their use for polymer production.

Masaki Hasegawa

Institute of Fiber Science and Technology

Keywords: vanillin, vanillic acid, epichlorohydrin, hexamethylene diamine

1958-014

アルカリ性亜硫酸ソーダ蒸解について

坂田 功、千手諒一

九州大学農学部

On the alkaline sulfite cooking.

Isao Sakata, Ryoichi Senjyu

Faculty of Agriculture, Kyusyu University

Keywords: *Castanopsis* sp., sulfonation, delignification

1958-015

未晒パルプより抽出されるリグニンの量的関係

佐藤孝一郎、三川 礼

国策パルプ株式会社

Amount of lignin extracted from unbleached pulps

Koichiro Sato, Rei Mikawa

Kokusaku Pulp Co., Ltd.

Keywords: unbleached pulp, beating, dimethylsulfoxide, extraction, lignin, lignin-carbohydrate complex

#### 第4回 (1959.11.13-14) 京大、楽友会館

1959-001

リグニンの生合成に関する研究— ユウガオ果実の木質化に関与する酵素と有機酸の消長について

館 勇、佐藤 惺

京都大学農学部

Studies on the biosynthesis of lignin – Changes in content of enzymes and organic acids related to lignification of kanpyo, a fruit of *Lagenaria siceraria* var. *hispidia*.

Isamu Tachi, Satoru Sato

Faculty of Agriculture, Kyoto University

Keywords: laccase, peroxidase, shikimic acid, quinic acid

1959-002

<sup>14</sup>C-アイソトープに依るリグニン生合成の研究

長谷川正男\*<sup>1</sup>、樋口隆昌\*<sup>2</sup>

\*<sup>1</sup>林業試験場、\*<sup>2</sup>岐阜大学農学部

Studies on the biosynthesis of lignin using <sup>14</sup>C-isotope.

Masao Hasegawa, Takayoshi Higuchi

\*<sup>1</sup>Forestry and Forest Product Research Institute, \*<sup>2</sup>Faculty of Agriculture, Gifu University

Keywords: phenylpropane, shikimic acid, protocatechuic acid, dehydroshikimic acid

1959-003

リグニン生成母体の形成について

石川久雄、沖 妙

愛媛大学農学部

On the biosyntheses of lignin precursors.

Hisao Ishikawa, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: *Bacillus cereus*, dehydroshikimic acid, protocatechuic acid, aromatic amino acids

1959-004

ミズナラ樹皮のリグニンについて

幡 克実、十河村男

香川大学農学部

On the lignin in the bark of Japanese oak (*Quercus cryspura*)

Katsumi Hata, Murao Sogo

Faculty of Agriculture, Kagawa University

Keywords: dioxane lignin, hydrochloric acid lignin, UV spectra, IR spectra

1959-005

下等植物のリグニンについて(第一報)へゴ及びコフキササルノコシカケのリグニン

川村一次、樋口隆昌、近藤雅春

岐阜大学農学部

On the lignin of lower plants. I. Lignin in *Cythea spinulosa* and *Fomea applanatus*.

Ichiji Kawamura, Takayoshi Higuchi, Masaharu Kondo

Faculty of Agriculture, Gifu University

Keywords: wood rotting fungi, color reaction, Klason lignin, dioxane lignin, nitrobenzene oxidation

1959-006

リグニンと炭水化物との化学結合に関する研究

林 暁、館 勇

京都大学農学部

Studies on the chemical linkages between lignin and carbohydrates

Faculty of Agriculture, Kyoto University

Akira Hayashi, Isamu Tachi

Keywords: wheat straw, lignin-carbohydrate complex, sugar composition

1959-007

酢化した木材粉とエチレンオキサイドの反応について

石川久雄、山下謙三

愛媛大学農学部

On the reaction of ethylene oxide with acetylated wood meal.

Hisao Ishikawa, Kenzo Yamashita

Faculty of Agriculture, Kagawa University

Keywords: beech, hydroxyethyl lignin, hydroxyethyl cellulose, Brauns' s native lignin

1959-008

リグニンの単離及びリグニンの反応性について

福渡七郎、竹田貴美、宮崎親二郎

島根農科大学

On the isolation of lignins and their reactivity.

Shichiro Fukuwatari, Takami Takeda, Sinjiro Miyazaki

Shimane Agricultural University

Keywords: kraft lignin, lignosulfonic acid, Purves lignin,  $\gamma$ -ray irradiated lignin

1959-009

脱リグニン反応とその過程について

福渡七郎、安田徳郎、石野荘造、柳浦千里

島根農科大学

On the delignification reaction and its process.

Shichiro Fukuwatari, Tokuro Yasuda, Shozo Ishino, Chisato Yagiura

Shimane Agricultural University

Keywords: chlorination, holocellulose, *Tilia japonica*, *Pinus densiflora*, *Eucalyptus*, *Populus Sieboldii*, *Quercus crispula*

1959-010

リグニンスルホン酸に関する研究(第一報)

舘 勇<sup>\*1</sup>、林 昶<sup>\*1</sup>、小島義一<sup>\*2</sup>、東辻 健<sup>\*2</sup>

<sup>\*1</sup>京都大学農学部、<sup>\*2</sup>丸菱油脂工業株式会社

Studies on the lignin sulfonic acid. I.

Isamu Tachi<sup>\*1</sup>, Akira Hayashi<sup>\*1</sup>, Giichi Kojima<sup>\*2</sup>, Ken Higashitsuji<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyoto University, <sup>\*2</sup>Marubishi Oil and Fat Co. Ltd.

Keywords: sulfite waste liquor, separation by extraction, dicyclohexylamine salt

1959-011

リグニンスルホン酸に関する研究(第二報)

舘 勇<sup>\*1</sup>、林 昶<sup>\*1</sup>、小島義一<sup>\*2</sup>、東辻 健<sup>\*2</sup>

<sup>\*1</sup>京都大学農学部、<sup>\*2</sup>丸菱油脂工業株式会社

Studies on the lignin sulfonic acid. II.

Isamu Tachi<sup>\*1</sup>, Akira Hayashi<sup>\*1</sup>, Giichi Kojima<sup>\*2</sup>, Ken Higashitsuji<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyoto University, <sup>\*2</sup>Marubishi Oil and Fat Co. Ltd.

Keywords: molecular weight, melting point depression method, ethylene carbonate

1959-012

未晒パルプよりジメチルスルホオキサイド抽出した成分について

佐藤孝一郎、小林晃夫

国策パルプ株式会社

Component of dimethylsulfoxide extract of unbleached pulps

Koichiro Sato, Akio Kobayashi

Kokusaku Pulp Co., Ltd.

Keywords: beating, extraction, lignin, lignin-carbohydrate complex

1959-013

未晒 SP より抽出したリグニンスルホン酸の分子量について

佐藤孝一郎、小林晃夫、三川 礼

国策パルプ株式会社

Molecular weight of lignin sulfonic acid extracted from unbleached sulfite pulp

Koichiro Sato, Akio Kobayashi, Rei Mikawa

Kokusaku Pulp Co., Ltd.

Keywords: dimethylsulfoxide, extraction, lignosulfonic acid

1959-014

リグニンの物理化学的研究(第1報)微分容量より見たリグニンスルホン酸塩の一考察  
上田静男、辻 福寿、林 暁、渡辺 昌、中井章能  
京都大学農学部

Physicochemical studies on lignin. I. Differential capacity of lignosulfonate.

Shizuo Ueda, Fukujyu Tsuji, Akira Hayashi, Akira Watanabe, Akiyoshi Nakai

Faculty of Agriculture, Kyoto University

Keywords: dropping mercury electrode, electrical double layer, surface active property

1959-015

リグニンの物理化学的研究(第2報)微分容量より見たリグニンスルホン酸塩の一考察  
上田静男、辻 福寿、林 暁、渡辺 昌、中井章能  
京都大学農学部

Physicochemical studies on lignin. I. Differential capacity of lignosulfonate.

Shizuo Ueda, Fukujyu Tsuji, Akira Hayashi, Akira Watanabe, Akiyoshi Nakai

Faculty of Agriculture, Kyoto University

Keywords: electric frequency

1959-016

チオリグニンのポーラログラフイー(第7報) 接触波の活性基について(I)  
神田 孝、寺島典二、川上日出国  
名古屋大学農学部

Polarography of lignin. VII. On the active group of thiolignin catalytic wave. (1)

Takashi Kanda, Noritsugu Terashima, Hidekuni Kawakami

Faculty of Agriculture, Nagoya University

Keywords: *Pinus densiflora*, reduction, sodium borohydride, Raney nickel

1959-017

ニトロリグニンのポーラログラフイー  
永田美之介、北尾弘一郎、舘 勇  
京都大学農学部

Polarography of nitrolignin.

Yoshinosuke Nagata, Kouichiro Kitao, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: m-nitrophenol, low molecular nitrocompounds

1959-018

Vanillin より高分子化合物の合成に関する研究(第4報)  
村上浩二、舘 勇  
京都大学農学部

Studies on the synthesis of high polymer from vanillin. IV.

Koji Murakami, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: vanillic acid, polyamide, solubility

1959-019

リグニンとメルカプタンとの反応

石原達夫

林業試験場

Reaction of lignin and mercaptan.

Tatsuo Ishihara

Forestry and Forest Product Research Institute

Keywords: mercaptolysis, ethyl mercaptan, mercaptol, lignin model compounds

1959-020

リグニンの臭素化について

中村徳郎、北浦貞夫

九州大学農学部

On the bromination of lignin.

Tokuro Nakamura, Sadao Kitaura

Faculty of Agriculture, Kyusyu University

Keywords: protolignin, sodiumborohydride

1959-021

アルカリリグニンの $\alpha$ 位にカルボニル基をもつた側鎖構造について

右田伸彦、石津 敦

東京大学農学部

On the  $\alpha$ -carbonyl side chain structure in alkali lignin.

Nobuhiko Migita, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: condensation, acetovanillone, propiovanillone, 3,4-dihydroxypropiovanillone

1959-022

広葉樹リグニンの分解生成物について

田中治郎

林業試験場

On the alkali degradation products of hardwood lignin.

Jiro Tanaka

Forestry and Forest Product Research Institute

Keywords: beech, alkali degradation, syringyl ethane

1959-023

バニリンの酸素酸化について

舘 勇、村上浩二、阿部圭二

京都大学農学部

On the oxidation of vanillin with oxygen.

Isamu Tachi, Koji Murakami, Keiji Abe

Faculty of Agriculture, Kyoto University

Keywords: oxidation with oxygen, UV absorption spectrum

1959-024

リグニンとフェノールスルホン酸の反応

中島浩二\*<sup>1</sup>、八浜義和\*<sup>2</sup>

\*<sup>1</sup> 山陽パルプ株式会社、\*<sup>2</sup> 大阪大学工学部

Reaction of lignin with phenol sulfonic acid.

Koji Nakajima\*<sup>1</sup>, Yoshikazu Hachihama\*<sup>2</sup>

\*<sup>1</sup>Sanyo Pulp Co. Ltd, \*<sup>2</sup>Faculty of Engineering, Osaka University

Keywords: Brauns' s native lignin, condensation, Japanese red pine

1959-025

高分子凝集剤によるリグニンの沈澱(第2報)

佐々木壮吉

東京工業試験所

Precipitation of lignin by polymer flocculant.

Sokichi Sasaki

The Government Chemical Industrial Research Institute, Tokyo

Keywords: sulfite waste liquor, dicyanodiamide, formalin, semichemical pulp waste liquor

1959-026

広葉樹リグニンスルホン酸に関する研究

京極与寿郎、位田博敏、八浜義和

大阪大学工学部

Studies on the hardwood lignin sulfonic acid.

Yoshiro Kyogoku, Hirotochi Ida, Yoshikazu Hachihama

Faculty of Engineering, Osaka University

Keywords: beech, heterogeneity, polymolecularity, nitrobenzene oxidation

1959-027

リグニンの利用に関する研究

舘 勇、林 暁、山本 昭

京都大学農学部

Studies on the utilization of lignin.

Isamu Tachi, Akira Hayashi, Akira Yamamoto

Faculty of Agriculture, Kyoto University

Keywords: tanning agent, lignin sulfonic acid, oxidized lignin sulfonic acid

1959-028

リグニン及び木材に対する放射線の作用

高椋節夫、八浜義和

大阪大学工学部

Effect of radiation on lignin and wood.

Setsuo Takamuku, Yoshikazu Hachihama

Faculty of Engineering, Osaka University

Keywords: Japanese red pine, spruce, cobalt 60, Brauns' s native lignin, infrared spectrometry

1959-029

リグニンに対する放射線照射効果

祖父江寛、上埜武夫

日本放射線高分子研究協会

Effect of radiation on lignin.

Hiroshi Sobue, Takeo Ueno

Japan Radiation Polymer Research Association

Keywords:  $\gamma$ -ray, irradiation, paramagnetic resonance spectroscopy, free radical

## 第5回 (1960.11.19-20) 名古屋、商工会議所

1960-001

リグニンの高圧水素添加分解

鹿島 寛、長田 武、田畑晴朗、渡辺 浩、久保輝雄

野口研究所

Hydrocracking of lignin.

Satoru Kashima, Takeshi Nagata, Haruo Tabata, Hiroshi Watanabe, Teruo Kubo

Noguchi Institute

Keywords: liquefaction rate, *p*-cresol, 4-ethylphenol, pyrocatechol

1960-002

リグニンの高圧水添分解に関する研究

榊原 彰、荒木 正

林業試験場

Studies on the hydrogenolysis of lignin.

Akira Sakakibara, Tadashi Araki

Forestry and Forest Product Research Institute

Keywords: phenol, cresols, catechols, xylenols, ethylphenol

1960-003

リグニンスルホン酸に関する研究 (VII) 水溶液の電導度並びに拡散係数について

小島義一、中井章能、館 勇

京都大学農学部

Studies on the lignin sulfonic acid. VII. Electric conductivity and diffusion coefficient of the aqueous solution

Giichi Kojima, Akiyosi Nakai, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: electric conductivity, diffusion coefficient, micelle formation, association

1960-004

リグニンスルホン酸に関する研究 (VIII) 非水溶媒中による分別

小島義一、東辻 健、林 暁、館 勇

京都大学農学部

Studies on the lignin sulfonic acid. VIII. Fractionation by nonaqueous solvents.

Gi-ichi Kojima, Ken Azumatsuji, Akira Hayashi, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: dicyclohexylamine salt, molecular weight, fractional precipitation, molecular weight

1960-005

リグニンスルホン酸に関する研究 (IX) 非水溶媒中における粒度の測定

小島義一、林 暁、館 勇

京都大学農学部

Studies on the lignin sulfonic acid. IX. Determination of particle size in nonaqueous solvents.

Gi-ichi Kojima, Akira Hayashi, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: dicyclohexylamine salt, dicyclohexylamine hydrochloric acid salt, dissociation

1960-006

光散乱法によるリグニンスルホン酸塩の研究

鈴木 勇<sup>\*1</sup>, 京極与寿郎<sup>\*2</sup>, 八浜義和<sup>\*2</sup>

<sup>\*1</sup> 国策パルプ株式会社, <sup>\*2</sup> 大阪大学工学部

Studies on light scattering spectrophotometry of lignosulfonate

Isamu Suzuki<sup>\*1</sup>, Yoshiro Kyogoku<sup>\*2</sup>, Yoshikazu Hachihama<sup>\*2</sup>

<sup>\*1</sup>Kokusaku Pulp Co., Ltd., <sup>\*2</sup>Osaka University, Faculty of Technology

Keywords: light scattering spectrophotometry, lignosulfonate, molecular weight

1960-007

リグニンの物理化学的研究(第3報)

上田静男、渡辺 昌、辻 福寿

京都大学化研究所

Physicochemical study of lignin. III.

Shizuo Ueda, Akira Watanabe, Fukutoshi Tsuji

Institute for Chemical Research, Kyoto University

Keywords: electric conductivity, micelle formation, molecular weight

1960-008

リグニンのポーラログラフイー(第9報)接触波の活性基について(3)

神田 孝、寺島典二、川上日出国

名古屋大学農学部

Polarography of lignin. IX. On the active group of thiolignin catalytic wave (3).

Takashi Kanda, Noritsugu Terashima, Hidekuni Kawakami

Faculty of Agriculture, Gifu University

Keywords: thiolignin, sodalignin, lignin model compounds, carbonyl group

1960-009

ナギ、ラカンマキ及びイチヨウ材のリグニンについて

川村一次、樋口隆昌

岐阜大学農学部

On the lignin in *Podocarpus nagi*, *Podocarpus chinensis* and *Ginkgo biloba*.

Ichiji Kawamura, Takayoshi Higuchi

Faculty of Agriculture, Gifu University

Keywords: Mäule color reaction, nitrobenzene oxidation, milled wood lignin, UV absorption spectrum, IR absorption spectrum

1960-010

アカマツ樹皮フェノール酸の性状

幡 克美、十河村男

香川大学農学部

Properties of phenolic acids in the bark of red pine.

Katsumi Hata, Murao Sogo

Faculty of Agriculture, Kagawa University

Keywords: ethanolysis, protocatechualdehyde, methoxyl group content

1960-011

リグニンと炭水化物との化学結合に関する研究

林 昶

立命館大学理工学部

Studies on the chemical bonds between lignin and carbohydrates.

Akira Hayashi

College of Science and Engineering, Ritsumeikan University

Keywords: DMF extractives, phenol glucoside bond, uronic acid ester bond

1960-012

リグニンの単離及び反応性について(II)フェノール及びアニリンとの結合反応について

福渡七郎、渡辺 寿、安田徳郎

島根農科大学

On isolation and reactivity of lignin. II. Reaction with phenol and anilin.

Hichirou Fukuwatari, Hisashi Watanabe, Tokurou Yasuda

Shimane University of Agriculture

Keywords: soda pulp lignin, sulfate pulp lignin, sulfuric acid lignin,  $\gamma$ -ray lignin

1960-013

グアヤコールの塩素水による塩素化について

佐藤孝一郎, 小林晃夫, 三川 礼

国策パルプ株式会社

Chlorination of guaiacol with aqueous chlorine solution

Koichiro Sato, Akio Kobayashi, Rei Mikawa

Kokusaku Pulp Co., Ltd.

Keywords: guaiacol, aqueous chlorine solution, chlorination, methoxyl group, methanol

1960-014

リグニン中のフェノール性水酸基のヒドロオキシエチル化について

石川久雄、沖 妙

愛媛大学農学部

On the hydroxyethylation of phenolic hydroxyl groups in lignin.

Hisao Ishikawa, Tae Oki,

Faculty of Agriculture, Ehime University

Keywords: beech, neutral sulfite pulping, guaiacyl-syringyl lignin, UV spectrum

1960-015

芳香核カルボン酸形成に関与する酵素系について

石川久雄、沖 妙

愛媛大学農学部

On the enzymes participate in formation of aromatic carboxylic acids.

Hisao Ishikawa, Tae Oki,  
Faculty of Agriculture, Ehime University

Keywords: *Bacillus cereus*, shikimic acid, 5-dehydroshikimic acid, dehydroshikimic acid  
dehydrase

1960-016

リグニンの生合成に関する研究、ユウガオ果実の木質化に関する酵素とコニフェリルアルコールの酸化について

佐藤 惺、館 勇

京都大学農学部

Studies on the biosynthesis of lignin. Enzymes related to lignification of kanpyo, a fruit of *Lagenaria siceraria* var. *hispida* and oxidation of coniferyl alcohol.

Akira Sato, Isamu Tachi

Faculty of Agriculture, Kyoto University

Keywords: laccase, peroxidase, dehydrogenative polymerization products (DHP)

1960-017

過酸化物によるリグニンの酸化

尾上史郎, 大久保正道, 池田健郎

山陽パルプ株式会社

Oxidation of lignin with peroxides

Shiro Onoe, Masamichi Okubo, Kenro Ikeda

Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, lignin, peroxide, barium peroxide, oxidation, vanillin, vanillic acid

1960-018

過マンガン酸カリ酸化分解による榎リグニンの *p*-ヒドロキシフェニル核の検索

藤井俊太郎<sup>\*1</sup>、京極与寿郎<sup>\*2</sup>、八浜義和<sup>\*2</sup>

<sup>\*1</sup>興国人絹パルプ株式会社、<sup>\*2</sup>大阪大学工学部

Search of *p*-hydroxyphenyl nucleus in beech lignin by potassium permanganate oxidation.

<sup>\*1</sup>Shuntaro Fujii, <sup>\*2</sup>Yojyuro Kyogoku, <sup>\*2</sup>Yoshikazu Hachihama

<sup>\*1</sup>Koukoku Jinken Pulp Co. Ltd, <sup>\*2</sup>Faculty of Engineering, Osaka University

Keywords: *p*-hydroxyphenyl nucleus, paper chromatography, condensed structure

1960-019

硫化物により生成するアセトバニロン構造の起源

右田伸彦、石津 教

東京大学農学部

Origin of acetovanillone structure formed by sodium hydrosulfide cooking of wood

Nobuhiko Migita, Atsusi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: retro-aldol reaction, lignin model compounds

1960-020

リグニン加水分解物としてのコニフェリルアルコールの生成

榊原 彰、中山信子

林業試験場

Formation of coniferyl alcohol as a hydrolysis product of lignin.

Akira Sakakibara, Nobuko Nakayama

Forestry and Forest Product Research Institute

Keywords: Yezo spruce, *Picea jezoensis*, coniferyl aldehyde, dehydrodiconiferyl alcohol

1960-021

アルカリ分解物としてのシリングルエタン

田中治郎

林業試験場

Syringylethane as an alkaline degradation product of lignin

Jiro Tanaka

Forestry and Forest Product Research Institute

Keywords: beech, *Fagus crenata*, syringylethane

## 第 6 回 (1961.11.18-19) 大阪、府立農林会館

1961-001

Björkman リグニンについて

John S. Fujii, 中野準三、Bengt Rånby

ニューヨーク州立大学

Studies on the Björkman lignin.

John S. Fujii, Junzo Nakano, Bengt Rånby

New York State University

Keywords: polystyrene, change of molecular weight, free-radical, toluene

1961-002

リグニンのポーラログラフイー

寺島典二、神田 孝

名古屋大学農学部

Polarography of lignin.

Noritsugu Terashima, Takashi Kanda

Faculty of Agriculture, Nagoya University

Keywords: thiolignin, imine cobalt chelate compound,

1961-003

幼植物のリグニンについて(第 3 報)ニセアカシアの MWL の赤外および紫外線吸収曲線について

川村一次、樋口隆昌

岐阜大学農学部

On the juvenile plant lignin. III. Infrared and ultraviolet absorption spectra of MWL from locust tree.

Ichiji Kawamura, Takayoshi Higuchi

Faculty of Agriculture, Gifu University

Keywords: Mayapis, *Shorea palosapis*, Ginkgo, *Ginkgo biloba*

1961-004

リグニンの単離および単離リグニンの反応性

福渡七郎、久下 喬

島根農科大学

Isolation and reactivity of lignin.

Shichiro Fukuwatari, Takashi Kuge

Shimane University of Agriculture

Keywords: soda lignin, thiolignin, sulfuric acid lignin

1961-005

クラフト蒸煮における硫化物の役割

石津 敦、右田伸彦

東京大学農学部

Role of sulfide in kraft cooking.

Atsushi Ishizu, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compound, veratrylglycerol- $\beta$ -guaiacyl ether,  $\alpha$ -(2-methoxyphenoxy)- $\beta$ -hydroxypropioveratrone, pH, sulfidity

1961-006

亜硫酸パルプ廃液よりリグニンを採取する方法について

久保輝雄、鹿島 寛

野口研究所

Separation of lignin from sulfite pulping black liquor.

Teruo Kubo, Hiroshi Kashima

Noguchi Institute

Keywords: lignosulfonate, concentrated black liquor

1961-007

リグニン水素添加分解生成物の分析 - モノフェノール類について

渡辺 浩、鹿島 寛

野口研究所

Analysis of lignin hydrogenolysis products. - Monophenols.

Hiroshi Watanabe, Hiroshi Kashima

Noguchi Institute

Keywords: phenol, *o*-cresol, *p*-cresol, *p*-ethylphenol, 2,4-xyleneol, *p*-*n*-propylphenol

1961-008

リグニンの水素添加分解について

尾上史郎、大久保正道、岡部次郎

山陽パルプ株式会社

Hydrocracking of lignin

Shiro Onoe, Masamichi Okubo, Jiro Okabe

Sanyo Pulp Co., Ltd.

Keywords: wood meal, hydrochloric acid lignin, sulfuric acid lignin, lignosulfonic acid, Raney-nickel

1961-009

リグニンの水素添加分解に関する研究

榊原 彰\*<sup>1</sup>、阿部 勲\*<sup>2</sup>

\*<sup>1</sup> 林業試験場、\*<sup>2</sup> 北海道林産試験場

Hydrogenolysis of lignin.

Akira Sakakibara<sup>\*1</sup>, Isao Abe<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Hokkaido Forest Products Research Institute

Keywords: catalyst, low-boiling point phenols

1961-010

ジオキサンー水によるリグニンの加水分解(第2報)

榊原 彰、中山信子

林業試験場

Hydrolysis of lignin with dioxane and water.

Akira Sakakibara, Nobuko Nakayama

Forestry and Forest Product Research Institute

Keywords: Klason lignin, Yezo spruce, *Picea jezoensis*, beech, *Fagus crenata*

1961-011

木材のアセチルブロマイドによる分解

田中治郎、榊原 彰

林業試験場

Degradation of wood by acetyl bromide.

Jiro Tanaka, Akira Sakakibara

Forestry and Forest Products Research Institute

Keywords: syringyl ethane, beech, degradation by alkali

1961-012

木材加水分解リグニンの利用について 1. アルカリによる活性化

森 滋<sup>\*1</sup>、山岸祥恭<sup>\*1</sup>、半沢道郎<sup>\*2</sup>、川瀬 清<sup>\*2</sup>、笹谷宣志<sup>\*2</sup>

<sup>\*1</sup>北海道林産試験場、<sup>\*2</sup>北海道大学農学部

Utilization of wood hydrolysis lignin. I. Activation by alkali treatment.

Shigeru Mori<sup>\*1</sup>, Yoshiyasu Yamagishi<sup>\*1</sup>, Michio Hanzawa<sup>\*2</sup>, Kiyoshi Kawase<sup>\*2</sup>, Takashi Sasaya<sup>\*2</sup>

<sup>\*1</sup>Hokkaido Forest Products Research Institute, <sup>\*2</sup>Faculty of Agriculture, Hokkaido University

Keywords: *Betula platyphylla*, acid hydrolysis lignin, phenol resin

1961-013

木材加水分解リグニンの利用について 2. 硫酸による活性炭の製造

半沢道郎、里中聖一、氏家雅男

北海道大学農学部

Utilization of wood hydrolysis lignin. II. Production of activated charcoal using sulfuric acid.

Michio Hanzawa, Seiichi Satonaka, Masao Ujiie

Faculty of Agriculture, Hokkaido University

Keywords: white birch, *Betula platyphylla*, acid hydrolysis lignin, methylene blue

1961-014

中性亜硫酸セミケミカルパルプ廃液中のリグニンの性状並びに定量法の検討

幡 克美、十河村男

香川大学農学部

Properties and quantitative analysis of lignin in waste liquor of neutral sulfite semi-chemical pulping.

Katsumi Hata, Murao Sogo

Faculty of Agriculture, Kagawa University

Keywords: tannin, tannin sulfonic acid, lignin sulfonic acid, colloid titration method

1961-015

中性亜硫酸セミケミカルパルプ廃液のイオン交換樹脂膜透析

幡 克美、十河村男

香川大学農学部

Dialysis of waste liquor of neutral sulfite semi-chemical pulping through ion-exchange resin membranes

Katsumi Hata, Murao Sogo

Faculty of Agriculture, Kagawa University

Keywords: lignin sulfonic acid, free inorganic salt

1961-016

リグニンスルホン酸による可溶化(I)

林 暁、館 勇、小島義一、東辻 健、坂口 享

京都大学農学部

Solubilization by lignosulfonate. I.

Akira Hayashi, Isamu Tachi, Giichi Kojima, Ken Higashitsuji, Toru Sakaguchi

Faculty of Agriculture, Kyoto University

Keywords: electric conductivity, diffusion coefficient, surface tension

1961-017

リグニンスルホン酸による可溶化(II)

林 暁、館 勇、東辻 健、坂口 享、小島義一

京都大学農学部

Solubilization by lignosulfonate. II.

Akira Hayashi, Isamu Tachi, Takeshi Azumatsuji, Ken Higashitsuji, Giichi Kojima

Faculty of Agriculture, Kyoto University

Keywords: pinocyanol chloride, micelle formation

1961-018

重クロム酸加里によるリグニンのゲル化機構について

千手諒一、阿部 光

九州大学農学部

Gelation mechanism of lignin by potassium dichromate.

Ryoichi Senjyu, Hikaru Abe

Faculty of Agriculture, Kyusyu University

Keywords: electric conductivity, thiolignin, cross linking

1961-019

リグニンスルホン酸の分子形態についての考察

京極与寿郎、八浜義和

大阪大学工学部

Consideration for molecular configuration of lignin sulfonic acid.

Yoshiro Kyogoku, Yoshikazu Hachihama

Faculty of Engineering, Osaka University.

Keywords: molecular weight, sedimentation coefficient, viscosity

1961-020

リグニンの物理化学的研究(第3報)微分容量と吸着動力学

上田静男、辻 福寿、渡辺 昌

京都大学化学研究所

Physicochemical study of lignin. III. Differential capacity and adsorption dynamics.

Shizuo Ueda, Fukujyu Tsuji, Akira Watanabe

Chemistry Institute, Kyoto University

Keywords: dropping mercury electrode

1961-021

リグニンの物理化学的研究(第4報)リグニンスルホン酸(LSA)イオンの水銀面への吸着エネルギー

上田静男、辻 福寿、渡辺 昌

京都大学化学研究所

Physicochemical study of lignin. IV. Adsorption energy of lignin sulfonic acid ion on mercury surface.

Shizuo Ueda, Fukujyu Tsuji, Akira Watanabe

Institute for Chemical Research, Kyoto University

Keywords: surface active agent, electrical double layer

1961-022

単離した塩素化リグニンスルホン酸バリウムについて

佐藤孝一郎、小林晃夫、三川 礼

国策パルプ株式会社

Properties of isolated chlorinated barium lignosulfonate.

Koichiro Sato, Akio Kobayashi, Rei Mikawa

Kokusaku Pulp Co., Ltd.

Keywords: acidic groups, carboxylic group, molecular weight, potentiometric titration

特別講演

米国リグニン化学討論会に出席して

鹿島 寛

野口研究所

1961-Invited lecture:

A report on the Lignin Chemistry Symposium in USA.

Hiroshi Kashima

Noguchi Institute

## 第7回(1962.10.04-05) 北海道大学クラーク会館

1962-001

リグニンの単離及び単離リグニンの反応性(IV) 特にジメチルスルfoxide・リグニンについて

福渡七郎、久下 喬、神保幹夫

島根農科大学

Isolation of lignin and reactivity of the isolated lignin. IV. On the dimethylsulfoxide-lignin.

Shichiro Fukuwatari, Takashi Hisashita, Mikio Jinbo

Shimane University of Agriculture

Keywords: red pine, *Pinus densiflora*, methoxyl content, UV absorption spectrum, hydroxyl group content

1962-002

Mäule 反応の呈色機構(VI)

中野準三、右田伸彦

東京大学農学部

Mechanism of Mäule color reaction. VI.

Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo.

Keywords: biosynthetic lignin, DHP, infrared absorption spectrum

1962-003

デオキサンー水によるリグニンの加水分解(第4報)

榊原 彰、中山信子

林業試験場

Hydrolysis of lignin by dioxane-water, IV,

Akira Sakakibara, Nobuko Nakayama

Forestry and Forest Products Research Institute

Keywords: guaiacylglycerol

1962-004

液体アンモニア中の金属ナトリウムによるリグニンの分解

榊原 彰、山口 彰

林業試験場

Degradation of lignin by metallic sodium in liquid ammonia.

Akira Sakakibara, Akira Yamaguchi

Forestry and Forest Products Research Institute

Keywords: *Picea jezoensis*, dihydroeugenol, guaiacylglycerol

1962-005

リグニンの水素化分解に関する研究

榊原 彰<sup>\*1</sup>、尾田勝夫<sup>\*1</sup>、阿部 勲<sup>\*2</sup>

<sup>\*1</sup> 林業試験場、<sup>\*2</sup> 北海道林産試験場

Hydrogenolysis of lignin.

Akira Sakakibara<sup>\*1</sup>, Masao Oda<sup>\*1</sup>, Isao Abe<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Hokkaido Forest Products Research Institute

Keywords: catalyst, nickel carbonyl, iron carbonyl, catechols

1962-006

リグニンのメルカプトリシスについて

石原達夫、榊原 彰

林業試験場

Mercaptolysis of lignin.

Tatsuo Ishihara, Akira Sakakibara

Forestry and Forest Products Research Institute

Keywords: *Picea jezevensis*, mercaptolysis products, structure of products

1962-007

竹リグニンに関する研究(第2報)ニトロベンゼン酸化による*p*-ヒドロキシベンズアルデヒの成因  
前田信夫、五十野善四郎、大野一月

大阪府立大学農学部

Studies on the bamboo lignin. II. Origin of *p*-hydroxybenzaldehyde by nitrobenzene oxidation.

Nobuo Maeda, Zenshiro Isono, Kazuki Ono

Faculty of Agriculture, Osaka Prefecture University

Keywords: *p*-hydroxyphenyl nucleus, Hibbert's ketones, *p*-coumaric acid

1962-008

リグニンスルホン酸バリウムの分散性

小林晃夫、葉賀忠昭、佐藤孝一郎

国策パルプ株式会社

Dispersing ability of barium lignosulfonate

Akio Kobayashi, Tadaaki Haga, Koichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: molecular weight, sulfonic group

1962-009

リグニンスルホン酸のポーラログラフによる定量

林 暁、山条弘子<sup>\*1</sup>、小島義一<sup>\*2</sup>

<sup>\*1</sup>立命館大学理工学部、<sup>\*2</sup>丸菱油脂株式会社

Quantitative determination of lignin sulfonic acid by polarography

Akira Hayashi<sup>\*1</sup>, Hiroko Yamajyo<sup>\*1</sup>, Gi-ichi Kojima<sup>\*2</sup>

<sup>\*1</sup>College of Science and Engineering, Ritsumeikan University, <sup>\*2</sup>Marubishi Oil Chemical Co. Ltd

Keywords: methylene blue, catalytic wave

1962-010

リグニンスルホン酸のキレート作用(1)

林 暁、山条弘子、羽下利勝

立命館大学理工学部

Chelating property of lignosulfonic acid. I.

Akira Hayashi, Hiroko Yamajyou, Toshikatsu Hage

College of Science and Engineering, Ritsumeikan University

Keywords: polarography, ferric ion, catalytic wave

1962-011

リグニンスルホン酸のキレート作用(2)

林 暁、山条弘子、扇孝三郎

立命館大学理工学部

Chelating property of lignosulfonic acid. II.

Akira Hayashi, Hiroko Yamajyou, Kozaburo Ougi

College of Science and Engineering, Ritsumeikan University

Keywords: polarography, ferric ion, catalytic wave, titration curve, ionic linkage

1962-012

リグニンスルホン酸と塩素との反応

尾上史郎, 大久保正道, 中島浩二

山陽パルプ株式会社

Reaction of lignosulfonic acid with chlorine.

Shiro Onoe, Masamichi Okubo, Koji Nakajima

Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, lignosulfonic acid, chlorination, oxidation, substitution

1962-013

イオン交換繊維によるリグニンスルホン酸の吸着

平山謙三郎, 日向明, 加藤正明

東洋紡績株式会社

Adsorption of lignosulfonates with ion-exchange cellulose fiber.

Kenzaburo Hirayama, Akira Hyuga, Masaaki Kato

Toyobo Co., Ltd.

Keywords: sulfite spent liquor, lignosulfonates, anion-exchange resin, ion-exchange cellulose, aminoethyl cellulose

1962-014

腐朽材のリグニン

川瀬 清

北海道大学農学部

Lignin in rotten wood.

Kiyoshi Kawase

Faculty of Agriculture, Hokkaido University

Keywords: UV spectrometric analysis

1962-015

モクマオウ及びバッカリス材のリグニンについて

川村一次, 樋口隆昌

岐阜大学農学部

Studies on the lignin in *Casuarina equisetifolia* and *Baccharis halimifolia*.

Takamasa Higuchi, Ichiji Kawamura

Faculty of Agriculture, Gifu University

Keywords: Mäure color reaction, Cross Bevan color reaction, IR absorption spectrum, dioxane lignin

1962-016

セミケミカルパルプ廃液中のリグニンの性状 ーとくにメトキシル基について

幡 克美, 十河村男

香川大学農学部

Properties of lignin in waste liquor of semi-chemical pulping, especially on the methoxyl content.

Katsumi Hata, Murao Sogo

Faculty of Agriculture, Kagawa University

Keywords: chestnut, beech, nitrobenzene oxidation, syringaldehyde, vanillin

1962-017

N-L 材混合チオリグニンの IR 吸収

杉松昭人, 岩田秀子

国策パルプ株式会社

Infrared spectroscopy of a mixture of softwood and hardwood thiolignins

Akihito Sugimatsu, Hideko Iwata

Kokusaku Pulp Co., Ltd.

Keywords: thiolignin, softwood, hardwood, mixture ratio, infrared spectroscopy

1962-018

チオリグニンの過安息香酸分解について

鍵野豊祐, 中野準三, 右田伸彦

東京大学農学部

Degradation of thiolignin by perbenzoic acid.

Toyosuke Kagino, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: acetovanillone, acetoveratrone, propiovanillone, propioveratrone

1962-019

アルカリリグニン中のカルボニル構造

石津 敦, 仙頭 明, 右田伸彦

東京大学農学部

Carbonyl structure in alkali lignin.

Atsushi Ishizu, Akira Sento, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: spruce, thiolignin, soda lignin,  $\Delta E_r$  spectrum

1962-020

サルフェート蒸解における硫化物の役割

石津 敦, 中野準三, 右田伸彦

東京大学農学部

Role of sulfides in sulfate cooking.

Atsushi Ishizu, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compounds, guaiacylglycerol- $\beta$ -guaiacyl ether

1962-021

木材加水分解リグニンの水溶性処理

中野準三, 佐々木和仁, 右田伸彦

東京大学農学部

Solubilization of wood hydrolysis lignin.

Junzo Nakano, Kazuhito Sasaki, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: sulfonation, sodium sulfite

1962-022

濃硫酸法木材加水分解リグニンの物理化学的性状について(その一)

布村昭夫、阿部 勲、長谷川勇、峰村伸哉、北村維朗  
北海道林業試験場

Physicochemical properties of wood hydrolysis lignin with concentrated sulfuric acid. I.  
Akio Nunomura, Isao Abe, Isamu Hasegawa, Nobuya Minemura, Tadao Kitamura  
Hokkaido Forestry Research Institute  
Keywords: white birch, *Betula platyphylla*, methoxyl content

1962-023

リグニン樹脂に関する研究  
岡田稔, 後藤孝, 白岩治巳, 高安信義  
興国人絹パルプ株式会社

Studies on lignin resin.  
Minoru Okada, Takashi Goto, Harumi Shiroiwa, Nobuyoshi Takayasu  
Kokoku Jinken Pulp Co., Ltd.  
Keywords: sulfite lignin, sulfite spent Liquor, polyamine lignin complex, lignin-phenol-  
formaldehyde resin

1962-024

リグニンスルホン酸-フェノール縮合物の鞣皮性能  
京極与寿郎、加藤正之、八浜義和  
大阪大学工学部

Tanning property of condensation product of lignosulfonic acid and phenol.  
Yoshiro Kyougoku, Masayuki Kato, Yoshikazu Hachihama  
Faculty of Engineering, Osaka University  
Keywords: red pine, *Pinus densiflora*, waste lignin from neutral sulfite cooking, phenolic hydroxyl  
content

特別講演、  
木材加水分解工業の二、三の知見  
保坂秀明  
北海道木材化学株式会社

1962-Invited lecture:  
Information concerning wood hydrolysis industry.  
Hideaki Hosaka  
Hokkaido Wood Chemical Co. Ltd.

## 第 8 回(1963.11.5-6)松江市、島根自治会館

1963-001

ペルオキシダーゼによるコニフェリルアルコールの脱水素重合 1. タケノコのペルオキシダーゼの  
精製と脱水素重合物の分光学的検索法  
野津祐三、中村 亘、奥貫一男  
大阪大学理学部

Dehydrogenative polymerization of coniferyl alcohol by peroxidase. I. Purification of bamboo  
peroxidase and spectroscopic investigation of dehydrogenative polymer.

Yuzo Nozu, Wataru Nakamura, Kazuo Okunuki  
Faculty of Science, Osaka University  
Keywords: DHP, UV spectroscopy, optimum pH

1963-002

パーオキシダーゼによるリグニン及びモデル化合物の酵素的分解

石川久雄、沖 妙

愛媛大学農学部

Enzymatic degradation of lignin and lignin model compounds by peroxidase.

Hisao Ishikawa, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: radish, horse radish, *Collybia velutipes*

1963-003

アカマツ外皮リグニンスルホン酸の性状について

十河村男、幡 克美

香川大学農学部

Properties of lignosulfonic acid from outer bark of red pine.

Murao Sogo, Katsumi Hata

Faculty of Agriculture, Kagawa University

Keywords: nitrobenzene oxidation, molecular weight

1963-004

ポリサルファイドリグニンの性状

中野準三、右田伸彦

東京大学農学部

Properties of lignin from polysulfide cooking liquor.

Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compound, vanillyl alcohol, apocynol

1963-005

タバコリグニンの性状について

加藤邦雄<sup>\*1</sup>、中野準三<sup>\*2</sup>、右田伸彦<sup>\*2</sup>

<sup>\*1</sup>専売公社中央研究所、<sup>\*2</sup>東京大学農学部

Properties of lignin in tobacco plant.

Kunio Kato<sup>\*1</sup>, Junzo Nakano<sup>\*2</sup>, Nobuhiko Migita<sup>\*3</sup>

<sup>\*1</sup>Central Research Institute, Japan Tobacco and Salt Public Corporation,

<sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: milled wood lignin, elemental composition, UV absorption spectrum, IR absorption spectrum

1963-006

ササのリグニンの性質

氏家雅男

北海道大学農学部

Properties of lignin in *Sasa kurilensis*.

Masao Uji-ie

Faculty of Agriculture, Hokkaido University

Keywords: *Sasa kurilensis*, milled wood lignin, color reaction, UV absorption spectrum, IR absorption spectrum

1963-007

木材の MWL の赤外線吸収曲線について

川村一次、樋口隆昌

岐阜大学農学部

Infrared absorption spectra of milled wood lignins.

Ichiji Kawamura, Takamasa Higuchi

Faculty of Agriculture, Gifu University

Keywords: softwood, hardwood, monocotyledons, dioxane lignin

1963-008

アルカリリグニンのカルボキシル基

石津 敦、中野準三、右田伸彦

東京大学農学部

Carboxyl group in alkali lignin.

Atsushi Ishizu, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: protolignin, decarboxylation, Mannich reaction

特別講演

リグニンの工業的利用

野村順次

山陽パルプ株式会社

1963- Invited lecture:

Industrial utilization of lignin.

Junji Nomura

Sanyo Pulp Co. Ltd.

パネル討論会、リグニンの利用開発

司会者: 八浜義和(大阪大学工学部)

1963- Panel discussion: Development of lignin utilization.

Moderator: Yoshikazu Hachihama, Faculty of Engineering, Osaka University

1963-009

リグニンのゲル化、特にその活性中心について

田中浩雄、千手諒一

九州大学農学部

Gelation of lignin, especially on the active center for gel formation.

Hirowo Tanaka, Ryouichi Senju

Faculty of Agriculture, Kyushu University

Keywords: liginosulfonic acid, thioglignin, potassium dichromate, desulfonation, carboxymethylation, methylation, chlorination

1963-010

リグニンスルホン酸塩の分散性

小林晃夫、山川 功、葉賀忠昭、佐藤孝一郎

国策パルプ株式会社

Dispersing ability of lignosulfonate.

Akio Kobayashi, Isao Yamakawa, Tada-aki Haga, Kouichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: cement, molecular weight,

1963-011

リグニンに対する放射線グラフト共重合

越島哲夫、村木永之介

大阪工業技術試験所

Radiation-induced graft copolymerization onto lignin.

Tetsuo Koshijima, Einosuke Muraki

Osaka National Research Institute.

Keywords: methyl metacrylate, styrene, vinyl acetate, cobalt 60

1963-012

糖化リグニンの溶解とIRスペクトル（リグニンの単離及び単離リグニンの反応性、V）

福渡七郎、雑賀宏昌

島根農科大学

Isolation of lignin and reactivity of the isolated lignin. V. Solubilization of wood-hydolysis lignin, and its infrared absorption spectroscopy.

Shichiro Fukuwatari, Hiromasa Saika

Shimane University of Agriculture

Keywords: sulfuric acid lignin, IR spectroscopy

1963-013

ポリサルファイド2段蒸解におけるリグニンの挙動

宮尾再青<sup>\*1</sup>、中野準三<sup>\*2</sup>、右田伸彦<sup>\*2</sup>

<sup>\*1</sup>東洋パルプ株式会社、<sup>\*2</sup>東京大学農学部

Behavior of lignin during two-stage polysulfide cooking.

Saisei Miyao<sup>\*1</sup>, Junzo Nakano<sup>\*2</sup>, Nobuhiko Migita<sup>\*2</sup>

<sup>\*1</sup>Toyo Pulp Co. Ltd., <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: Polysulfide, two-stage cooking, vanillyl alcohol.

1963-014

特別講演、

リグニン化学の一動向

石川久雄

愛媛大学農学部

Invited lecture:

Trend of lignin chemistry.

Hisao Ishikawa

Faculty of Agriculture, Ehime University

1963-015

土壤処理剤としてのリグニンスルホン酸塩の研究 2. ゲル化による砂質土の処理

赤羽政亮、黒沢 彰、矢野弘子

鉄道技術研究所

Studies on lignosulfonate as a soil-stabilizer. II. Treatment of sandy soil by gelation.

Masasuke Akabane, Akira Kurosawa, Hiroko Yano

Railway Technical Research Institute

Keywords: potassium dichromate, aluminum chloride, cupric chloride, ferric chloride, aging test

1963-016

土壤処理剤としてのリグニンスルホン酸塩の研究 3. クロムリグニン及び処理土からの溶 脱

赤羽政亮、黒沢 彰、矢野弘子

鉄道技術研究所

Studies on lignosulfonate as a soil-stabilizer. III. Chrom-lignin and its leaching from treated soil.

Masasuke Akabane, Akira Kurosawa, Hiroko Yano

Railway Technical Research Institute

Keywords: potassium dichromate, aluminum chloride, cupric chloride, ferric chloride, aging test

1963-017

クラフトリグニンの水素添加分解について

藤岡靖雄

日本パルプ工業株式会社

Hydrocracking of kraft lignin.

Yasuo Fujioka

Nippon Pulp Industry Co., Ltd.

Keywords: hydrocracking, kraft lignin, oil yield, catalyst, phenols

1963-018

連続試験装置によるリグニンの水素化分解(予報)

榊原 彰、宮崎 信、石原達夫、尾田勝夫、山口 章、高橋 敏

林業試験場

Continuous hydrocracking of lignin by small-scale pilot plant. (Preliminary report)

Akira Sakakibara, Sin Miyazaki, Tatsuo Ishihara, Masao Oda, Akira Yamaguchi, Satoshi Takahashi

Forestry and Forest Product Research Institute

特別講演

1963- Invited Lecture:

The Swedish Wood Research Center, a Brief Review of Organization and Research.

J. L. Samuelsson

The Central Laboratory of the Swedish Cellulose Industry

## 第9回 (1964.11.11-12) 紙パルプ会館

1964-001

コニフェリルアルコールの脱水素重合に関する酵素系について

中村 亘、野津祐三、奥貫一男

大阪大学理学部

Enzymes participating in dehydrogenative polymerization of coniferyl alcohol.

Wataru Nakamura, Yuzo Nozu, Kazuo Okunuki

Faculty of Science, Osaka University

Keywords: peroxidase, laccase, Japanese lacquer, bamboo shoot, mushroom

1964-002

植物の組織培養中のリグニンの生合成

樋口隆昌

岐阜大学農学部

Biosynthesis of lignin during tissue culturing of plants.

Takayoshi Higuchi

Faculty of Agriculture, Gifu University

Keywords: strobus pine (*Pinus strobus*), sequoia (*Sequoia sempervirens*), paulownia (*Paulownia tomentosa*), syringe (*Syringa pekinensis*), rosa (*Rosa grauca*), pelargonium (*Pelargonium grandiflorum*), poplar (*Populus nigra*), <sup>14</sup>C-phenylalanine, ethanolysis, nitrobenzene oxidation

1964-003

赤外線吸収曲線に基づくリグニンの分別と化学的性質との関係

川村一次、樋口隆昌

岐阜大学農学部

Relationship between classification of lignin based on IR absorption spectra and their chemical properties.

Ichiji Kawamura, Takayoshi Higuchi

Faculty of Agriculture, Gifu University

Keywords: fern plant (Pteridophyta), cycads (*Cycas revoluta*), ginkgo (*Ginkgo biloba*), ephedra (*Ephedra sinica*), Mäule color reaction, nitrobenzene oxidation

1964-004

リグニンのポーラログラフ的研究(第 11 報)モデル化合物の KP 蒸解とポーラログラフ的性質

寺島典二、玉生征人、神田 孝

名古屋大学農学部

Polarography of lignin. XI. Kaft cooking of lignin model compounds and their polarographic properties.

Noritsugu Terashima, Masato Tamao, Takashi Kanda

Faculty of Agriculture, Nagoya University

Keywords: imine-cobalt chelate compound

1964-005

リグニン中のピノレジノール構造について

荻山紘一、近藤民雄

九州大学農学部

Pinoresinol structural units in lignin molecule.

Koichi Ogiyama, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: red pine, *Pinus densiflora*, *Cryptomeria japonica*, white birch, *Betula tauschii*, *Symplocos lucida*, alcohol lignin, nitric acid oxidation, dilactone

1964-006

低分子量リグニンスルホン酸の分離(主としてペーパークロマトグラフィによる知見)

田中治郎

林業試験場

Separation of low molecular lignosulfonic acid, and information obtained by paper chromatography.

Jiro Tanaka

Forestry and Forest Product Research Institute

Keywords: *Abies sachariensis*, sulfite cooking, paper chromatography

1964-007

ブナリグニンスルホン酸に関する研究(第1報)

秦 邦男、中村孝一

東北パルプ株式会社

Studies on beech lignosulfonates. I

Kunio Hata, Koichi Nakamura

Tohoku Pulp Co., Ltd.

Keywords: sulfite spent liquor, barium lignosulfonate, beech, *Fagus crenata*

1964-008

クラフト蒸解における硫化物の役割

石津 敦、中野準三、右田伸彦

東京大学農学部

Role of sulfides in kraft cooking.

Atsushi Ishizu, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: *Abies sachariensis*, milled wood lignin,  $\Delta E_r$  spectrum

1964-009

ポリスルフィドリグニンの性状

\*<sup>1</sup>中野準三、\*<sup>1</sup>右田伸彦、\*<sup>2</sup>宮尾再青

\*<sup>1</sup>東京大学農学部、\*<sup>2</sup>東洋パルプ株式会社

Characterization of lignin from polysulfide cooking liquor.

Junzo Nakano, Nobuhiko Migita, Saisei Miyao

\*<sup>1</sup>Faculty of Agriculture, the University of Tokyo, \*<sup>2</sup>Toyo Pulp Co, Ltd.

Keywords: vanillyl alcohol, thioglignin, sulfur content

1964-010

チオリグニンとフェノールとの反応

小林晃夫、葉賀忠昭、佐藤孝一郎

国策パルプ株式会社

Reaction of thioglignin with phenol

Akio Kobayashi, Tadaaki Haga, Kouichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: thioglignin, phenol, reaction, formaldehyde

1964-011

リグニンをベースとした接着剤について

秋野精也、岩崎揮一、三輪一迪  
東海パルプ株式会社

Lignin base adhesive.

Seiya Akino, Terukazu Iwasaki, Kazumichi Miwa

Tokai Pulp & Paper Co., Ltd.

Keywords: thiolignin, phenol-formaldehyde resin, resol resin, softwood black liquor

1964-012

セメントに対する亜硫酸パルプ排液の作用

町原 晃、中島浩二

山陽パルプ株式会社

Dispersing ability of sulfite spent liquor on cement slurry

Akira Machihara, Koji Nakajima

Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, cement, dispersing effect, lignosulfonic acid, sulfonated carbohydrate, aldonic acid

1964-013

エゾマツ粗酢酸リグニンより得た低分子化合物および高分子化合物について

福住俊郎、芝本武夫

東京大学農学部

Low and high molecular weight compounds obtained from crude acetic acid lignin of Yezo spruce.

Toshio Fukuzumi, Takeo Shibamoto

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, vanilloyl methyl ketone, vanillin, molecular weight

1964-014

リグニンの過酢酸分解について

畠山兵衛、中野準三、右田伸彦

東京大学農学部

Degradation of lignin with peracetic acid.

Hyo Hatakeyama, Jyunzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compounds, vanillyl alcohol, veratryl alcohol

1964-015

リグニンの酸化分解に関する研究(III) 過酸化物による高収率パルプの漂白時における脱リグニンの機作について

石川久雄、沖 妙

愛媛大学農学部

Studies on the oxidative degradation of lignin. III. Delignification mechanism of peroxide bleaching of high yield pulp.

Hisao Ishikawa, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: chemigroundwood pulp, dioxane lignin, peracetic acid

1964-016

## 硫酸糖化リグニンの化学「シェルモールド用材料としての基礎的知見」

宮崎安太郎<sup>\*1</sup>、勝田千昭<sup>\*1</sup>、森松久徳<sup>\*2</sup>、上ヶ島慶一<sup>\*2</sup>

<sup>\*1</sup>東京教育大学農学部、<sup>\*2</sup>北海道木材化学工業株式会社

Chemistry of sulfuric acid hydrolysis lignin: Basic knowledge on the material for shell mold process.

Yasutaro Miyazaki<sup>\*1</sup>, Chiaki Katuta<sup>\*1</sup>, Hisanori Morimatsu<sup>\*2</sup>, Keiichi Jyogasima<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Education, <sup>\*2</sup>Hokkaido Wood Chemical Engineering Co. Ltd.

1964-0017

リグニンの水素化分解に関する研究(第6報)鉄カーボニルを触媒とした場合のリグニンスルホン酸に対する各要因の検討

榊原 彰<sup>\*1</sup>、田中治郎<sup>\*2</sup>、古屋信子<sup>\*2</sup>、宮崎 信<sup>\*2</sup>、石原達夫<sup>\*2</sup>、尾田勝夫<sup>\*2</sup>、山口 彰<sup>\*2</sup>、高橋敏<sup>\*2</sup>、志水一允<sup>\*2</sup>

<sup>\*1</sup>北海道大学農学部、<sup>\*2</sup>林業試験場

Hydrogenolysis of lignin. VI. Investigation of factors affecting on reaction during hydrogenolysis of lignosulfonic acid using iron carbonyl as a catalyst.

Akira Sakakibara<sup>\*1</sup>, Jiro Tanaka<sup>\*2</sup>, Nobuko Furuya<sup>\*2</sup>, Shin Miyazaki<sup>\*2</sup>, Tatsuo Ishihara<sup>\*2</sup>, Masao Oda<sup>\*2</sup>, Akira Yamaguchi<sup>\*2</sup>, Satoshi Takahashi<sup>\*2</sup>, Kazumasa Simizu<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Forestry and Forest Products Research Institute

Keywords: addition of sulfur, yield of phenolic compounds

1964-018

リグニンの水素化分解に関する研究(第7報)モデル化合物の水素化分解によって得られた2、3の知見

石原達夫、宮崎 信、田中治郎、尾田勝夫、山口 彰、古屋信子、高橋 敏、志水一允  
林業試験場

Hydrocracking of lignin. VII. Information obtained by hydrocracking of lignin model compounds.

Tatsuo Ishihara, Shin Miyazaki, Jiro Tanaka, Masao Oda, Akira Yamaguchi, Nobuko Furuya, Satoshi Takahashi, Kazumasa Simizu

Forestry and Forest Products Research Institute

Keywords: lignin model compounds, structure of side chain

1964-019

重クロム酸リグニンのゲル化機構について(その一)

林 暁<sup>\*1</sup>、D.A.I.Goring<sup>\*2</sup>

<sup>\*1</sup>立命館大学理工学部、<sup>\*2</sup>カナダ紙パルプ研究所

Gelling mechanism of lignin by dichromate. I.

Akira Hayashi<sup>\*1</sup>, D.A.I. Goring<sup>\*2</sup>

<sup>\*1</sup>College of Science and Engineering, Ritsumeikan University, <sup>\*2</sup>Pulp and Paper Research Institute of Canada

Keywords: viscosity, hydrophilicity, sulfonic acid group content, catechol group

1964-020

重クロム酸リグニンのゲル化機構について(その二)

林 暁<sup>\*1</sup>、D. A. I. Goring<sup>\*2</sup>

<sup>\*1</sup>立命館大学理工学部、<sup>\*2</sup>カナダ紙パルプ研究所

Gelation mechanism of lignin by dichromate. II.

Akira Hayashi\*<sup>1</sup>, D.A.I. Goring\*<sup>2</sup>

\*<sup>1</sup>College of Science and Engineering, Ritsumeikan University, \*<sup>2</sup>Pulp and Paper Research Institute of Canada

Keywords: active group, tannin, molybdate, tungstate

1964-021

過硫酸塩によるリグニンのゲル化について

田中浩雄、千手諒一

九州大学農学部

Gelation of lignin by persulfate.

Hiroo Tanaka, Ryoichi Senjyu

Faculty of Agriculture, Kyusyu University

Keywords: ammonium persulfate, lignin sulfonic acid, thiolignin

1964-022

土壌処理剤としてのリグニンスルホン酸塩の研究、第5報、カビ性試験について

赤羽政亮、河村肇、八木舜治

鉄道技術研究所

Studies on lignosulfonates for soil stabilizer. V. Result of fungus resistance test.

Masasuke Akabane, Hajime Kawamura, Shunji Yagi

Railway Technical Research Institute

Keywords: soil stabilizer, chromium lignin, fungus, lignin sulfonate, gelatinizer

1964-023

特別講演：リグニンの研究に対する要望

1. 大学から民間研究機関へ

三川 礼

大阪大学産業科学研究所

2. 民間から国公立研究機関へ

秦 邦男

東北パルプ株式会社

Invited lecture: Requests to the research on lignin.

1. From university to private research institutes.

Rei Mikawa,

Institute of Scientific and Industrial Research, Osaka University

2. From private research institutes to university.

Kunio Hata

Tohoku Pulp Co. Ltd.

## 第 10 回 (1965.11.8-9)大阪科学技術センター

1965-001

加水分解リグニン系樹脂製造に関する研究(第 2 報)リグニンのアルカリ活性化試験

阿部 勲、窪田 実、布村昭夫、森 滋

北海道林産試験場

Preparation of plastics from wood hydrolysis lignin. II. Activation of lignin by treatment with alkali.

Isao Abe, Minoru Kubota, Akio Nunomura, Shigeru Mori  
Hokkaido Forest Products Research Institute  
Keywords: thermosetting plastic, sulfuric acid lignin

1965-002

加水分解リグニン系樹脂製造に関する研究(第3報)活性化リグニンの縮合試験  
阿部 勲、北村維朗、布村昭夫、森 滋  
北海道林産試験場

Preparation of plastics from wood hydrolysis lignin. III. Condensation of activated lignin.  
Isao Abe, Minoru Kubota, Akio Nunomura, Shigeru Mori  
Hokkaido Forest Products Research Institute  
Keywords: thermosetting plastic, sulfuric acid lignin, phenol, formaldehyde

1965-003

リグニン樹脂のシェルモールドへの応用  
広瀬正尚  
日本合成化工株式会社

Application of lignin resin for shell mold.  
Masanao Hirose  
Nihon Gosei Kako Co., Ltd.  
Keywords: lignin resin, shell mold, phenylpropane radical

1965-004

チオリグニンおよびフェノール化チオリグニンとホルムアルデヒドの反応  
小林晃夫、葉賀忠昭、佐藤孝一郎  
国策パルプ株式会社

Reaction of thiolignin and phenolated thiolignin with formaldehyde.  
Akio Kobayashi, Tadaaki Haga, Kouichiro Sato  
Kokusaku Pulp Co., Ltd.  
Keywords: thiolignin, phenolated thiolignin, formaldehyde, reaction

1965-005

アルカリ電池中のリグニンの挙動  
林 暁、名村好文、山下大二郎  
立命館大学理工学部

Behavior of lignin in alkaline battery.  
Akira Hayashi, Yosifumi Namura, Daijiro Yamashita  
College of Science and Engineering, Ritsumeikan University  
Keywords: thiolignin, electrode reaction

1965-006

亜硫酸パルプ排液の粘結性について  
町原 晃、岡部次郎  
山陽パルプ株式会社

Adhering ability of sulfite spent liquor.  
Akira Machihara, Jiro Okabe  
Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, adhering ability, casting sand, lignosulfonic acid, xylose

1965-007

亜硫酸パルプ廃液の 2、3 の粉体に対する分散効果について

猪狩俣将、小川博嗣、生源寺延

東京工業試験所

Dispersion ability of sulfite waste liquor to some kinds of powder material.

Yoshimasa Ikari, Hirotsugu Ogawa, Susumu Shogenji

Government Chemical Industrial Research Institute, Tokyo

Keywords: calcium carbonate, calcium hydroxide, Portland cement

1965-008

亜硫酸パルプ廃液およびリグニンスルホン酸の界面活性

小山 実、生源寺延

東京工業試験所

Surface activity of sulfite waste liquor and lignin sulfonic acid.

Minoru Koyama, Susumu Shogenji

Government Chemical Industrial Research Institute, Tokyo

Keywords: surface tension, interfacial surface tension, solubilization capacity, emulsifying capacity, dispersion force, osmotic force, foaming power

1965-009

加水分解リグニンから製造した陰イオン交換樹脂

載 清華、中野準三、右田伸彦

東京大学農学部

Anion exchange resin prepared from wood hydrolysis lignin.

Seika Tai, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: white birch (*Betula platyphylla*), chloromethylated lignin, quaternary ammonium-strong basic ion-exchange resin

1965-010

リグニンの水素化分解に関する研究(第 8 報)再生重質油をペースト油に使用するくりかえし運転について

宮崎 信<sup>\*1</sup>、石原達夫<sup>\*1</sup>、尾田勝夫<sup>\*1</sup>、田中治郎<sup>\*1</sup>、山口 彰<sup>\*1</sup>、高橋 敏<sup>\*1</sup>、古屋信子<sup>\*1</sup>、志水 一允<sup>\*1</sup>、榊原 彰<sup>\*2</sup>

<sup>\*1</sup> 林業試験場、<sup>\*2</sup> 北海道大学農学部

Hydrogenolysis of lignin. VIII. Repeated operation using recovered heavy oil as paste oil.

Shin Miyazaki<sup>\*1</sup>, Tatsuo Ishihara<sup>\*1</sup>, Masao Oda<sup>\*1</sup>, Jiro Tanaka<sup>\*1</sup>, Akira Yamaguchi<sup>\*2</sup>, Satoshi Takahashi<sup>\*1</sup>, Nobuko Furuya<sup>\*1</sup>, Kazumasa Simizu<sup>\*1</sup>, Akira Sakakibara<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Faculty of Agriculture, Hokkaido University

Keywords: SP waste lignin

1965-011

リグニンの水素化分解に関する研究(第 9 報)リグニンペーストの粘度

山口 彰<sup>\*1</sup>、宮崎 信<sup>\*1</sup>、石原達夫<sup>\*1</sup>、尾田勝夫<sup>\*1</sup>、田中治郎<sup>\*1</sup>、高橋 敏<sup>\*1</sup>、古屋信子<sup>\*1</sup>、志水一允<sup>\*1</sup>、榊原 彰<sup>\*2</sup>

\*<sup>1</sup> 林業試験場、\*<sup>2</sup> 北海道大学農学部

Hydrogenolysis of lignin. IX. Viscosity of lignin paste.

Akira Yamaguchi\*<sup>2</sup>, Shin Miyazaki\*<sup>1</sup>, Tatsuo Ishihara\*<sup>1</sup>, Masao Oda\*<sup>1</sup>, Jiro Tanaka\*<sup>1</sup>, Satoshi Takahashi\*<sup>1</sup>, Nobuko Furuya\*<sup>1</sup>, Kazumasa Simizu\*<sup>1</sup>, Akira Sakakibara\*<sup>2</sup>

\*<sup>1</sup>Forestry and Forest Products Research Institute, \*<sup>2</sup>Faculty of Agriculture, Hokkaido University

Keywords: SP waste lignin

1965-012

スチレンのリグニンへの放射線グラフト共重合における溶媒効果

村木永之介、越島哲夫

大阪工業技術試験所

Solvent effect of styrene on radiation-induced graft copolymerization onto lignin.

Einosuke Muraki, Tetsuo Koshijima

Government Industrial Research Institute, Osaka

Keywords: red pine (*Pinus densiflora*), hydrochloric acid lignin, methylated lignin, styrene

1965-013

塩酸リグニン・スチレングラフト重合生成物の性状と官能基

越島哲夫、村木永之介

大阪工業技術試験所

Properties and functional groups of hydrochloric acid lignin-styrene graft copolymer.

Tetsuo Koshijima, Einosuke Muraki

Government Industrial Research Institute, Osaka

Keywords: nitrobenzene oxidation, chlorite oxidation

1965-014

リグニンモデルのゲル化機構について

田中浩雄、千手諒一

九州大学農学部

Gelation mechanism of lignin model compounds.

Hiroo Tanaka, Ryoichi Senjyu

Faculty of Agriculture, Kyusyu University

Keywords: poly-(4-hydroxy)-styrene, novolac type phenolic resin

1965-015

モデル化合物のアルカリ分解生成物より見たリグニン側鎖の構造

田中治郎

林業試験場

Side chain structure of lignin estimated by alkaline degradation of model compounds.

Jiro Tanaka

Forestry and Forest Product Research Institute

Keywords: guaiacylthane

1965-016

広葉樹リグニンのアリルグリセロール-β-アリルエーテル型構造について

中野準三、何 照 =、右田伸彦

東京大学農学部

Arylglycerol- $\beta$ -aryl ether structure in hardwood lignin.

Junzo Nakano, Zhao Jun He, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: guaiacyl nucleus, syringyl nucleus, acetoguaiacone, acetosyringone

1965-017

リグニン中のピノレジノール構造について(第2報)

荻山紘一、近藤民雄

九州大学農学部

Pinoresinol structural units in lignin molecule. II.

Koichi Ogiyama, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: ethanol lignin, acetic acid lignin, dioxane lignin, milled wood lignin

1965-018

リグニンの色に関する研究(第2報)官能基がチオリグニンの色に及ぼす影響

飯山賢治、中野準三、右田伸彦

東京大学農学部

Studies on the color of lignin. II. Effect of functional groups on the color of thiolignin.

Kenji Iiyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: methylated lignin, chromophore, auxochrome

1965-019

リグニンの酸・アルカリ変性について

福渡七郎、瀬崎一敏

兵庫農科大学

Modification of lignin by treatment with acid and alkali.

Shichiro Fukuwatari, Kazutoshi Sezaki

Hyogo University of Agriculture

Keywords: sulfuric acid lignin, solubility

1965-020

リグニンの酸化分解に関する研究(第5報)過酢酸による模型化合物の酸化

石川久雄、沖 妙

愛媛大学農学部

Studies on the oxidative degradation of lignin. V. Oxidation of lignin model compounds by peracetic acid.

Hisao Ishikawa, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: guaiacyl methyl carbinol, vanillyl alcohol, acetovanillone, vanillin, vanillic acid

1965-021

リグニンの酸化分解に関する研究(第6報)過酸化漂白によるパルプからの脱リグニンについて

石川久雄、大久保克美、沖 妙

愛媛大学農学部

Studies on the oxidative degradation of lignin. VI. Delignification of pulp by peracetic acid bleaching.

Hisao Ishikawa, Katsumi Okubo, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: high yied pulp, semichemical pulp, groundwood pulp, dioxane lignin

1965-022

リグニンの過酢酸分解について(コハク酸の起源構造の追求)

畠山兵衛、中野準三、右田伸彦

東京大学農学部

Degradation of lignin by peracetic acid – Investigation of original structure from which succinic acid is derived.

Hyoe Hatakeyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: Yezo spruce (*Picea jezoensis*), succinic acid, vanillyl alcohol, veratryl alcohol

1965-023

リグニンに対する過酢酸の作用(第2報)

坂井克己、近藤民雄

九州大学農学部

Action of peracetic acid on lignin. II.

Kokki Sakai, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: red pine (*Pinus densiflora*), white birch (*Betula platyphylla*), dioxane lignin, infrared absorption spectrum

1965-024

MWL およびその抽出残渣リグニンの分解物における比較

榊原 彰、松倉紀男

北海道大学農学部

Comparison of degradation products from MWL and residual lignin.

Akira Sakakibara, Motoo Matsukura

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce (*Picea jezoensis*), veratric acid, isohemipic acid, dehydrodiveratric acid

1965-025

ジオキサン-水によるリグニンの加水分解(第5報)モデル物質の分解およびリグニン中における結合形態に対する2、3の考察

榊原 彰、武山浩武、諸星紀幸

北海道大学農学部

Hydrolysis of lignin with dioxane and water. V. Hydrolysis of lignin model compounds and discussion of linkage types in lignin.

Akira Sakakibara, Hirotake Takeyama, Noriyuki Morohoshi

Faculty of Agriculture, Hokkaido University

Keywords: coniferyl alcohol, veratrylglycerol- $\beta$ -guaiacyl ether, disproportionation reaction

1965-026

チオ・リグニンの反応、(その1)スルホ・メチル化反応

品部義秋、小川昭弘

東洋パルプ株式会社

Reaction of thioglignin. I. Sulfomethylation

Yoshiaki Shinabe, Akihiro Ogawa

Toyo Pulp Co., Ltd.

Keywords: dispersing agent, thioglignin, hydrophilicity, sulfomethylation, methylol group, air-entraining ability

1965-027

チオ・リグニンの反応、(その2) アミノ・メチル化反応

品部義秋, 小川昭弘

東洋パルプ株式会社

Reaction of thioglignin. II. Aminomethylation.

Yoshiaki Shinabe, Akihiro Ogawa

Toyo Pulp Co., Ltd.

Keywords: thioglignin, asphalt emulsifier, cationic surfactant, Mannich reaction

1965-028

チオリグニンのスルホメル化について

老田 靖、中野準三、右田伸彦

東京大学農学部

Sulfomethylation of thioglignin.

Yasushi Oita, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: softwood thioglignin, hardwood thioglignin, surface tension, dispersion force

1965-029

竹の維管束および柔細胞のリグニンの化学的性質

木村長治、樋口隆昌、川村一次

岐阜大学農学部

Chemical properties of lignin in vascular bundle and parenchyma of bamboo.

Choji Kimura, Takayoshi Higuchi, Ichiji Kawamura

Faculty of Agriculture, Gifu University

Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, nitrobenzene oxidation, ethanolysis

1965-030

種々のリグニン中の *p*-ヒドロキシフェニルグリセロール- $\beta$ -アリルエーテル構造

樋口隆昌、川村一次

岐阜大学農学部

*p*-Hydroxyphenylglycerol structures in lignin of various plants.

Takayoshi Higuchi, Ichiji Kawamura

Faculty of Agriculture, Gifu University

nitrobenzene oxidation, ethanolysis, gaschromatography, *Gramineae*

1965-031

ペルオキシダーゼによるコニフェリルアルコールの脱水素重合

野津祐三、中村 亘、奥貫一男

## 大阪大学理学部

Dehydrogenative polymerization of coniferyl alcohol by peroxidase.

Yuzo Nozu, Wataru Nakamura, Kazuo Okunuki

Faculty of Science, Osaka University

Keywords: laccase, molecular weight, sinapyl alcohol

### 1965-総合講演

- A リグニン研究の最近の動向  
中野準三(東京大学農学部)
- B リグニン生合成研究の現状と問題点  
樋口隆昌(岐阜大学農学部)
- C リグニンの利用と物性について  
林 暁(立命館大学)
- D 最近のパルプ廃液処理の動向  
野村順次(山陽パルプ株式会社)

### 1965-Plenary lectures:

- A Recent trends in research of lignin.  
Junzo Nakano (Faculty of Agriculture, the University of Tokyo)
- B Current situation of research in lignin biosynthesis and related problems.  
Takayoshi Higuchi (Faculty of Agriculture, Gifu University)
- C Physical properties and utilization of lignin.  
Akira Hayashi (Ritsumeikan University)
- D Recent trends in pulp waste liquor treatment.  
Junji Nomura (Sanyo Pulp Co. Ltd.)

## 第11回 (1966.10.31-11.1) 広島大学会館

### 1966-001

リグニンの色に関する研究(第3報) 蒸煮および単離条件がチオリグニンの色に及ぼす影響

飯山賢治、中野準三、右田伸彦

東京大学農学部

Studies on the color of lignin. III. Effect of cooking and isolation conditions on the color of thiolignin.

Kenji Iiyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: red pine (*Pinus densiflora*), beech (*Fagus crenata*), reflectance spectra, visible light transmittance, sulfur

### 1966-002

リグニンの色に関する研究(IV) 材のシーズニングがリグノスルホン酸の色に及ぼす影響について

中野準三、飯塚堯介、右田伸彦

東京大学農学部

Studies on the color of lignin. IV. Effect of seasoning on the color of liginosulfonic acid.

Junzo Nakano, Gyosuke Meshitsuka, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: *Abies firma*, *Pinus densiflora*, *Fagus crenata*, *Betula Maximowiziana*, brightness, wavelength, excitation purity

1966-003

重金属イオンとリグニンスルホン酸の色

林 暁、三成 紘

立命館大学理工学部

Heavy metal ion and color of lignosulfonic acid.

Akira Hayashi, Hiro Mitsunari

College of Science and Engineering, Ritsumeikan University

Keywords: chelation, iron, copper, nickel, cobalt, manganese, chromium, catechol group

1966-004

リグニンのオゾン分解について

畠山兵衛、外岡豊穂、中野準三、右田伸彦

東京大学農学部

Degradation of lignin by ozone.

Hyo Hatakeyama, Toyoho Tonooka, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: vanillyl alcohol, veratryl alcohol, muconic acid lactone

1966-005

リグノスルホン酸およびチオリグニンの過酢酸分解

鈴木金道<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>、中野準三<sup>\*2</sup>、右田伸彦<sup>\*2</sup>

<sup>\*1</sup>東北パルプ株式会社研究所、<sup>\*2</sup>東京大学農学部

Degradation of lignosulfonic acid and thiolignin by peracetic acid.

Kanemichi Suzuki<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>, Junzo Nakano<sup>\*2</sup>, Nobuhiko Migita<sup>\*2</sup>

<sup>\*1</sup>Institute of Tohoku Pulp Co. Ltd., <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: carboxyl group, phenolic hydroxyl group, methoxyl group, UV absorption spectrum

1966-006

二酸化塩素漂白に関する研究(I)モデル物質の二酸化塩素酸化について

石川俊彦、住本昌之、近藤民雄

九州大学農学部

Studies on the bleaching by chlorine dioxide.I. Oxidation of model compounds by chlorine dioxide.

Toshihiko Ishikawa, Masayuki Sumimoto, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: vanillin, vanillyl alcohol, syringyl alcohol, p-quinone structure

1966-007

リグノスルホン酸ゲル化反応中の脱メチル

林 暁、名村好夫、上北忠之

立命館大学理工学部

Demethylation during gelation reaction of lignosulfonic acid.

Akira Hayashi, Yoshio Namura, Tadayuki Uekita

College of Science and Engineering, Ritsumeikan University

Keywords: catechol group, dichromate, guaiacol, vanillin, vanillyl alcohol

1966-008

リグニン及びリグニンモデル物質の高分解能 NMR スペクトル

武谷 愿、横山 晋、石井忠雄

北海道大学工学部

High resolution NMR spectroscopy of lignin and lignin model compounds.

Gen Taketani, Shin Yokoyama, Tadao Ishii

Faculty of Engineering, Hokkaido University

Keywords: *Abies sachalinensis*, *Fagus crenata*, *Quercus crispula*, milled wood lignin, DMSO

1966-009

リグニンと炭水化物との結合について

寺島典二<sup>\*1</sup>、H.I. Bolker<sup>\*2</sup>

<sup>\*1</sup>名古屋大学農学部、<sup>\*2</sup>カナダ紙パルプ研研究所

Linkages between lignin and carbohydrates.

Noritsugu Terashima<sup>\*1</sup>, Henry I. Bolker<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Nagoya University, <sup>\*2</sup> Pulp and Paper Research Institute of Canada

Keywords: acetal, 2,2-dimethoxypropane, 2,2-diethoxypropane, solvolysis

1966-010

リグニン中のカルボキシル基定量

福渡七郎、錦織 勇

島根大学農学部

Determination of carboxyl group in lignin.

Shichiro Fukuwatari, Isamu Nishikori

Faculty of Agriculture, Shimane University

Keywords: Infrared absorption spectroscopy, potassium thiocyanate, soda-lignin, thiolignin

1966-011

稲科植物 MWL の化学的性質

樋口隆昌<sup>\*1</sup>、島田幹夫<sup>\*1</sup>、川村一次<sup>\*1</sup>、井藤佳美<sup>\*2</sup>

<sup>\*1</sup>岐阜大学農学部、<sup>\*2</sup>岐阜大学工学部

Chemical properties of milled wood lignin from gramineous plants.

Takayoshi Higuchi<sup>\*1</sup>, Mikio Shimada<sup>\*1</sup>, Ichiji Kawamura<sup>\*1</sup>, Yoshimi Itoh<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Gifu University, <sup>\*2</sup> Faculty of Engineering, Gifu University

Keywords: UV absorption spectroscopy, IR absorption spectroscopy, p-coumaric acid, ferulic acid, ester bond

1966-012

熱帯より温帯にわたり自然分布しているユーカリのリグニンの化学的性質について

川村一次<sup>\*1</sup>、D.E. Bland<sup>\*2</sup>

<sup>\*1</sup>岐阜大学農学部、<sup>\*2</sup>オーストラリア CSIRO 林産研究所

Chemical properties of lignin of eucalyptus distributed from tropical to temperate zone.

Ichiji Kawamura<sup>\*1</sup>, D.E. Bland<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Gifu University, <sup>\*2</sup> Forest Product Research Institute, CSIRO, Australia

Keywords: IR absorption spectroscopy, S/V ratio, Klason lignin, altitude effect

1966-013

樹皮リグニンの化学的性質

樋口隆昌<sup>\*1</sup>、島田幹夫<sup>\*1</sup>、川村一次<sup>\*1</sup>、井藤佳美<sup>\*2</sup>

\*<sup>1</sup>岐阜大学農学部、\*<sup>2</sup>岐阜大学工学部

Chemical properties of bark lignin.

Takayoshi Higuchi\*<sup>1</sup>, Mikio Shimada\*<sup>1</sup>, Ichiji Kawamura\*<sup>1</sup>, Yoshimi Itoh\*<sup>2</sup>

\*<sup>1</sup> Faculty of Agriculture, Gifu University, \*<sup>2</sup> Faculty of Engineering, Gifu University

Keywords: black pine, *Pinus Thunbergii*, fir, *Abies firma*, hemlock, *Tsuga heterophylla*, Alder, *Alnus japonica*, beech, *Fagus crenata*, ethanolysis

1966-014

ダグラスファー樹皮のエタノリシス生成物

藤井ミチヒロ\*<sup>1</sup>, E. F. Kurth\*<sup>2</sup>

\*<sup>1</sup>北越製紙, \*<sup>2</sup>オレゴン州立大

Ethanolysis products from Douglas fir bark.

Michihiro Fujii\*<sup>1</sup>, E. F. Kurth\*<sup>2</sup>

\*<sup>1</sup>Hokuetsu Paper Mills Co., Ltd., \*<sup>2</sup>Oregon State University

Keywords: Douglas fir, *Pseudotsuga taxifolia*, ethanolysis, Hibbert' s ketones

1966-015

ブナリグニンスルホン酸に関する研究(第2報)ブナリグニンスルホン酸分割物のニトロベンゼン酸化

秦邦男, 中村孝一

東北パルプ株式会社

Studies on beech lignosulfonates. II. Nitrobenzene oxidation of fractionated lignosulfonate portions.

Kunio Hata, Koichi Nakamura

Tohoku Pulp Co., Ltd.

Keywords: beech lignosulfonates, alkaline nitrobenzene oxidation, vanillin, syringyl aldehyde, *p*-hydroxybenzaldehyde

1966-016

リグニンに対するアルカリ蒸解の影響 (IX) アリルアルキル- $\beta$ -アリルエーテルの開裂に関するモデル実験

中野準三、鈴木 磨、佐伯節夫、右田伸彦

東京大学農学部

Effect of alkali cooking on lignin. IX. Model experiments on cleavage of arylalkyl- $\beta$ -aryl ether.

Junzo Nakano, Migaku Suzuki, Setsuo Saheki, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: kraft cooking, sulfidity, reaction temperature, paper chromatography, UV absorption spectroscopy

1966-017

ジオキサナー水によるリグニンの加水分解(第6報)

佐野嘉拓、榊原 彰

北海道大学農学部

Hydrolysis of lignin with dioxane and water. VI.

Yoshihiro Sano, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: coniferyl alcohol, isoeugenol, paper chromatography

1966-018

プロトリグニンの水素化分解に関する研究(第1報)ビフェニール結合体を中心として  
和田 功、太田路一、榊原 彰  
北海道大学農学部

Hydrogenolysis of protolignin. I. On the biphenyl type products.

Isao Wada, Michikazu Ota, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*, paper chromatography, 5,5'-biphenyl compounds

1966-019

モデル化合物のアルカリ分解生成物からみたリグニン側鎖の構造(II)

田中治郎  
林業試験場

Side chain structure of lignin estimated from alkaline degradation products of model compounds. II.

Jiro Tanaka

Forestry and Forest Product Research Institute

Keywords: guaiacyl ethane, ferulic acid, acetoguaiacone

1966-020

リグニン中のピノレジノール構造について(第3報)2,3-[Bis-oxyvanillyl]-butane-diol(1,4)から  
*d*-Pinoresinol の合成について

萩山紘一、近藤民雄  
九州大学農学部

Pinoresinol structure in lignin. III. Synthesis of dl-pinoresinol from 2,3-[bis-oxyvanillyl]-butane-diol(1,4).

Koichi Ogiyama, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: thin layer chromatography, symplocosigenol, epipinoresinol

1966-021

$\beta$ -ナフタレンスルホン酸ホルムアルデヒド縮合体(リグニンスルホン酸塩類似物質)の薄層クロマト  
グラフィーによる分離ならびにそれらの分子量と分子構造について

根来健二、佐伯幸民  
広島大学工学部

Separation of a condensation product of  $\beta$ -naphthalene sulfonic acid and formaldehyde (a compound analogous to lignin sulfonic acid) by thin layer chromatography, and its molecular weight, and chemical structure.

Kenji Negoro, Yukitami Saiki

Faculty of Engineering, Hiroshima University

Keywords: Tamol NNO, Demol N, gel filtration

1966-022

稲科植物リグニンの *p*-ヒドロキシフェニルプロパン部の性質とその形成におけるチラーゼの役割  
樋口隆昌\*<sup>1</sup>、川村一次\*<sup>1</sup>、井藤佳美\*<sup>2</sup>

\*<sup>1</sup>岐阜大学農学部、\*<sup>2</sup>岐阜大学工学部

Properties of *p*-hydroxyphenylpropane moiety in gramineous plant lignin and role of tyrase in its formation.

Takayoshi Higuchi<sup>\*1</sup>, Ichiji Kawamura<sup>\*1</sup>, Yosimi Itoh<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Gifu University, <sup>\*2</sup> Faculty of Engineering, Gifu University

Keywords: *p*-coumaric acid, *p*-hydroxyphenyl nucleus, phenylalanine-G-<sup>14</sup>C, tyrosine-G-<sup>14</sup>C

1966-023

タケノコ中の 5-デヒドロシキミ酸還元酵素

樋口隆昌、島田幹夫

岐阜大学農学部

5-Dehydroshikimic acid reductase in bamboo shoots.

Takayoshi Higuchi, Mikio Shimada

Faculty of Agriculture, Gifu University

Keywords: *Phyllostachys reticulata*, shikimic acid pathway, NADP, EDTA

1966-024

酵素によるフェルラ酸およびシナップ酸の生成

樋口隆昌、島田幹夫

岐阜大学農学部

Formation of ferulic and sinapic acids by enzyme.

Takayoshi Higuchi, Mikio Shimada

Faculty of Agriculture, Gifu University

Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, S-adenosylmethinine, caffeic acid, 5-dehydroferulic acid

1966-025

キンイロアナタケによって腐朽されたトウヒ材から分離したリグニンについて

幡 克美<sup>\*1</sup>、F.F. Nord<sup>\*2</sup>

<sup>\*1</sup>香川大学農学部、<sup>\*2</sup>フォードム大学

Studies on the lignin isolated from spruce wood rotted by *Poria subacida* B11.

Katsumi Hata<sup>\*1</sup>, F.F. Nord<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa Universty, <sup>\*2</sup>Fordham University

Keywords: spruce, *Picea jezoensis*, milled wood lignin, UV absorption spectrum, IR absorption spectrum, nitrobenzene oxidation

1966-026

リグニンの水素添加分解

大島幹義、鹿島 寛、田畑晴郎、久保輝雄、渡部 浩

野口研究所

亜硫酸パルプ廃液、脱スルホンリグニン、触媒

Hydrocracking of lignin.

Mikiyoshi Oshima, Hiroshi Kajima, Haruo Tabata, Teruo Kubo, Hiroshi Watanabe

Noguchi Institute

Keywords: sulfite pulp waste liquor, desulfonated lignin, catalyst

1966-027

鉛蓄電池に対するリグニンの効果

林 昶、名村好文  
立命館大学理工学部

Effect of lignin on lead storage battery.

Akira Hayashi, Yoshifumi Namura

College of Science and Engineering, Ritsumeikan University

Keywords: alkaline lignin, catechol, maleic acid

1966-028

液相及び気相アルカリ蒸解黒液から単離したリグニンの性状について

岡本行雄<sup>\*1</sup>、李 宗藩<sup>\*2</sup>、中野準三<sup>\*2</sup>、右田伸彦<sup>\*2</sup>

<sup>\*1</sup>東洋パルプ株式会社、<sup>\*2</sup>東京大学農学部

Characteristics of lignins isolated from the black liquor of liquid-phase and vapor-phase alkaline cookings.

Yukio Okamoto<sup>\*1</sup>, Sohan Ri<sup>\*2</sup>, Junzo Nakano<sup>\*2</sup>, Nobuhiko Migita<sup>\*2</sup>

<sup>\*1</sup>Toyo Pulp Co. Ltd., <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: alkafide pulping, kraft pulping, polysulfide pulping

1966-029

Na-S 系によるリグニンの脱メチル反応

種田健造、長谷川勇

北海道林産試験場

Demethylation of lignin in aqueous alkaline solution containing sulfur.

Kenzo Taneda, Isamu Hasegawa

Hokkaido Forest Products Research Institute

Keywords: dimethyl sulfide, acid hydrolysis lignin, conversion to resin

1966-030

亜硫酸パルプ廃液のアルカリ溶液中での挙動について

猪狩俣将、小川博嗣、生源寺延

東京工業試験所

Behavior of lignin in alkaline sulfite black liquor.

Yoshimasa Ikari, Hirotsugu Ogawa, Susumu Shogenji

Tokyo Institute of Advanced Industrial Science and Technology

Keywords: calcium hydroxide, cement, conductivity titration

1966-031

粉体の分散に対するリグニンスルホン酸と糖変成物の作用

小川博嗣、猪狩俣将、生源寺延

東京工業試験所

Effect of lignin sulfonic acid and metamorphic product of carbohydrates on dispersion of powder.

Hirotsugu Ogawa, Yoshimasa Ikari, Susumu Shogenji

Tokyo Institute of Advanced Industrial Science and Technology

Keywords: zinc powder, light absorption

1966-032

亜硫酸パルプ排液の熱処理による分散剤の製造について

町原 晃、岡部次郎

山陽パルプ株式会社

Preparation of dispersant by heat treatment of sulfite spent liquor.

Akira Machihara, Jiro Okabe

Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, dispersant, heat treatment, spray drying, lignosulfonic acid

1966-033

針葉樹のクラフト黒液からチオリグニンの沈澱

品部義秋、西部隆文

東洋パルプ株式会社

Precipitation of thiolignin from black liquor of kraft cooking of conifer wood.

Yoshiaki Shinabe, Takafumi Nishibe

Toyo Pulp Co. Ltd.

Keywords: precipitant, sulfuric acid, carbon dioxide, cohesion property

1966-034

KP 黒液およびチオリグニンの界面活性

小山 実、生源寺延

東京工業試験所

Surface activity of sulfite waste liquor and lignin sulfonic acid.

Minoru Koyama, Susumu Shogenji

Tokyo Institute of Advanced Industrial Science and Technology

Keywords: surface tension, solubilization capacity, emulsifying capacity, dispersion force, osmotic force, foaming power

1966-035

チオリグニンの熱的挙動

岩見田 紘、佐藤孝一郎

国策パルプ株式会社

Thermal properties of thiolignin.

Tadashi Iwamida, Kouichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: thiolignin, thermal gravimetric analysis, differential thermal analysis, insolubility, oxygen content, softening temperature

1966-036

リグニンのエポキシ化について

戴 洋華、中野準三、右田伸彦

東京大学農学部

Epoxidation of lignin.

Seika Tai, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: softwood lignin, coniferous wood lignin, epichlorohydrin, infrared spectroscopy

1966-037

フェノール化チオリグニンとヘキサメチレンテトラミンとの反応

小林晃夫、葉賀忠昭、佐藤孝一郎

国策パルプ株式会社

Reaction of phenolated thiolignin with hexamethylene tetramine.

Akio Kobayashi, Tadaaki Haga, Kouichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: thiolignin, phenolated thiolignin, hexamethylene tetramine, formaldehyde

1966-038

加水分解リグニン系樹脂に関する研究(第4報)装置試験および製造原単位

森 滋、布村昭夫、阿部 勲、北村維郎、窪田 実、朝倉孝之、齊藤 勝

北海道林産試験場

Studies on the plastics from wood hydrolysis lignin. IV. Equipment test and production intensity.

Shigeru Mori, Akio Nunomura, Isao Abe, Tadao Kitamura, Minoru Kubota, Takayuki Asakura, Masaru

Saito

Hokkaido Forest Products Research Institute

Keywords: thermosetting resin, continuous activation reaction, production intensity, operation cost

1966-特別講演

A

鑄型粘結剤について

東 正十郎

広島県呉工業試験所

1966-Invited lecture: Binder for casting mold.

Shojuro Azuma

Kure Institute of Industrial Science and Technology, Hiroshima Prefecture.

Keywords: bentonite, water glass, sodium silicate, cement, starch, drying oil, lignin binder

B

最近の界面活性剤の物性研究の動向

根来健二

広島大学工学部

1966-Invited lecture: Recent trend in the research of physical property of surfactant.

Kenji Negoro

Faculty of Engineering, Hiroshima University

Keywords: surface tension, surface adsorption, contact angle, cloud point

## 第12回(1967.11.1-2)九州大学農学部

1967-001

SP 排液中のリグニンスルホン酸と非リグニン有機物の粉体の分散に対する作用

小川博嗣、猪狩俣将、生源寺延

東京工業試験所

要旨空白(中止)

1967-002

リグニンの過酢酸酸化生成物の性状について

石川久雄、木下良郎、沖 妙、大久保克美

愛媛大学農学部

Characteristics of peracetic acid oxidation product of lignin.

Hisao Ishikawa, Yoshiro Kinoshita, Tae Oki, Katumi Okubo

Faculty of Agriculture, Ehime University

Keywords: conifer, dioxane lignin, molecular weight

1967-003

SP 排液中のリグニンスルホン酸の分子量分布とアルカリ溶液中での挙動

猪狩倅将、小川博嗣、生源寺延

東京工業試験所

Molecular weight distribution of lignin sulfonic acid from sulfite waste liquor and its behavior in alkaline solution.

Yoshimasa Ikari, Hirotsugu Ogawa, Susumu Shogenji

Tokyo Institute of Advanced Industrial Science and Technology

Keywords: hyamine salt, quaternary ammonium salt, electric conductivity titration, cement dispersing agent

1967-004

リグニンスルホン酸のゲル化に関する研究

秦邦男、中村孝一

東北パルプ株式会社

Studies on gelation of lignosulfonates.

Kunio Hata, Koichi Nakamura

Tohoku Pulp Co., Ltd

Keywords: beech, *Fagus crenata*, sulfite cooking black liquor, gelation, dicyclohexylamine-n-butanol extraction, potassium dichromate

1967-005

亜硫酸パルプ排液と重クロム酸の反応に関する2, 3の考察

岡部次郎、町原 晃、三浦義之

山陽パルプ株式会社

Reaction of sulfite spent liquor with dichromate

Jiro Okabe, Akira Machihara, Yoshiyuki Miura

Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, dichromate, soil stabilizer, lignosulfonic acid, gelation, chelate

1967-006

フェノール類の酸化のカップリング反応

熊野谿徒、加藤 隆

東京大学工学部

Oxidative coupling reaction of phenolic compounds.

Ju Kumanotani, Takashi Kato

Faculty of Engineering, the University of Tokyo

Keywords: quinone quinhydrone, quinone methide, radical reaction

1967-007

リグニンモデル化合物と過酢酸との反応における側鎖の影響

鈴木金道<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>、中野準三<sup>\*2</sup>、右田伸彦<sup>\*2</sup>

<sup>\*1</sup> 東北パルプ株式会社、<sup>\*2</sup> 東京大学農学部

Effect of side chain structure on the reaction of lignin model compounds with peracetic acid.

Kanemichi Suzuki<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>, Junzo Nakano<sup>\*2</sup>, Nobuhiko Migita<sup>\*2</sup>

<sup>\*1</sup>Tohoku pulp Co.Ltd., <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo.

Keywords: vanillyl alcohol, barium vanillyl sulfonate, vanillyl ethyl sulfide

1967-008

リグニンモデル化合物の過酢酸酸化分解について

沖 妙、木下良郎、石川久雄

愛媛大学農学部

Oxidation of lignin model compounds by peracetic acid.

Tae Oki, Yosiro Kinoshita, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: vanillyl alcohol, vanillin, guaiacylglycerol, isoeugenol, Baeyer-Villiger Reaction

1967-009

プロトリグニンの水素化分解に関する研究(第2報) 1,2-Diaryl Propane 構造を有する分解物の単離

太田路一、榊原 彰

北海道大学農学部

Hydrogenolysis of protolignin. II. Isolation of 1,2-diaryl propane type products.

Michikazu Ota, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*, paper chromatography, 1,2-bis-(4-hydroxy-3-methoxyphenyl)-propanol-3

1967-010

クラフトパルプの塩素による漂白について

寺島典二<sup>\*1</sup>、篠田善彦<sup>\*2</sup>、神田 孝<sup>\*1</sup>

<sup>\*1</sup>名古屋大学農学部、<sup>\*2</sup>岐阜大学農学部

Bleaching of kraft pulp with chlorine.

Noritsugu Terashima<sup>\*1</sup>, Yoshihiko Shinoda<sup>\*2</sup>, Takashi Kanda<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>Faculty of Agriculture, Gifu University

Keywords: vanillyl alcohol, quinhydrone, stilbene, lignin-carbohydrate bond

1967-011

サルファイト蒸解における着色構造の生成について

飯塚堯介、中野準三、右田伸彦

東京大学農学部

Formation of chromopholic structures during sulfite cooking.

Gyosuke Meshitsuka, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: red pine, *Pinus densiflora*, birch, *Betula maximowiczii*, lignin sulfonic acid, combined sulfur dioxide, catechol, hemicellulose

1967-012

リグニン中のラジカルの温度依存性

畠山兵衛、中野準三、右田伸彦

東京大学農学部

Temperature dependence of stability of radical in lignin.

Hyoue Hatakeyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: electron spin resonance, broad line nuclear magnetic resonance, milled wood lignin, dioxane lignin, lignin sulfonic acid

1967-013

樹皮の難溶性リグニンについて

十河村男、幡 克美

香川大学農学部

Low-solubility lignin in tree bark.

Murao Sogo, Katsumi Hata

Faculty of Agriculture, Kagawa University

Keywords: red pine, *Pinus densiflora*, Yezo spruce, *Picea jezoensis*, *Acacia*, Japanese oak, *Quercus crispula*, *Quercus serrata*, chestnut, *Castanea crenata*, dioxane lignin

1967-014

MWL、LCC およびその抽出残渣リグニンの分解物における比較(第2報)

松倉紀男、榊原 彰

北海道大学農学部

Comparison of degradation products of MWL, LCC and lignin in extracted residue. II.

Motoo Matsukura, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: protolignin, potassium permanganate oxidation, nitrobenzene oxidation, ethanolysis, condensed structure

1967-015

リグニン樹脂発泡体製造に関する研究 —縮合に関する二、三の知見—

森 滋、阿部 勲、峯村伸哉、窪田 実

北海道林産試験場

Production of plastics form from lignin. — Results obtained from condensation test—.

Shigeru Mori, Isao Abe, Shinya Minemura, Minoru Kubota

Hokkaido Forest Products Research Institute

Keywords: kraft lignin, formaldehyde, hydroxymethylated lignin

1967-016

チオリグニンのイソシアネート化について

戴 清華、沢登丈夫、中野準三、右田伸彦

東京大学農学部

Reaction of thiolignin with triline diisocyanate.

Seika Tai, Takeo Sawanobori, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: urethane bond, allophanate bond, *m*-phenylenediamine, polyethyleneglycol

1967-017

リグニンと合成高分子化合物との共縮合に関する研究 —ポリメタアクリロクロライドと諸種水酸基とのエステル化反応

内藤寿夫、福住俊郎、南 享二

東京大学農学部

Studies on the copolymerization of lignin with synthetic polymer. —Esterification of several hydroxyl compounds with polymethacryloyl chloride.

Hisao Naito, Toshio Fukuzumi, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: phenol, methoxyphenol, vanillyl alcohol, NMR spectra

1967-018

放射線の空气中前照射によるリグニンのグラフト化

村木永之介、越島哲夫

大阪工業技術試験所

Grafting of lignin with pre-radiation in air.

Einosuke Muraki, Tetsuo Koshijima

Osaka Institute of Advanced Industrial Science and Technology

red pine, *Pinus densiflora*, hydrochloric acid lignin, lignin sulfonic acid, styrene

1967-019

リグニンモデル化合物のアルカリ蓄電池に対する作用

林 暁、木下恭介

立命館大学理工学部

Effect of lignin models on alkali storage battery.

Akira Hayashi, Kyosuke Kinoshita

College of Science and Engineering, Ritsumeikan University

Keywords: thioglignin, catechol, guaiacol, pyrogallol, maleic acid, chelate

1967-020

亜硫酸パルプ廃液活性炭について

岸本 定吉<sup>\*1</sup>、森 見二<sup>\*2</sup>

<sup>\*1</sup>東京教育大学農学部、<sup>\*2</sup>静岡大学農学部

Production of active carbon from sulfite waste liquor.

Teikichi Kishimoto, Kenji Mori

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Education, <sup>\*2</sup>Faculty of Agriculture, Shizuoka University

Keywords: activation by zinc chloride, water vapor activation

1967-021

フェニルプロパン誘導体のガスクロマトグラフィ

山口 彰、宮崎 信、高橋 敏

林業試験場

Gas chromatography of phenylpropane derivatives.

Akira Yamaguchi, Makoto Miyazaki, Satoshi Takahashi

Forestry and Forest Products Research Institute

Keywords: trimethylsilylether, side-chain structure, side-chain hydroxyl group

1967-022

リグニンの電子スペクトルの解析

飯山賢治、中野準三、右田伸彦

東京大学農学部

Resolution of electronic spectra of lignin.

Kenji Iiyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: Yezo spruce, *Picea jezoensis*, milled wood lignin, lignin sulfonic acid, absorption band, guaiacyl nucleus, syringyl nucleus

1967-023

チオリグニンのポーラログラフ的研究(第12報)アルカリ蒸解中におけるクアヤシル核5位置換構造の生成について

玉生征人、寺島典二、神田 孝

名古屋大学農学部

Polarography of lignin (XII). Formation of substructure with substitution at 5 position of guaiacyl nucleus during alkali pulping.

Masato Tamao, Noritsugu Terashima, Takashi Kanda

Faculty of Agriculture, Nagoya University

Keywords: red pine, *Pinus densiflora*, thiolignin, polarography, alkaline cooking, guaiacyl nucleus, condensed unit

1967-024

担子菌によるリグニンの分解における芳香族化合物添加の影響

原口隆英

東京農工大学農学部

Effect of addition of aromatic compounds on the degradation of lignin by basidiomycetes.

Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Pycnoporus coccineus*, Yezo spruce, *Picea jezoensis*, benzoic acid, *p*-hydroxybenzoic acid, vanillic acid, ferulic acid

1967-025

木材腐朽菌の酵素によるリグニンの分解 -リグニンのアリルアルキルエーテル結合の分解

福住俊郎、南 享二

東京大学農学部

Degradation of lignin by enzyme of wood-rotting fungi. -Cleavage of arylalkyl ether bond.

Toshio Fukuzumi, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: Yezo spruce, *Picea jezoensis*, *Perenniporia subacida*, veratrylglycerol- $\beta$ -guaiacyl ether, laccase

1967-026

タケノコの木化におけるO-メチルトランスフェラーゼの役割について

樋口隆昌、島田幹夫、大橋英雄

岐阜大学農学部

Role of *O*-methyltransferase in lignification of bamboo shoot.

Takayoshi Higuchi, Mikio Shimada, Hideo Ohashi

Faculty of Agriculture, Gifu University

Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, caffeic acid, S-adenosylmethionine, ferulic acid, sinapic acid

1967-027

タケノコの木化に伴う関連酵素の変動について

樋口隆昌、島田幹夫

岐阜大学農学部

Change of activity of enzymes involved in lignification of bamboo.

Takayoshi Higuchi, Mikio Shimada

Faculty of Agriculture, Gifu University

Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, phenylalanine ammonia-lyase, peroxidase

### 第 13 回 (1968.10.26-27)名古屋大学農学部

1968-001

リグニンのメキシル基生成に関する生化学的研究

樋口隆昌<sup>\*1</sup>、島田幹夫<sup>\*2</sup>、大橋英雄<sup>\*2</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>岐阜大学農学部

Biochemical study on the formation of methoxyl groups of lignin.

Takayoshi Higuchi<sup>\*1</sup>, Mikio Shimada<sup>\*2</sup>, Hideo Ohashi<sup>\*2</sup>

<sup>\*1</sup> Wood Research Institute, Kyoto University, <sup>\*2</sup> Faculty of Agriculture, Gifu University

Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, *Ginkgo biloba*, *Cryptomeria japonica*, *Podocarpus macrophyllus*, yew, *Taxus cuspidate*, autoradiography, *O*-methyltransferase

1968-002

稲科植物リグニン中の *p*-クマール酸のエステル結合に関する研究

樋口隆昌<sup>\*1</sup>、島田幹夫<sup>\*2</sup>、山崎 徹<sup>\*1</sup>、福塚 哲<sup>\*2</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>岐阜大学農学部

Studies on the *p*-coumaric ester bond of grass lignin.

Takayoshi Higuchi<sup>\*1</sup>, Mikio Shimada<sup>\*2</sup>, Toru Yamasaki<sup>\*1</sup>, Tetsu Fukuzuka<sup>\*2</sup>

<sup>\*1</sup> Wood Research Institute, Kyoto University, <sup>\*2</sup> Faculty of Agriculture, Gifu University

Keywords: bamboo, *Arundo donax*, *Coix*, *Phragmites*, DHP

1968-003

木材腐朽菌によるリグニンの分解

石原達夫、宮崎 信

林業試験場

Degradation of lignin by wood-rotting fungi.

Tatsuo Ishihara, Makoto Miyazaki

Forestry and Forest Product Research Institute

Keywords: *Polyporus versicolor*, milled wood lignin, catechol, *Pseudomonas*

1968-004

樹皮リグニンの定量について

十河村男、幡 克美

香川大学農学部

Determination of lignin content in bark.

Murao Sogo, Katsumi Hata

Faculty of Agriculture, Kagawa University

Keywords: *Japanese red pine*, *Pinus densiflora*, *Yezo spruce*, *Picea jezoensis*, *Quercus serrata*, *chestnut*, *Castanea crenata*, *cork oak*, *Quercus variabilis*, Klason lignin, dioxane lignin

1968-005

リグニンの親水性に関する研究

岡部次郎, 工藤正邦

山陽パルプ株式会社

Studies on hydrophilicity of lignin

Jiro Okabe, Masakuni Kudo

Sanyo Pulp Co., Ltd.

Keywords: dioxane lignin, hydrophilicity, hygroscoy

1968-006

多段漂白における塩素化-アルカリ抽出(III)塩素化された DL の吸湿性について

河内 進策、武井 斎

宮崎大学農学部

Chlorination-alkali extraction in multistage bleaching. III. Hygroscoy of chlorinated dioxane lignin.

Shinsaku Kawachi, Hitoshi Takei

Faculty of Agriculture, Miyazaki University

Keywords: red pine, *Pinus densiflora*, *Machilus thunbergii*, dioxane lignin

1968-007

可塑剤によるリグニンの可塑化について

坂田 功、青柳祥二、千手諒一

九州大学農学部

Plasticization of lignin by plasticizer.

Isao Sakata, Shoji Aoyagi, Ryoichi Senju

Faculty of Agriculture, Kyusyu University

Keywords: red pine, *Pinus densiflora*, dioxane lignin, thiolignin, phthalic acid ester, tributyl phosphate, softening temperature

1968-008

チオリグニンの加熱時における活性基量の変化について

岩見田 糺, 佐藤孝一郎

国策パルプ株式会社

Change in the amount of reactive groups during heat treatment of thiolignin.

Tadashi Iwamida, Koichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: reactive groups, alcoholic hydroxyl group, phenolic hydroxyl group, carboxyl group

1968-009

リグニンラジカルの性状について

畠山兵衛<sup>\*1</sup>、籾野 晃<sup>\*1</sup>、中野準三<sup>\*2</sup>、右田伸彦<sup>\*2</sup>

<sup>\*1</sup>アラスカパルプ株式会社、<sup>\*2</sup>東京大学農学部

Properties of radical in lignin.

Hyoë Hatakeyama<sup>\*1</sup>, Akira Hatano<sup>\*1</sup>, Junzo Nakano<sup>\*2</sup>, Nobuhiko Migita<sup>\*2</sup>

<sup>\*1</sup>Alaska Pulp Co. Ltd., <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compounds, electron spin resonance spectra, milled wood lignin, dioxane lignin, calcium lignosulfonate, thiolignin,  $\gamma$ -ray irradiation

1968-010

リグニン分子中のピノレジノール構造について(第5報)酸アルカリ処理とピノレジノール構造

荻山紘一、近藤民雄

九州大学農学部

On the pinoresinol type of structural units in lignin molecule. V. Effect of acid or alkali treatment on pinoresinol structures.

Koichi Ogiyama, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: Japanese red pine, *Pinus densiflora*, *Cryptomeria japonica*, *Betula Tauschii*, *Shorea negrosensis*, dioxane lignin, symplocosigenol

1968-011

アルカリ処理によるリグニン分子の変化 —NMRによる芳香環置換度の測定について

諸星紀幸、榊原 彰

北海道大学農学部

Change in lignin molecule by alkaline treatment. — Determination of condensed type unit by NMR spectroscopy.

Noriyuki Morohoshi, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*, milled wood lignin, assignment of proton signal

1968-012

液安中金属ナトリウムによるリグニンの分解

山口 彰、広居忠量、宮崎 信

林業試験場

Degradation of lignin with metallic sodium in liquid ammonia.

Akira Yamaguchi, Tadakazu Hiroi, Makoto Miyazaki

Keywords: Yezo spruce, *Picea jezoensis*, milled wood lignin, lignin carbohydrate complex, paper chromatography, gas chromatography

1968-013

プロトリグニンの水素化分解(第4報)フェニルクマラン開環型分解物の単離、同定について

松倉紀男、榊原 彰

北海道大学農学部

Hydrogenolysis of protolignin. IV. Isolation and identification of open-ring-phenylcoumaran type products.

Motoo Matsukura, Akira sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*, thin-layer chromatography, gas chromatography, 1-(4-hydroxy-3-methoxyphenyl)-2-(2'-hydroxy-3'-methoxy-5'-propylphenyl)-propane

1968-014

ジオキサン-水によるリグニンの加水分解(第8報)

佐野嘉拓、榊原 彰

北海道大学農学部

Hydrolysis of lignin with dioxane and water. VIII.

Yoshihiro Sano, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: column chromatography, *p*-hydroxyphenylglycerol, NMR, UV absorption spectroscopy

1968-015

Björkman リグニンの酸素酸化に関する研究

渡辺貞良、林 治助、戸坂圀夫、小林昌子

北海道大学工学部

Oxidation of Björkman lignin with oxygen.

Sadayoshi Watanabe, Jisuke Hayashi, Kunio Tosaka, Masako Kobayashi

Faculty of Engineering, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*, functional group, hydroxyl group, carboxyl group, infrared absorption spectroscopy

1968-016

リグニンスルホン酸の電解酸化

小川博嗣、富田由明

東京工業試験所

カルボキシル基、メトキシル基

Electrolytic oxidation of lignin sulfonic acid.

Hirotsugu Ogawa, Yoshiaki Tomita

Tokyo Institute of Advanced Industrial Science and Technology

Keywords: carboxyl group, methoxyl group,

1968-017

電子スペクトルの解析によるリグニンの着色機構の検討

飯山賢治、中野準三、右田伸彦

東京大学農学部

Studies on the coloring mechanism of lignin by the electronic spectral analysis.

Kenji Iiyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: thiolignin, milled wood lignin, lignin model compounds, adsorption band, vanillyl alcohol, assignment of absorption band

1968-018

リグニンに対する亜ニチオン酸塩の反応機構について

細谷修二、畠山兵衛、中野準三、右田伸彦

東京大学農学部

Reaction mechanism of sodium hydrosulfite with lignin.

Shuji Hosaya, Hyoe Hatakeyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: calcium lignosulfonate, lignin model compounds, vanillin, acetoguaiacone, isoeugenol,  $\alpha$ -quinone

1968-019

リグニン脱メチル生成物の着色について

林 暁、上北忠之

立命館大学理工学部

Coloring of demethylated lignin.

Akira Hayashi, Tadayuki Kamikita

College of Science and Engineering, Ritsumeikan University

Keywords: guaiacol, 1-cyclopentene carboxylic acid, catechol, quinhydrone, quinone

1968-020

サルファイト蒸解におけるリグニンの着色について

飯塚堯介、川上菊士、中野準三、右田伸彦

東京大学農学部

Coloring of lignin during sulfite cooking.

Gyosuke Meshitsuka, Kikuo Kawakami, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: fir, *Abies firma*, functional group, UV absorption difference spectroscopy

1968-021

Hydrotropic cooking について

村主信彦、近藤民雄

九州大学農学部

Studies on the hydrotropic cooking.

Nobuhiko Suguri, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: xylene sulfonic acid, toluene sulfonic acid, benzene sulfonic acid, benzoic acid, surface tension

1968-022

リグニンの蓄電池に及ぼす効果について

林 暁、木下恭介

立命館大学理工学部

Effect of addition of lignin to battery.

Akira Hayashi, Kyousuke Kinoshita

College of Science and Engineering, Ritsumeikan University

Keywords: polyphenol, chelating agent, catechol, resorcinol

1968-023

リグノスルホン酸塩の色におよぼす重金属イオンの影響

飯塚堯介、中野準三、右田伸彦

東京大学農学部

Effect of heavy metal ions on the color of lignosulfonate.

Gyosuke Meshitsuka, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo

Keywords: iron, copper, nickel, vanadium, manganese, chromium, visible light absorption spectra

1968-024

リグノスルホン酸類と各種金属イオンとの反応性

猪狩俣将, 横山正一郎, 室井和彦

東京工業試験所

Reactivity of various metal ions with lignosulfonic acid.

Yoshimasa Ikari, Shoichiro Yokoyama, Kazuhiko Muroi

Tokyo Institute of Advanced Industrial Science and Technology

Keywords: iron, calcium, cadmium, nickel, copper, chromium, manganese, UV light absorption spectroscopy

1968-025

亜硫酸パルプ排液と重クロム酸の反応に関する研究(第2報)

岡部次郎, 町原 晃, 三浦義之

山陽パルプ株式会社

Reaction of sulfite spent liquor with dichromate. Part.

Jiro Okabe, Akira Machihara, Yoshiyuki Miura

Sanyo Pulp Co., Ltd.

Keywords: soil stabilizer, lignosulfonic acid, sugar, gelation, chelate

1968-026

ポリフェノールの酸化カップリング反応

熊野谿従, 加藤 隆

東京工業大学

Oxidative coupling reaction of polyphenols.

Ju Kumanotani, Takashi Kato

Tokyo Institute of Technology

Keywords: urushiol, thin layer chromatography, *o*-quinone, nuclear magnetic resonance

1968-027

重クロム酸塩によるフェノールの酸化カップリング

田中浩雄, 坂田 功, 千手諒一

九州大学農学部

Oxidative coupling of phenols by potassium dichromate.

Hiroo Tanaka, Isao Sakata, Ryoichi Senjyu

Faculty of Agriculture, Kyusyu University

Keywords: *p*-cresol, creosol, manganese

1968-028

リグニンのゲル化機構

田中浩雄, 坂田 功, 千手諒一

九州大学農学部

Gelation mechanism of lignin.

Hiroo Tanaka, Isao Sakata, Ryoichi Senjyu

Faculty of Agriculture, Kyusyu University

Keywords: chromium, chelate, lignin sulfonic acid, polyhydroxystyrene sulfonic acid

## 第 14 回(1969.10.28-29)東京、日本化学会講堂

1969-001

アテ材リグニンの化学的特性に関する研究(第2報)

諸星紀幸、榊原 彰

北海道大学農学部

Chemical properties of of compression wood. II.

Noriyuki Morohoshi, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Abies mayriana*, *Fraxinus excelsissima*, milled wood lignin, lignin carbohydrate complex, potassium permanganate oxidation, ethanolysis, nitrobenzene oxidation, gas chromatography

1969-002

ジオキサソール水によるリグニンの加水分解(第9報)

佐野嘉柘、榊原 彰

北海道大学農学部

Hydrolysis of lignin with dioxane and water. IX.

Yoshihiro Sano, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: guaiacylglycerol, 1,2-bisguaiacylpropane1,3-diol, NMR, mass spectrometry

1969-003

AP 法廃液からのアルカリ・リグニンの性状について

香川詔士、内田 壮

関東学院大学工学部

Characteristics of alkali lignin in soda pulping waste liquor.

Shoji Kagawa, So Uchida

Faculty of Engineering, Kanto Gakuin University

Keywords: larch, *Larix Kaempferi*, soda pulping waste liquor, hydrochloric acid lignin, differential thermal analysis, nitrobenzene oxidation

1969-004

クラフト蒸解中におけるグアヤシル核 5 位置換型構造の生成について

玉生征人、寺島典二

名古屋大学農学部

Formation of guaiacyl nucleus with substitution at position 5 during kraft pulping.

Masato Tamao, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords:  $^{14}\text{C}$ -labeled lignin model compounds, guaiacylglycerol- $\beta$ -guaiacyl ether- $[\alpha\text{-}^{14}\text{C}]$ , guaiacylglycerol- $\beta$ -guaiacyl ether- $[\beta\text{-}^{14}\text{C}]$ , guaiacylglycerol- $\beta$ -guaiacyl ether- $[\gamma\text{-}^{14}\text{C}]$ ,

1969-005

リグニン中のピノレジノール構造について(第6報)KP蒸解とピノレジノール構造との関係  
荻山紘一、谷口栄一  
山形大学農学部

Pinoresinol structure in lignin. VI. Behavior of pinoresinol structure during kraft cooking.  
Koichi Ogiyama, Eichi Taniguchi  
Faculty of Agriculture, Yamagata University

Keywords: *Symplocos lucida*, *Pinus densiflora*, *Betula tauschii*, symplocosin, symplocosigenol, syringaresinol

1969-006

リグノスルホン酸塩中の共役二重結合について  
飯塚堯介、中野準三  
東京大学農学部

Conjugated double bonds in lignosulfonate.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: coniferaldehyde, coniferyl alcohol, stilbene, chalcone, phenylcoumaran

1969-007

リグニン分解木材腐朽菌(未同定菌)によるアセトン・リグニンの分解生成物  
福住俊郎、南 享二  
東京大学農学部

Degradation products of acetone lignin by a wood-rotting fungus (unidentified white rot type).

Toshio Fukuzumi, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: Yezo spruce, *Picea jezoensis*, jar-fermentor, hydroxymatairesinol

1969-008

カラタケ酵素のワニリン酸に対する挙動  
石原達夫、宮崎 信  
林業試験場

Behavior of enzyme of *Polyporus versicolor* on vanillic acid.

Tatsuo Ishihara, Makoto Miyazaki

Forestry and Forest Product Research Institute

Keywords: laccase, peroxidase, UV spectroscopy, IR spectroscopy, NMR

1969-009

広葉樹の葉における芳香核構造の季節的変動  
田中治郎、千野広子  
林業試験場

Seasonal change of aromatic structures in the leaves of hardwood.

Jiro Tanaka, Hiroko Chino

Forestry and Forest Product Research Institute

Keywords: sycamore, *Platanus occidentalis*, nitrobenzene oxidation, formation of aldehydes

1969-010

Hydrotropic Cooking について(II)

村主信彦、近藤民雄

九州大学農学部

Hydrotropic Cooking. II.

Nobuhiko Suguri, Tamio kondo

Faculty of Agriculture, Kyusyu University

Keywords: sodium xylenesulfonate, sodium benzoate, gel filtration chromatography

1969-011

リグニンの水溶性化に関する研究

工藤正邦, 岡部次郎

山陽パルプ株式会社

Studies on water solubilization of lignin.

Masakuni Kudo, Jiro Okabe

Sanyo Pulp Co., Ltd.

Keywords: solubilization, dioxane lignin, sulfonation, hygroscoy, sulfonic group

1969-012

ゲル濾過法によるリグノスルホン酸類の分別

猪狩俣将、横山正一郎

東京工業試験所

Fractionation of lignosulfonic acids by gel filtration chromatography.

Yoshimasa Ikari, Shoichiro Yokoyama

Tokyo Institute of Advanced Industrial Science and Technology

Keywords: molecular weight distribution, sephadex, affinity

1969-013

リグノスルホン酸とスチレンのグラフト共重合における Fe[III]イオンによる酸化の効果

村木永之介、越島哲夫

大阪工業技術試験所

Effect of oxidation with ferric ion on the copolymerization of lignosulfonic acid and styrene.

Einosuke Muraki, Tetsuo Koshijima

National Industrial Research Institute of Osaka

Keywords: vanillyl sulfonic acid, graft polymer

1969-014

フェノール系高分子(リグニンモデル)の合成とその重クロム酸塩によるゲル化

田中浩雄、坂田 功、千手諒一

九州大学農学部

Synthesis of phenolic polymers (lignin model) and their gelation by dichromate.

Hiroo Tanaka, Isao Sakata, Ryoichi Senju

Faculty of Agriculture, Kyusyu University

Keywords: poly-4-hydroxystyrenesulfonic acid, poly-4-hydroxy-3-methoxystyrene sulfonic acid, poly-4-hydroxy-3,5-dimethoxystyrene sulfonic acid, viscosity, molecular weight

1969-015

リグニンゲルとポリウロン酸ゲルの粘性について

石川久雄、木下良郎、大久保克美、沖 妙

愛媛大学農学部

Viscosity of lignin gel and polyuronide gel.

Hisao Ishikawa, Yoshiro Kinoshita, Katsumi Okubo, Tae Oki

Faculty of Agriculture, Ehime University

Keywords: *Abelmoschus manihot*, alginate, lignin sulfonic acid, calcium ion

1969-016

ベラトリルスルホン酸の電解酸化

小川博嗣、戸倉保司

東京工業試験所

Electrolytic oxidation of veratryl sulfonic acid.

Hiroshi Ogawa, Yasusi Tokura

National Industrial Research Institute of Tokyo

Keywords: pH, UV absorption spectra, demethylation

1969-017

チオリグニンの熱重合時における生成ガスについて

岩見田 紘

国策パルプ株式会社

Gases generated during polymerization of thiolignin by heat treatment.

Tadashi Iwamida

Kokusaku Pulp Co., Ltd.

Keywords: heat treatment, polymerization, gaschromatography

1969-018

リグニンの DSC による熱解析

畠山兵衛、久保田勝也

製品科学研究所

Thermal analysis of lignin by differential scanning calorimetry.

Hyo Hatakeyama, Masaya Kubota

Industrial Products Research Institute

Keywords: glass transition temperature, differential scanning calorimetry, milled wood lignin, dioxane lignin, thiolignin, calcium lignosulfonate

1969-019

リグニンモデル化合物の過酢酸酸化分解について

沖 妙、木下良郎、石川久雄

愛媛大学農学部

Oxidative degradation of lignin model compounds by peracetic acid.

Tae Oki, Yoshiro Kinoshita, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: Baeyer-Villiger reaction, dehydrodiisoeugenol, isoeugenol, UV absorption spectroscopy

1969-020

パルプ廃液の色に関する研究 (I) KP 晒廃液の色とオキシリグニン

鮫島一彦、近藤民雄

九州大学農学部

Studies on the color of pulping waste liquor. I. Color of waste liquor from kraft pulp bleaching and oxygignin.

Kazuhiko Sameshima, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: Japanese red pine, *Pinus densiflora*, *Betula Tauschii*, multistage bleaching, UV absorption spectroscopy

## 第 15 回(1970.10.8-9)札幌市民会館

1970-001

タケリグニンのメキシル基生成に関する生化学的研究

島田幹夫、樋口隆昌

京都大学木材研究所

Biochemical studies on the formation of methoxyl groups in bamboo lignin.

Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phyllostachys reticulata*, bamboo shoot, *O*-methyltransferase, caffeic acid-2-<sup>14</sup>C, ferulic acid-2-<sup>14</sup>C, *S*-adenosyl methionine

1970-002

タケ及びイネ科植物リグニン中の *p*-クマール酸エステル結合に関する研究

島田幹夫、樋口隆昌

京都大学木材研究所

Studies on the coumaric acid ester bonds in lignins of bamboo and gramineous plants.

Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: dehydrogenative polymer, coniferyl alcohol, UV absorption spectra, radio-labeled *p*-coumaric acid, methanolysis

1970-003

コニフェリルアルコールの脱水素重合におよぼすヘミセルロースの影響

樋口隆昌、荻野桂作

京都大学木材研究所

Effect of hemicelluloses on dehydrogenative polymerization of coniferyl alcohol.

Takayoshi Higuchi, Keisaku Ogino

Wood Research Institute, Kyoto University

Keywords: pectin, peroxidase, dehydrogenative polymer, molecular weight, UV absorption spectra

1970-004

酵素によるリグニンのエーテル結合の分解

松本 久、福住俊郎、南 享二

東京大学農学部

Cleavage of ether bonds in lignin by enzyme.

Hisashi Matsumoto, Toshiro Fukuzumi, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: wood rotting fungi, *Perenniporia subacida*, thin layer chromatography, gas chromatography

1970-005

放線菌の一種によるリグニンの分解

原口隆英

東京農工大学農学部

Degradation of lignin by *Actinomycetes* sp.

Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: potassium lignosulfonate, vanillic acid, UV absorption spectrometry, chemical oxygen demand

1970-006

ヒノキ-MWL 及び LCC の化学特性、その分子量分布について

広居忠量、宮崎 信

林業試験場

Chemical properties of MWL and LCC of Japanese cypress, and their molecular weight distribution.

Tadakazu Hiroi, Makoto Miyazaki

Forestry and Forest Products Research Institute

Keywords: Japanese cypress, *Chamaecyparis obtusa*, gel permeation chromatography, number average molecular weight, vapor pressure osmometry

1970-007

液安中の金属ナトリウムによるリグニンの分解(II)

山口 彰、宮崎 信

林業試験場

要旨なし(中止)

1970-008

サルファイト蒸解過程におけるリグニンの酸加水分解について

飯塚堯介、中野準三

東京大学農学部

Acid hydrolysis of lignin during sulfite cooking process.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: red pine, *Pinus densiflora*, repeating unit, lignosulfonic acid, molecular weight distribution, gel filtration chromatography

1970-009

塩化アルミニウムによるリグノスルホン酸塩の凝集沈澱について

飯塚堯介、徐道太郎、中野準三

東京大学農学部

Precipitation of lignisulfonate by coagulation with aluminum chloride.

Gyosuke Meshitsuka, Michitaro Jo, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: softwood, conifer, gel filtration, pH, phenolic hydroxyl group, alcoholic hydroxyl group

1970-010

リグノスルホン酸塩とメタクリル酸メチルのフエントン試薬によるグラフト重合反応(その1)

南正院、斉藤雅康、村木永之介、越島哲夫

大阪工業技術試験所

Graft polymerization of lignosulfonate and methyl methacrylates by Fenton's reagent. I.

Zeong-Woun Nam, Masayasu Saito, Einosuke Muraki, Tetsuo Koshijima

Osaka Institute of Advanced Industrial Science and Technology

Keywords: softwood, conifer, molecular weight, veratryl sulfonic acid *p*-hydroxybenzylsulfonic acid

1970-011

木材パルプのアクリルアミドグラフト重合にたいするリグニンの影響

小林晃夫<sup>\*1</sup>、W. Brown<sup>\*2</sup>、V. Stannett<sup>\*3</sup>

<sup>\*1</sup>国策パルプ株式会社、<sup>\*2</sup>Uppsala 大学、<sup>\*3</sup>North Carolina 州立大学

Influence of lignin on graft polymerization of acrylamide to wood pulp

Akio Kobayashi<sup>\*1</sup>, W. Brown<sup>\*2</sup>, V. Stannett<sup>\*3</sup>

<sup>\*1</sup>Kokusaku Pulp Co., Ltd., <sup>\*2</sup>Uppsala University, <sup>\*3</sup>North Carolina State University

Keywords: spruce, *Picea engelmannii*, KP, kraft pulp, BKP, bleached kraft pulp, DP, dissolve pulp, GP, ground wood pulp, cotton linter, electron spin resonance spectroscopy

1970-012

二、三のリグニンモデル化合物合成の試み —グアヤシルプロペン類の合成—

福住俊郎、小宅茂夫、南 享二

東京大学農学部

Synthesis of a few lignin model compounds. —Synthesis of guaiacyl propenes—

Toshio Fukuzumi, Shigeo Koyake, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: guaiacyl vinyl ketone, vanilloyl acetoaldehyde, coniferyl alcohol

1970-013

次亜塩素酸ナトリウムによるリグニンモデル化合物の反応について

細谷修二、中野準三

東京大学農学部

Reaction of lignin model compounds with sodium hypochlorite.

Shuji Hosaya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: pH, vanillyl alcohol, veratryl alcohol, gaschromatography

1970-014

リグニンスルホン酸の二酸化塩素による酸化 —モデル化合物の酸化反応

中村孝一、横田金吾、秦 邦男

十条製紙株式会社

Oxidation of lignosulfonates with chlorine dioxide — Oxidation of model compounds

Koichi Nakamura, Kingo Yokota, Kunio Hata,

Jyujo Pulp Co., Ltd.

Keywords: lignosulfonates, chlorine dioxide, vanillyl sulfonate, syringyl sulfonate

1970-015

2-(2-Methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanol の過酢酸酸化について

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Oxidation of 2-(2-methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanol by peracetic acid.

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: Baeyer-Villiger reaction, paper chromatography, UV absorption chromatography

1970-016

パルプ廃液の色に関する研究(II)塩素オキシリグニンの着色について

鮫島一彦、近藤民堆

九州大学農学部

Studies on the color of pulping waste liquor. II. On the color of chlorin-oxylignin.

Kazuhiko Sameshima, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: *Pinus densiflora*, *Betula Tauschii*, oxylignin, pH dependence, functional groups

1970-017

ハイドロトロピック蒸解におけるリグニンの可溶化

石川久雄、沖 妙、大久保克美

愛媛大学農学部

Solubilization of lignin during hydrotropic cooking.

Hisao Ishikawa, Tae Oki, Katsumi Okubo

Faculty of Agriculture, Ehime University

Keywords: beech, *Fagus crenata*, sodium *m*-xylenesulfonate, dioxane lignin, sodium salicylate

1970-018

Hydrotropic Cooking について(III)より強力なハイドロトロピック剤へのアプローチ

山田洋三、近藤民雄

九州大学農学部

Hdrotropic cooking. III. Approach toward more effective hydrotropic reagent.

Yozo Yamada, Tamio Kondo

Faculty of Agriculture, Kyusyu University

Keywords: sodium salicylate, sodium aminobenzene sulfonate, viscosity

1970-019

アルカリ蒸解における酸素と硫黄の役割

飯山賢治、中山忠光、中野準三

東京大学農学部

Role of oxygen and sulfur in alkaline cooking.

Kenji Iiyama, Tadimitsu Nakayama, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compounds, vanillyl alcohol, acetoguaiacone, creosol, soda cooking, kraft cooking

1970-020

リグニンの脱メチル反応について

林 暁、谷口 彰

立命館大学理工学部

Demethylation reaction of lignin.

Akira Hayashi, Akira Taniguchi

College of Science and Engineering, Ritsumeikan University

Keywords: *Pinus densiflora*, dioxane lignin, soda cooking,  $\sigma$ -quinone

1970-021

リグニンのメチロール化反応について

阿部 勲、窪田 実

北海道林産試験場

Introduction of methylol groups onto lignin.

Isao Abe, Minoru Kubota

Hokkaido Forest Products Research Institute

Keywords: kraft lignin, formaldehyde, vanillic acid, ferulic acid, *p*-coumaric acid

1970-022

チオリグニンの鑄型への利用

岩見田 紘、佐藤 孝一郎

国策パルプ株式会社

Utilization of thiolignin for shell mold.

Tadashi Iwamida, Kouichiro Sato

Kokusaku Pulp Co., Ltd.

Keywords: shell mold, sand, binder, phenol

1970-023

アルカリリグニンからバニリンの製造について

香川 詔士、六川 真佐行、堀井 淑子

関東学院大学工学部

Production of vanillin from alkali lignin.

Shoji Kagawa, Masayuki Mutsukawa, Toshiko Horii

Faculty of Engineering, Kanto Gakuin University

Keywords: larch, *Larix Kaempferi*, nitrobenzene oxidation, air oxidation, UV absorption spectroscopy

1970-024

バニリン製造における副生リグニンの性状について

品川 和夫、工藤 正邦

山陽パルプ株式会社

Properties of residual lignin during production of vanillin

Kazuo Shinagawa, Masakuni Kudo

Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, vanillin, by-product, chemical structure

1970-025

蓄電池添加剤としてのリグニンの効果

木下恭介、林 暁

立命館大学理工学部

Effect of lignin as lead-acid battery additive.

Kyousuke Kinoshita, Akira Hayashi

College of Science and Engineering, Ritsumeikan University

Keywords: polyphenol, novolac type phenolic resin, poly-4-hydroxy-3-methoxystyrene

## 第 16 回 (1971.11.4-5) 高松電機ビル

1971-001

植物体に投与されたフェルラ酸のデメトキシ、およびメトキシレーションに関する研究

島田幹夫、伏木秀文、樋口隆昌

京都大学木材研究所

Studies on the demethoxylation and methoxylation of ferulic acid fed to a plant.

Mikio Shimada, Hidefumi Fushiki, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phyllostachys pubescens*, sinapic acid, 5-hydroxyferulic acid, guaiacyl nucleus, syringyl nucleus, hardwood, softwood

1971-002

広葉樹、および針葉樹リグニンのメトキシル基形成に関する比較生化学的研究

島田幹夫、伏木秀文、樋口隆昌

京都大学木材研究所

Comparative biochemical studies on the formation of methoxyl groups in hardwood and softwood lignins.

Mikio Shimada, Hidefumi Fushiki, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phyllostachys pubescens*, *Pinus Thunbergii*, *Ginkgo biloba*, *O*-methyltransferase, *S*-adenosylmethionine

1971-003

ポプラリグニン中のパラヒドロキシ安息香酸の生合成

寺島典二、森 勇

名古屋大学農学部

Biosynthesis of *p*-hydroxybenzoic acid in poplar lignin.

Noritsugu Terashima and Isamu Mori

Faculty of Agriculture, Nagoya University

Keywords: *Populus nigra* x *Populus Maximowiczii*, phenylalanine ammonia-lyase, *t*-cinnamic acid, *p*-coumaric acid

1971-004

広葉樹リグニン生合成についての一考察

寺沢 実、古賀卓哉、奥山 寛、三宅基夫

帯広畜産大学

Studies on the biosynthesis of lignin in hardwood.

Minoru Terasawa, Takuya Koga, Hiroshi Okuyama, Motoo Miyake

Obihiro University of Agriculture and Veterinary Medicine

Keywords: *Larix Kaempferi*, *Magnolia obobata*, *p*-glucocoumaryl alcohol, coniferin, syringin, cambial sap, softwood, hardwood

1971-005

MWL, LCC の磨砕に対する挙動

広居忠量、宮崎 信

林業試験場

Behavior of MWL and LCC during milling.

Tadakazu Hiroi, Makoto Miyazaki

Government Forest Experiment Station

Keywords: *Chamaecyparis obtusa*, glucomannan, ball mill, IR spectra, molecular weight distribution

1971-006

種子リグニンの特性

萩山紘一、畠山隆一、故 谷口栄一

山形大学農学部

Characteristic properties of lignin in seeds.

Koichi Ogiyama, Ryuichi Hatakeyama, the late Eiichi Taniguchi

Faculty of Agriculture, Yamagata University

Keywords: *Pinus densiflora*, *Juglans Sieboldiana*, UV spectra, IR spectra, nitrobenzene oxidation

1971-007

竹リグニンのアシドリシス (第 2 報) アシドリシス生成物の分離同定

中坪文明、棚橋光彦、樋口隆昌

京都大学木材研究所

Acidolysis of bamboo lignin. II. Isolation and identification of acidolysis products.

Fumiaki Nakatsubo, Mitsuhiko Tanahashi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: gel filtration, NMR, IR, *p*-coumaric acid, arylglycerol- $\beta$ -aryl ether substructure

1971-008

竹リグニンのアシドリシス (第 3 報) アリルグリセロール- $\beta$ -アリルエーテルの合成とそのアシドリシス

樋口隆昌、棚橋光彦、中坪文明

京都大学木材研究所

Acidolysis of bamboo lignin. III. Synthesis of arylglycerol- $\beta$ -aryl ether and its acidolysis.

Takayoshi Higuchi, Mitsuhiko Tanahashi, Fumiaki Nakatsubo

Wood Research Institute, Kyoto University

Keywords: *Phyllostachys pubescens*, model compounds, acidolysis in dioxane-water

1971-009

プロトリグニンの水素化分解に関する研究 (第 9 報) 新 2, 3 量体の単離・同定について

松倉紀男<sup>\*1</sup>、榊原 彰<sup>\*2</sup>

<sup>\*1</sup>十條製紙株式会社, <sup>\*2</sup>北海道大学農学部

Hydrogenolysis of protolignin. IX. Isolation and identification of new dimeric and trimeric products.

Motoo Matsukura<sup>\*1</sup>, Akira Sakakibara<sup>\*2</sup>,

<sup>\*1</sup>Jujo Paper Co. Ltd., <sup>\*2</sup>Faculty of Agriculture, Hokkaido University

Keywords: NMR, jezo spruce, *Picea jezoensis*, paper chromatography, thin-layer chromatography,

1971-010

リグニン-炭水化物複合体に関する研究 ジオキサン-水による加水分解物からの単離-

武山浩武、榊原 彰

北海道大学農学部

Studies on the lignin-carbohydrate complex. -Isolation from hydrolysis products with dioxane-water.

Hirotake Takeyama, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Picea jezoensis*, paper chromatography, thin-layer chromatography

1971-011

NMR を用いた MWL の測定

佐藤 惺、北村晃子、樋口隆昌

京都大学木材研究所

NMR analysis of MWL.

Akira Sato, Teruko Kitamura, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Metasequoia glyptostroboides*, *Fagus crenata*, *Phyllostachys*, molecular weight distribution

1971-012

チオリグニンの熱的性質に及ぼす分子量の影響について

岩下建二<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>、中野準三<sup>\*1</sup>

<sup>\*1</sup>東京大学農学部、<sup>\*2</sup>製品科学研究所

Effect of molecular weight on thermal properties of thiolignin.

Kenji Iwashita<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>, Junzo Nakano<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo <sup>\*2</sup>Industrial Products Research Institute

Keywords: *Abies mayriana*, *Fagus crenata*, gel filtration, differential scanning calorimetry

1971-013

リグニンモデル化合物の酸化電位について

小川博嗣

東京工業試験所

Oxidation potential of lignin model compounds.

Hirotsugu Ogawa

Government Chemical Industrial Research Institute, Tokyo

Keywords: polarography, vanillin, vanillic acid, vanillyl sulfonic acid

1971-014

サルファイト蒸解におけるリグニン・糖複合体の挙動について

飯塚堯介、白銀英明、中野準三

東京大学農学部

Behavior of lignin-carbohydrate complex during sulfite cooking

Gyosuke Meshitsuka, Hideaki Shirogane, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Pinus densiflora*, gel filtration, peracetic acid treatment

1971-015

サルファイト系高歩留りパルプ製造時のリグニンの挙動

岩見田 紘<sup>\*1</sup>, 浜田忠平<sup>\*1</sup>, 李 宗藩<sup>\*2</sup>, 中野準三<sup>\*2</sup>

<sup>\*1</sup>国策パルプ株式会社, <sup>\*2</sup>東京大学農学部

Behavior of lignin during sulfite chemimechanical pulping

Tadashi Iwamida<sup>\*1</sup>, Tadahira Hamada<sup>\*1</sup>, Sohan Ri<sup>\*2</sup>, Junzo Nakano<sup>\*2</sup>

<sup>\*1</sup>Kokusaku Pulp Co., Ltd., <sup>\*2</sup>the University of Tokyo, Faculty of Agriculture

Keywords: defibration, sulfonic acid group, middle lamella, secondary wall

1971-016

クラフト蒸解における残存および溶出リグニンの性状

飯山賢治、中野準三

東京大学農学部

Properties of dissolved and residual lignin in kraft pulp.

Kenji Iiyama, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Pseudotsuga taxifolia*, color of lignin, color of pulp, MWL, molecular weight distribution

1971-017

ソーダ蒸解によるリグニンの着色機構

林 暁、木下恭介、谷口 彰

立命館大学理工学部

Coloring mechanism of lignin during soda cooking.

Akira Hayashi, Kyosuke Kinoshita, Akira Taniguchi

Faculty of Science and Engineering, Ritsumeikan University

Keywords: model compound, quinone, catechol, chromophoric groups

1971-018

2-(2-Methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanol とそのメチル化物の過酢酸酸化について

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Peracetic acid oxidation of 2-(2-Methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanol.

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: TLC, NMR, IR absorption spectroscopy

1971-019

$\beta$ -アリアルエーテル型リグニンモデル化合物の過酢酸酸化

坂井克己<sup>\*1</sup>、黒田健一<sup>\*1</sup>、岸本定吉<sup>\*2</sup>

<sup>\*1</sup>九州大学農学部, <sup>\*2</sup>東京教育大学農学部

Peracetic acid oxidation of  $\beta$ -aryl ether type lignin model compounds.

Kokki Sakai<sup>\*1</sup>, Ken-ichi Kuroda<sup>\*1</sup>, Sadakichi Kishimoto<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Education

Keywords: conifer lignin, guaiacylglycerol- $\beta$ -guaiacyl ether, gas chromatography, mass spectrometry

1971-020

酸化漂白剤によるビフェニル型リグニンモデル化合物の反応について

細谷修二、中野準三

東京大学農学部

Reaction of biphenyl type lignin model compounds with oxidative bleaching agents.

Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: dehydrodivanillyl alcohol, dehydrodiveratryl alcohol, sodium hypochlorite, hydrogen peroxide

1971-021

高歩留パルプの漂白機構について—漂白剤添加量と白色度増加との関係

加納直<sup>\*1</sup>, 細谷修二<sup>\*2</sup>, 中野準三<sup>\*2</sup>

<sup>\*1</sup>国策パルプ, <sup>\*2</sup>東京大学農学部

Mechanism of bleaching of high yield pulp – Relation between dosage of bleaching agent and increase of brightness.

Tadashi Kano<sup>\*1</sup>, Shuji Hosoya<sup>\*2</sup>, Junzo Nakano<sup>\*2</sup>

<sup>\*1</sup>Kokusaku Pulp Co.,Ltd., <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: chemimechanical pulp, cold soda process, hydrogen peroxide, MWL

1971-022

塩素化リグニンのアルカリ抽出におよぼす熱処理の影響について(II)

河内進策

宮崎大学農学部

Effect of thermal treatment on alkali extraction of chlorinated lignin. II.

Shinsaku Kawachi

Faculty of Agriculture, Miyazaki University

Keywords: *Pinus densiflora*, dioxane lignin, holocellulose

1971-023

ゲルろ過法による針葉樹と広葉樹リグノスルホン酸類の比較

猪狩倅将、横山正一郎

東京工業試験所

Comparison of lignosulfonic acids prepared from softwood and hardwood by gel filtration.

Government Chemical Industrial Research Institute, Tokyo

Yoshimasa Ikari, Shoichirou Yokoyama

Keywords: sephadex

1971-024

リグノスルホン酸塩とメタクリル酸メチルのフェントン試薬によるグラフト重合反応(その2)

越島哲夫、南正院、村木永之介

大阪工業技術試験所

Graft copolymerization of methyl methacrylate onto lignosulfonate by Fenton reagent. II.

Tetsuo Koshijima, Chongwon Nam, Einosuke Muraki,

Government Industrial Research Institute, Osaka

Keywords: barium *p*-hydroxybenzylsulfonate, barium vanillylsulfonate, barium veratrylsulfonate,

1971-025

金属酸化物触媒の存在下におけるリグニンスルホン酸塩のアルカリ酸化分解 —酸化銅触媒の表面特性がバニリン生成反応に及ぼす影響

高橋英郎、渡辺昭雄

東京工業試験所

Alkaline oxidative degradation of lignosulfonate in presence of metal oxide catalyst. —Effect of surface properties of copper oxide catalyst on vanillin production.

Hideo Takahashi, Akio Watanabe

Government Chemical Industrial Research Institute, Tokyo

Keywords: volatile acid, oxygen consumption

1971-026

アルカリリグニンの空気酸化について

香川詔士、古梶 誠

関東学院大学工学部

Air oxidation of alkali lignin.

Shoji Kagawa, Makoto Kokaji

Faculty of Engineering, Kanto Gakuin University

Keywords: *Larix Kaempferi*, gas chromatography

1971-027

バニリン製造における副生リグニンの性状に関する研究(第2報)

品川和夫、工藤正邦、岡部次郎

山陽パルプ

Properties of residual lignin during production of vanillin, Part 2

Kazuo Shinagawa, Masakuni Kudo, Jiro Okabe

Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, vanillin, by-product, lignin, molecular weight, sulfopropylation

1971-028

濃縮 SP 廃液とフェノールによる耐水性接着剤の製造に関する研究

榊原 彰、佐野嘉拓

北海道大学農学部

Preparation of water resistant adhesives from concentrated sulfite waste liquor and phenol

Akira Sakakibara, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Keywords: chest nut powder, formaldehyde

1971-029

カワラタケのラッカーゼによる MWL の分解

石原達夫、宮崎 信

林業試験場

Degradation of MWL by laccase of *Polyporus versicolor*.

Tatsuo Ishihara, Makoto Miyazaki

Forestry and Forest Product Research Institute

Keywords: *Acer palmatum* Thunb, wood rotting fungi, milled wood lignin, GPC

1971-030

加水分解酵素によるリグニンの分解

福住俊郎、南 享二

東京大学農学部

Degradation of lignin by hydrolase.

Toshio Fukuzumi, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, *Polystictus sanquineus*, *Perenniporia subacida*, Brauns' s lignin

1971-031

放線菌によるリグニンの分解(第2報)

原口隆英、諸星紀幸

東京農工大学農学部

Degradation of lignin by *Actinomycetes*. II.

Takafusa Haraguchi, Noriyuki Morohoshi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: lignosulfonic acid, gel filtration, UV absorption spectra, *p*-hydroxybenzoic acid, vanillic acid

1971-032

パルプ廃液の色に関する研究(II) 塩素化オキシリグニンの着色について(2)

鮫島一彦、住本昌之、近藤民雄

九州大学農学部

Studies on the color of pulping waste liquor. II. Color of chlorinated oxylignin. (2)

Kazuhiko Sameshima, Masashi Sumimoto, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: benzoquinone, auxochrome, complex chromophore

1971-033

パルプ製造排水の凝集処理に関する研究

徐道太郎、飯塚堯介、中野準三

東京大学農学部

Treatment of pulp and paper mill wastewater by coagulation-flocculation.

Michitaro Jo, Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: lignosulfonate, chlorine treatment, alkali treatment, gel filtration

1971-034

パルプ廃水の清水化に関する研究 ークラフトリグニンの活性炭による吸着

壁谷 洋、藤井利郎、久保隆昌

四国工業技術試験所

Purification of pulp and paper mill wastewater – Adsorption of kraft lignin by activated carbon.  
Hiroshi Kabeya, Toshirou Fujii, Takamasa Kubo  
Government Industrial Research Institute, Shikoku  
Keywords: adsorption isotherm

## 第 17 回(1972.11.4-5)京都大学農学部

1972-001

広葉樹材生長過程における S/V 比の変動

田中治郎, 宮崎 信

林業試験場

Variation of S/V ratio during growing of hardwood.

Jiro Tanaka, Makoto Miyazaki

Government Forest Experiment Station

Keywords: *Platanus occidentalis*, nitrobenzene oxidation

1972-002

加水分解酵素による木粉よりのリグニン分解物

福住俊郎

東京大学農学部

Degradation products from lignin in wood meal by hydrolase.

Toshiro Fukuzumi

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, cellulase from *Trametes sanguineus*, Meicelase

1972-003

南洋材リグニンの特性について(2)南洋材広葉樹の 1%-NaOH 易溶性リグニンについて

荻山紘一、安江保民

山形大学農学部

Characteristics of the tropical wood lignins II. Lignin soluble in 1% NaOH in tropical hardwood.

Koichi Ogiyama, Moritami Yasue

Faculty of Agriculture, Yamagata University

*Parashorea melaanonan*, *Shorea rubroshorea*, white lauan, red lauan, 1%NaOH-extract, polymer

1972-004

リグニンの水素化分解に関する研究(第 10 報)新二, 三量体の単離について

須藤賢一、榊原 彰

北海道大学農学部

Hydrogenolysis of protolignin. X. Isolation of new dimer and trimer.

Kenichi Sudo, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*, TLC, <sup>1</sup>H-NMR, UV spectroscopy

1972-005

広葉樹リグニンの加水分解物から新リグナン型化合物およびシリルグリセロール-β-シリル

#### ルグリセロールエーテルの単離

大森茂俊、榊原 彰

北海道大学農学部

Isolation of a new lignan-type compound and syringylglycerol- $\beta$ -syringyl ether from hydrolysis products of hardwood lignin.

Shigetoshi Omori, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Fraxinus excelsissima*,  $^1\text{H-NMR}$ , UV spectroscopy, IR spectroscopy, mass spectrometry

1972-006

#### ジオキサン-水によるリグニンの加水分解・スチルベン分解物について

佐野嘉拓、榊原 彰

北海道大学農学部

Hydrolysis of lignin with dioxane-water. On the stilbene type degradation products.

Yoshihiro Sano, Akira Sakakibara,

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*, MWL,  $^1\text{H-NMR}$ , UV spectroscopy, IR spectroscopy

1972-007

#### 液安中金属ナトリウムによるリグニンの分解-III

山口 彰

林業試験場

Degradation of lignin by metallic sodium in liquid ammonia. III.

Akira Yamaguchi

Government Forest Experiment Station

Keywords: Yezo spruce, *Picea jezoensis*, guaiacyl-1,3-propanediol,  $^1\text{H-NMR}$ ,

1972-008

#### リグニンの分子運動におよぼす置換基の影響に関する研究

畠山兵衛

製品科学研究所

Effect of substituent group on molecular motion of lignin molecule.

Hyo Hatakeyama

Industrial Products Research Institute

Keywords: dioxane lignin, thiolignin, polystyrene, GPC

1972-009

#### 塩素化リグニンの光化学反応による脱ハロゲン

島田謹爾<sup>\*1</sup>、稲田 治<sup>\*2</sup>

<sup>\*1</sup> 林業試験場, <sup>\*2</sup> 東京農工大学農学部

Dehalogenation of chlorolignin by photochemical reaction.

Kinji Shimada<sup>\*1</sup>, Osamu Inada<sup>\*2</sup>

<sup>\*1</sup> Government Forest Experiment Station, <sup>\*2</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Pinus densiflora*, *Fagus crenata*, MWL, irradiation of UV light, GLC

1972-010

過酢酸酸化のさいの $\beta$ -アリルエーテル型構造の挙動

坂井克己、近藤民雄

九州大学農学部

Behavior of  $\beta$ -aryl ether type structure in peracetic acid oxidation.

Kokki Sakai, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Pinus densiflora*, *Betula Tauschii*, MWL, acidolysis,

1972-011

特別講演、リグニン化学の進歩と今後の進路

榊原 彰

北海道大学農学部

Invited lecture: Progress and future prospects of lignin chemistry.

Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: occurrence, distribution, formation, lignin in reaction wood, carbohydrates, structural model

1972-012

亜硫酸パルプ排液よりキシロースの単離

加藤孝二郎、工藤正邦、岡部次郎

山陽国策パルプ

Isolation of xylose from sulfite spent liquor.

Koujiro Kato, Masakuni Kudo, Jiro Okabe

Sanyo Kokusaku Pulp Co., Ltd.

Keywords: sugar composition, pentose, hexose, extraction solvent

1972-013

リグニン中のキノイド構造

飯山賢治、中野準三

東京大学農学部

Quinoid structure in lignin.

Kenji Iiyama, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, MWL, thioglignin, lignosulfonic acid, visible light absorption spectrometry,  $\sigma$ -quinone,

1972-014

高歩留パルプの酸化および還元漂白中におけるキノン類の挙動に関する研究

細谷修二、清家孝一、中野準三

東京大学農学部

Behavior of quinones during oxidative and reductive bleaching of high yield pulp.

Shuji Hosoya, Koichi Seike, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: methoxy-*p*-quinone, 2,6-dimethoxy-*p*-quinone, 2-6-dimethoxybibenzoquinone, hydrogen peroxide

1972-015

パルプ廃液の色に関する研究(第4報)オキシリグニンと金属塩(2)

鮫島一彦、住本昌之、近藤民雄

九州大学農学部

Studies on the color of pulp waste liquor. IV. Oxy lignin and metal salt. II.

Kazuhiko Sameshima, Masashi Sumimoto, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: aluminum ion, calcium ion, pH, gel filtration, lignin aluminum complex

1972-016

パルプ製造排水の凝集処理に関する研究

徐道太郎、飯塚堯介、中野準三

東京大学農学部

Studies on coagulation treatment of waste liquor from pulp mill.

Michitaro Jyo, Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Pinus densiflora*, sulfite pulping, chlorine treatment, ferric sulfate, aluminum sulfate, pH

1972-017

ソーダ、酸素蒸解におけるリグニンの挙動について

十河村男、幡 克美

香川大学農学部

Behavior of lignin during soda-oxygen cooking.

Murao Sogo, Katsumi Hata

Faculty of Agriculture, Kagawa University

Keywords: *Pinus densiflora*, *Fagus crenata*, MWL, UV absorption spectroscopy, IR absorption spectroscopy

1972-018

アミノベンゼンスルホン酸塩リグニンについて(II)

黒田健一、坂井克己、近藤民雄

九州大学農学部

On aminobenzenesulfonate lignin. II.

Ken-ichi Kuroda, Kokki Sakai, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Fagus crenata*, dioxane lignin, UV absorption spectroscopy, IR absorption spectroscopy

1972-019

高歩留り蒸煮木材のリファイニングにおいて剥離される中間層について

岩見田 紘<sup>\*1</sup>, 中野準三<sup>\*2</sup>

<sup>\*1</sup> 山陽国策パルプ, <sup>\*2</sup> 東大農

Properties of middle lamella peeling during refining of steamed wood in sulfite semichemical process.

Tadashi Iwamida<sup>\*1</sup>, Junzo Nakano<sup>\*2</sup>

<sup>\*1</sup>Sanyo Kokusaku Pulp Co., Ltd., <sup>\*2</sup> Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, sulfite cooking, cell wall layers, electron microscope

1972-020

特別講演: Tappi Chromophores セミナーおよび酸素-アルカリ蒸解・漂白セミナーに参加して  
中野準三

東京大学農学部

Invited lecture: Reports as an attendant at the Tappi Chromophore Seminar and Oxygen-Alkali  
Cooking and Bleaching Seminar

Junzo Nakano

Faculty of Agriculture, the University of Tokyo

## 第 18 回 (1973.11.3-4)九州大学農学部

1973-A01

シナップ酸の還元および針葉樹におけるシリングルリグニンの生成

中村吉紀、樋口隆昌

京都大学木材研究所

Reduction of sinapic acid and formation of syringyl lignin in conifer.

Yoshiki Nakamura, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keyword: poplar, *Populus* spp., cherry, *Prunus densiflora*, red pine, *Pinus densiflora*, *Ginkgo biloba*, acidolysis, GC-MS analysis

1973-A02

*p*-クマリルアルコールの脱水素重合(II). Coumaran の Configuration

中坪文明、樋口隆昌

京都大学木材研究所

Dehydrogenative polymerization of *p*-coumaryl alcohol. II. Configuration of coumaran substructures.

Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keyword: synthesis of coumarans, <sup>1</sup>H-NMR

1973-A03

*p*-ヒドロキシシナミルアルコール類の酵素的脱水素反応によるアリルグリセロールの生成

樋口隆昌、中坪文明、池田良久

京都大学木材研究所

Formation of arylglycerol by enzymatic dehydrogenation of *p*-hydroxycinnamyl alcohols.

Takayoshi Higuchi, Fumiaki Nakatsubo, Yoshihisa Ikeda

Wood Research Institute, Kyoto University

Keywords: synthesis of arylglycerols, <sup>1</sup>H-NMR, laccase, peroxidase

1973-A04

プロトリグニンの水素化分解に関する研究(第 12 報)-炭素・炭素結合を有する二、三の 2 量体、3 量体の単離、同定について

須藤賢一、榊原 彰

北海道大学農学部

Hydrogenolysis of protolignin. XII. Isolation and identification of some dimmers and trimers having

carbon-carbon bond.

Kenichi Sudo, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Picea jezoensis*, UV absorption spectrometry, <sup>1</sup>H-NMR, gas chromatography-mass spectrometry

1973-A05

磨碎木粉の酵素分解(1)

佐野嘉拓、榊原 彰

北海道大学農学部

Enzymatic degradation of milled wood. I.

Yoshihiro Sano, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: hemicellulase, cellulase, nitrobenzene oxidation

1973-A06

竹 MWL アシドリシス残渣のオゾン分解

棚橋光彦、中坪文明、樋口隆昌

京都大学木材研究所

Ozonolysis of acidolysis residue of bamboo MWL.

Mitsuhiko Tanahashi, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: <sup>1</sup>H-NMR, synthesis of phenyl coumarone compound, UV absorption spectrometry

1973-A07

ヤチダモ材の加水分解物よりリグナン型化合物の単離

大森茂俊<sup>\*1</sup>、榊原 彰<sup>\*2</sup>

<sup>\*1</sup>岩手大学農学部、<sup>\*2</sup>北海道大学農学部

Isolation of lignan type compounds from hydrolysis products of *Fraxinus excelsissima*.

Shigetoshi Omori<sup>\*1</sup>, Akira Sakakibara<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Iwate University, <sup>\*2</sup>Faculty of Agriculture, Hokkaido University

Keywords: <sup>1</sup>H-NMR, column chromatography, mass spectrometry, UV absorption spectrometry, IR absorption spectrometry, <sup>1</sup>H-NMR

1973-A08

Björkman LCC の分別

越島哲夫、夜久富美子、田中龍太郎

大阪工業試験所

Fractionation of Björkman LCC.

Tetsuo Koshijima, Fumiko Yaku, Ryutaro Tanaka

Government Industrial Research Institute, Osaka

Keywords: gel filtration, paper electrophoresis, molecular weight

1973-A09

リグニンの抗腫瘍作用

村上浩紀

九州大学農学部

Antitumor activity of lignin.

Hiroki Murakami

Faculty of Agriculture, Kyushu University

Keywords: *Sasa veitchii*, *Pinus densiflora*, calcium lignosulfonate, mouse

1973-A10

南洋材リグニンの特性について(3) -*Eucalyptus Calophylla* の KINO 成分-

萩山紘一、安江保民

山形大学農学部

Characteristics of the tropical wood lignins. III. Kino of *Eucalyptus calophylla*.

Koichi Ogiyama, Moritami Yasue

Faculty of Agriculture, Yamagata University

Keywords: anthocyanidine, leucoanthocyanidine, polymer

1973-A11

広巾 NMR によるリグニンの分子運動に及ぼす置換基の影響についての研究

村越 康、畠山兵衛

製品科学研究所

Studies on the effect of substituent on molecular motion of lignin by broad band NMR.

Yasushi Murakoshi, Hyoe Hatakeyama

Industrial Products Research Institute

Keywords: polystyrene, model polymer, substituted styrene

1973-A12

アセトグアヤコン、イソオイゲノールおよび関連アリアルエーテル類の光分解

佐分義正、善本知孝、南 享二

東京大学農学部

Photodegradation of acetoguaiacone, isoeugenol and related arylethers.

Yoshimasa Saburi, Tomotaka Yoshimoto, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compounds, gas liquid chromatography,

1973-A13

放射性同位元素標識リグニンの反応 -リグニンを構成する各炭素のKP蒸解中の挙動

寺島典二、荒木 広、菅沼伸夫、神田 孝

名古屋大学農学部

Radiotracer experiments on lignin reactions. The behavior of lignin carbons during kraft cooking process.

Noritsugu Terashima, Hiroshi Araki, Nobuo Suganuma, Takashi Kanda

Faculty of Agriculture, Nagoya University

Keywords: *Pinus Thunbergii*, radiotracer, carbon 14, gel filtration

1973-A14

放射性同位元素標識リグニンの反応 -KP蒸解中のリグニンと炭水化物との反応-

寺島典二、菅沼伸夫、荒木 広、神田 孝

名古屋大学農学部

Radiotracer experiments on lignin reactions. The reaction of lignin with carbohydrates during kraft

cooking process.

Noritsugu Terashima, Nobuo Suganuma, Hiroshi Araki, Takashi Kanda

Faculty of Agriculture, Nagoya University

Keywords: *Pinus Thunbergii*, carbon 14, gel filtration, MWL, DHP, guaiacylglycerol- $\beta$ -guaiacyl ether

1973-A15

リグニン及びフェノール類の着色

林 昶、木下恭介、中村卓司

立命館大学工学部

Coloring of lignin and phenols.

Akira Hayashi, Kyosuke Kinoshita, Takuji Nakamura

Faculty of Science and Engineering, Ritsumeikan University

Keywords: quinone polymer, ferric chloride, thioglignin, polarography

1973-A16

過酸化水素漂白における高歩留パルプ中のリグニンの反応に関する研究 –リグニン中間位モデル物質の反応–

細谷修二、中野準三

東京大学農学部

Reaction of lignin during bleaching of high yield pulp by hydrogen peroxide. –Reaction of intermediate lignin model compounds.

Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: model compounds, Mass spectrometry, GC-Mass, TLC, NMR spectroscopy

1973-A17

Guaiacylglycerol- $\beta$ -guaiacyl ether の過酢酸酸化

沖 妙、大久保 克美、石川 久雄

愛媛大学農学部

Peracetic acid oxidation of guaiacylglycerol- $\beta$ -guaiacyl ether

Tae Oki, Katsumi Okubo, Hisao Ishikawa,

Faculty of Agriculture, Ehime University

Keywords: lignin model compounds, vapor-phase oxidation, liquid phase oxidation

1973-A18

分子量分別したリグニンスルホン酸の電解酸化について

小川博嗣

東京工業試験所

Electrolytic oxidation of lignosulfonic acids fractionated by molecular weight.

Hirotsugu Ogawa

Government Chemical Industrial Research Institute, Tokyo

Keywords: oxidation potential, pH

1973-A19

リグニンのオゾン処理 –溶媒の影響–

田中 治郎

#### 林業試験場

Ozone treatment of lignin. -Effect of solvent.

Jiro Tanaka

Government Forest Experiment Station

Keywords: larch, *Larix Kaempferi*, red pine, *Pinus densiflora*, wettability test

1973-B01

過酢酸気相漂白とその特色について

大久保克美、沖 妙、石川久雄

愛媛大学農学部

Vapor phase bleaching by peracetic acid, and its special feature.

Katsumi Okubo, Tae Oki, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: Douglas fir, *Pseudotsuga taxifolia*, UKP, dioxane lignin

1973-B02

各種ベースによるホロパルプ製造

松浦洋

日本紙パルプ研究所

Holopulping process using different bases

Hiroshi Matsuura

Japan Pulp and Paper Research Institute, Inc.

Keywords: holopulp, holocellulose, chlorine dioxide, recovery process, Na-base holopulp, Mg-base holopulp

1973-B03 中止

1973-B04

酸素・アルカリ処理によるアカマツ MWL の分解

十河 村男、幡 克美

香川大学農学部

Degradation of MWL of Japanese red pine by oxygen-alkali treatment.

Murao Sogo, Katsumi Hata

Faculty of Agriculture, Kagawa University

Keywords: *Pinus densiflora*, MWL, UV spectroscopy, gel filtration

1973-B05

針葉樹クラフトパルプの酸素漂白

永野正、石井彰一、宮尾再青、松井泰彦

東洋パルプ株式会社

Oxygen bleaching of softwood kraft pulp.

Tadashi Nagano, Shoichi Ishi, Saisei Miyao, Yasuhiko Matsui

Toyo Pulp Co., Ltd

Keywords: COD, cooking spent liquor, green liquor, kappa number

1973-B06

酸素漂白について

田渕博, 川島功, 山田洋三

紀州製紙株式会社

On the oxygen bleaching.

Horoshi Tabuchi, Isao Kawashima, Yozo Yamada

Kishu Paper Co., Ltd.

Keywords: heavy metal ion, cellulose protecting agents, brightness stability

1973-B07

パルプ工業の無公害化へのアプローチ

御田昭雄<sup>\*1</sup>、平井久雄<sup>\*2</sup>

<sup>\*1</sup> 東京工業試験所、<sup>\*2</sup> チッソエンジニアリング株式会社

Approaches to pollution free pulp industry.

Akio Mita<sup>\*1</sup>, Hisao Hirai<sup>\*2</sup>

<sup>\*1</sup>Government Chemical Industrial Research Institute, Tokyo, <sup>\*2</sup>Chisso Engineering Co.Ltd.

Keywords: closed system, unit process,

1973-B08

SO<sub>2</sub>+MgSO<sub>4</sub> 蒸解廃液からの薬品の回収と活性炭の製造について

林 治助<sup>\*1</sup>、戸坂圀夫<sup>\*1</sup>、伴内正樹<sup>\*2</sup>

<sup>\*1</sup> 北海道大学工学部、<sup>\*2</sup> プロセス資材株式会社

Recovery of chemicals and production of activated carbon from waste liquor of pulping with SO<sub>2</sub> + MgSO<sub>4</sub>.

Jisuke Hayashi<sup>\*1</sup>, Kunio Tosaka<sup>\*1</sup>, Masaki Bannai<sup>\*2</sup>

<sup>\*1</sup>Faculty of Engineering, Hokkaido University, <sup>\*2</sup>Process Shizai Co. Ltd.

Keywords: white birch, *Betula Tauschii*,

1973-B09

γ線照射によるパルプ製造廃水の淡色化に関する研究

飯塚堯介、中野準三

東京大学農学部

Reduction of color intensity of pulp mill effluent liquor by γ-ray irradiation.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: thiolignin, liginosulfonic acid, cobalt 60, peroxide radical

1973-B10

亜硫酸系パルプ廃液中の有機物成分の分取

猪狩俣将、横山正一郎

東京工業試験所

Separation of organic components from sulfite pulp waste liquor.

Yoshimasa Ikari, Shoichiro Yokoyama

Government Chemical Industrial Research Institute, Tokyo

Keywords: Yezo spruce, *Picea jezoensis*, *Abies Mayriana*, NSCP, BOD,

1973-B11

パルプ製造廃水の凝集処理に関する研究 —凝集機構について—

徐道太郎、飯塚堯介、中野準三

東京大学農学部

Studies on the coagulation treatment of pulp mill effluent liquor. -Mechanism of coagulation.

Jyo Michitaro, Gyosuke Meshitsuka, Junzo Nakano.

Faculty of Agriculture, the University of Tokyo

Keywords: lignosulfonate, thioglignin, sulfomethyl thioglignin, zeta potential, electrokinetic potential, aluminum ion

1973-B12

クラフトパルプ廃水のオゾン併用活性汚泥処理 -処理効率と諸パラメーターについて-

上嶋 洋、赤松 勲

四国工業技術試験所

Treatment of kraft pulp mill effluent by activated sludge combined with ozone treatment. -Efficiency and parameters of the treatment.

Hiroshi Kamishima, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords: BOD, COD(Mn),

1973-B13

製紙スラッジを原料とする吸着剤の製造研究 -各種スラッジの示差熱分析結果と製造条件について-

前松陸郎、曾我部隆紀、芳地全保、谷 静男

愛媛県製紙試験所

Production of adsorbent from pulp mill sludge. -Differential thermal analyses of various sludge and conditions of preparation.

Mutsuo Maematsu, Takanori Sogabe, Masayasu Hochi, Shizuo Tani

Pulp and Paper Research Institute of Ehime Prefecture.

Keywords: recycled paper sludge, straw pulp sludge,

1973-B14

クラフトパルプ廃水の石灰処理(V)-廃水中のリグニンの分子量分布の石灰処理に及ぼす影響-

加藤俊作、久保隆昌、木村 裕

四国工業技術試験所

Treatment of kraft pulp mill effluent with lime. V. Effect of molecular weight distribution of lignin in the effluent on lime treatment.

Shunsaku Kato, Takamasa Kubo, Yutaka Kimura

Government Industrial Research Institute, Shikoku

Keywords: COD, TOC, gel filtration,

1973-B15

BKP 製造における工程別排水の性状およびその凝集沈澱処理

上埜武夫、守屋正夫、竹下 登

山陽国策パルプ株式会社

Properties and sedimentation treatment of effluents from kraft pulping and bleaching processes.

Takeo Ueno, Masao Moriya, Noboru Takeshita

Sanyo Kokusaku Pulp Co., Ltd.

Keywords: *Pseudotsuga taxifolia*, COD, chromaticity, lignin, sugar, color analysis

1973-B16

パルプ廃水処理

白川精一, 木村勇, 川添早苗, 荒牧幹男

三菱重工業株式会社

Pulp effluents treatment.

Seiichi Shirakawa, Isamu Kimura, Sanae Kawazoe, Mikio Aramaki

Mitsubishi Heavy Industries, Ltd.

Keywords: sedimentation, KP, SP, SCP, fermentation spent liquor, flocculant, colloid titration

## 第 19 回 (1974.10.19-20) 秋田大学教育学部

1974-101

ヤドリギ (*Viscum album*) のリグニンと *O*-メチル基転位酵素

黒田宏之、樋口隆昌

京都大学木材研究所

Lignin in *Viscum album*, and *O*-methyl transferase.

Hiroyuki Kuroda, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: ferulic acid, sinapic acid, OMT inhibitor

1974-102

シラカンバ新生組織へのフェニールアラニン-<sup>14</sup>C(U)の取り込みとリグニン形成

三宅基夫、寺沢 実、奥山 寛

帯広畜産大学

Incorporation of phenylalanine-<sup>14</sup>C(U) into newly formed xylem tissue of *Betula Tauschii* and lignin formation.

Motoo Miyake, Minoru Terasawa, Hiroshi Okuyama

Obihiro University of Agriculture and Veterinary Medicine

Keywords: platyophylloside, platyphyllidiolside, betuloside

1974-103

ポプラリグニンのパラヒドロオキシ安息香酸の生合成

寺島典二、岡田基光、神田 孝

名古屋大学農学部

Biosynthesis of *p*-hydroxybenzoic acid in poplar lignin.

Noritsugu Terashima, Motomitsu Okada, Takashi Kanda

Faculty of Agriculture, Nagoya University

Keywords: *Populus nigra* X *Populus Maximowiczii*, <sup>14</sup>C-labeled precursor

1974-104

Non-Woody リグニンについて -ナシの石細胞とモモの内果皮リグニン-

黒田宏之、近藤民堆

九州大学農学部

On the non-woody lignin. -Lignins in stone cell of pear (*Pyrus pyrifolia* var. *culta*) and in endocarp of peach (*Amygdalus persica*).

Hiroyuki Kuroda, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: dioxane lignin, nitrobenzene oxidation, ethanolysis

1974-105

圧縮アテ材リグニンの化学構造について

安田征市、榊原 彰

北海道大学農学部

Chemical structure of lignin in compression wood.

Seichi Yasuda, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Larix leptolepis*, *p*-hydroxyphenyl nucleus, guaiacyl nucleus, MWL, NMR

1974-106

カラマツアルカリリグニンの GPC について

香川詔士、長谷川修

関東学院大学工学部

On gel permeation chromatography of alkali lignin from larch.

Shoji Kagawa, Osamu Hasegawa

Kanto Gakuin University

Keywords: *Larix leptolepis*, molecular weight distribution, air oxidation of alkali lignin, IR spectrum

1974-107

プロトリグニンの水素化分解に関する研究(第 13 報)-2, 3 量体の単離、同定について-

須藤賢一、榊原 彰

北海道大学農学部

Hydrogenolysis of protolignin. XIII. -Isolation and identification of dimers and trimers.

Kenichi Sudo, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*,  $\alpha$ -conidendrin, matairesinol

1974-108

液安中金属ナトリウムによるリグニンの分解 -G 核及び P 核を有する二量体の単離-

山口 彰

林業試験場

Degradation of lignin by metallic sodium in liquid ammonia. - Isolation of dimer containing G and P units-

Akira Yamaguchi

Government Forest Experiment Station

Keywords: Yezo spruce, *Picea jezoensis*,  $^1\text{H-NMR}$ , mass spectrometry

1974-109

竹リグニンのアシドリシス残渣のオゾン分解

棚橋光彦、中坪文明、樋口隆昌

京都大学木材研究所

Ozonolysis of acidolysis residue of bamboo lignin.

Mitsuhiko Tanahashi, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: lignin model compound,

1974-110

ジオキサン-水によるリグニンの加水分解

佐野嘉拓、榊原 彰

北海道大学農学部

Hydrolysis of lignin with dioxane-water.

Yoshihiro Sano, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: synthesis of compounds related hydrolysis products, gel chromatography

1974-111

リグニンの加溶媒分解 (第3報) -トレーサー法による反応の検討-

可知省吾<sup>\*1</sup>, 荒木廣<sup>\*2</sup>, 寺島典二<sup>\*2</sup>

日本紙パルプ研究所<sup>\*1</sup>, 名古屋大学農学部<sup>\*2</sup>

Solvolytic of lignin. (Part 3), Examination of reaction by the radioisotope tracer techniques.

Shogo Kachi<sup>\*1</sup>, Hiroshi Araki<sup>\*2</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>Japan Pulp and Paper Research Institute, Inc, <sup>\*2</sup> Faculty of Agriculture, Nagoya University

Keywords: MWL, radioisotope, carbon-14, tritium

1974-112

1,2-Diarylpropane-1,3-diols の合成

中坪文明、樋口隆昌

京都大学木材研究所

Synthesis of 1,2-diarylpropane-1,3-diols.

Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: <sup>1</sup>H-NMR, configuration, preparative TLC

1974-113

グアヤシルグリセロール-β-グアヤシルエーテルの合成

細谷修二、中野準三

東京大学農学部

Synthesis of guaiacylglycerol-β-guaiacyl ether.

Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: <sup>1</sup>H-NMR, mass spectrometry

1974-114

Guaiacylglycerol-β-guaiacyl ether の酸素アルカリ分解

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Degradation of guaiacylglycerol-β-guaiacyl ether by oxygen-alkali.

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: peracetic acid oxidation, thin layer chromatography, gas chromatography

1974-115

リグニン分子運動のモデルポリマーによる考察

畠山兵衛<sup>\*1</sup>、木村 実<sup>\*2</sup>

<sup>\*1</sup> 製品科学研究所, <sup>\*2</sup> 東京大学農学部

Simulation of molecular motion of lignin using a model polymer.

Hyoë Hatakeyama<sup>\*1</sup>, Minoru Kimura<sup>\*2</sup>

<sup>\*1</sup>National Institute of Advanced Industrial Science and Technology, <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: TBA, torsion brade analysis, DSC, broad band NMR,

1974-116

特別講演、Past and Present Challenges in Lignin Chemistry.

Conrad Schuerch

ニューヨーク州立大、米、シラキウス

Invited lecture: Past and Present Challenges of Lignin Chemistry

Conrad Schuerch

New York State University, Syracuse. USA

Keywords: Klason, Staudinger, Freudenberg, Hibbert, Erdtman, heterogeneity, macromolecule, molecular weight, cellulose, UV spectroscopy, IR spectroscopy, protolignin, milled wood lignin, biphenyl structure, phenolic hydroxyl group content, <sup>13</sup>C-NMR, microscopy, pulping, bleaching

1974-201

酸素アルカリ蒸解におけるブナリグニンの挙動

十河村男、幡 克美

香川大学農学部

Behavior of beech lignin during oxygen-alkali cooking.

Murao Sogo, Katsumi Hata

Faculty of Agriculture, Kagawa University

Keywords: *Fagus crenata*, MWL, UV spectroscopy, gaschromatography

1974-202

酸素アルカリ蒸解におけるリグニンの挙動

青柳哲夫、細谷修二、中野準三

東京大学農学部

Behavior of lignin during oxygen-alkali cooking.

Tetsuo Aoyagi, Syuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: apocinol, acetovanillon, gas chromatography, quinone, radical

1974-203

アルカリ酸素漂白におけるプロテクターの保護機構

林 治助<sup>\*1</sup>、山田紹良<sup>\*1</sup>、戸坂圀夫<sup>\*1</sup>、小泉正弘<sup>\*2</sup>

<sup>\*1</sup> 北海道大学工学部, <sup>\*2</sup> 東洋パルプ株式会社

Mechanism of protection of cellulose degradation by protectors in oxygen-alkali bleaching.

Jisuke Hayashi<sup>\*1</sup>, Akira Yamada<sup>\*1</sup>, Kunio Tosaka<sup>\*1</sup>, Masahiro Koizumi<sup>\*2</sup>

<sup>\*1</sup> Faculty of Engineering, Hokkaido University, <sup>\*2</sup>Toyo Pulp Co. Ltd.

Keywords: magnesium carbonate, glucose, xylose, reducing monosaccharide, water soluble lignin

1974-204

クラフトパルプのオゾン漂白 –針葉樹と広葉樹パルプの漂白性について

上嶋 洋、藤井利郎、赤松 勲

四国工業技術試験所

Ozone bleaching of kraft pulp. –Bleachability of softwood pulp and hardwood pulp.

Hiroshi Kamishima, Toshiro Fujii, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords: Japanese red pine, *Pinus densiflora*, beech, *Fagus crenata*,

1974-205

酸素アルカリ処理に関する研究(V)–酸素漂白シーケンスについて(2)–

西田友昭、坂井克己、近藤民堆

九州大学農学部

Studies on oxygen-alkali treatment. V. Peracetic acid bleaching of kraft pulp prebleached by oxygen-alkali (2).

Tomoaki Nishida, Kokki Sakai, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: white birch, *Betula Tauschii*, analysis of variance, brightness

1974-206

高収率パルプに関する研究

御田昭雄<sup>\*1</sup>、山本登久男<sup>\*2</sup>、勝地光雄<sup>\*2</sup>、勝山敦弘<sup>\*2</sup>、平井久夫<sup>\*3</sup>、赤羽利昭<sup>\*3</sup>

<sup>\*1</sup> 東京工業試験所、<sup>\*2</sup> 静岡県製紙工業試験所、<sup>\*3</sup> チッソエンジニアリング

Studies on the high yield pulp.

Akio Mita<sup>\*1</sup>, Tokuo Yamamoto<sup>\*2</sup>, Mitsuo Katsuji<sup>\*2</sup>, Atsuhiko Katsuyama<sup>\*2</sup>, Hisao Hirai<sup>\*3</sup>, Toshiaki Akabane<sup>\*3</sup>

<sup>\*1</sup>Government Industrial Research Institute, Tokyo, <sup>\*2</sup>Paper Research Institute of Shizuoka Prefecture, <sup>\*3</sup>Chisso Engineering Co. Ltd.

Keywords: Douglas fir, *Pseudotsuga taxifolia*, lauan, *Shorea sp.*, straw, bagasse, SOX chemimechanical pulp,

1974-207

南洋材リグニンの特性について(4)–パルプ排液の着色に及ぼす高分子ロイコアントシアニジンの影響–

荻山紘一、安江保民

山形大学農学部

Characteristics of the tropical wood lignins. IV. –Effect of high molecular leuco-anthocyanidins on coloring of pulp waste liquor.

Koichi Ogiyama, Moritami Yasue

Faculty of Agriculture, Yamagata University

Keywords: *Eucalyptus calophylla*, UV spectroscopy, benzoquinone

1974-208

SCP 廃液について(4)–廃液中の Xylan–

稲田 治、鮫島一彦、近藤民雄  
九州大学農学部

On the waste liquor of SCP. IV. -Xylan in waste liquor.

Osamu Inada, Kazuhiko Sameshima, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Carpinus* sp. white birch, *Betula Tauschii*, beech, *Fagus crenata*, kapur, *Doryobalanops*, white lauan, *Pentacme* sp.

1974-209

石巻地先における底質汚染の調査結果について

上柿明子、渡辺丈夫、佐藤春雄、曾根 光

宮城県公害技術センター

Report of sediment contamination survey at Onshore of Ishinomaki.

Akiko Kamigaki, Takeo Watanabe, Haruo Sato, Hikaru Sone

Pollution Reserch Center of Miyagi Prefecture

Keywords: pulp effluent, COD, TOC, sulfide

1974-210

秋田湾海域汚染とスス水発生について

加藤治男

秋田県水産試験場

Sea water pollution and cause of sooty water at Akita bay.

Haruo Kato

Akita Fisheries Experiment station

Keywords: COD, SS, suspended substance,

1974-211 中止

1974-212

BKP 製造工程から発生する各種漂白排水の性状及びその排水処理

竹下 登, 上埜武夫, 守屋正夫

山陽国策パルプ株式会社

Properties and treatment of effluents from kraft pulp bleaching processes.

Noboru Takeshita, Takeo Ueno, Masao Moriya

Sanyo Kokusaku Pulp Co., Ltd.

Keywords: molecular weight distribution, sedimentation process, activated sludge process

1974-213

パルプ廃液の色に関する研究 -廃液処理時の色の挙動について-

鮫島一彦、石崎貞二、住本昌之、近藤民雄

九州大学農学部

Studies on the color of pulping waste liquor. -Behavior of coloring matter during treatment of waste liquor.

Kazuhiko Sameshima, Teiji Ishizaki, Masashi Sumimoto, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords:: activated carbon, dialysis, aluminum sulfate

1974-214

パルプ廃水の炭素質材料等による浄化

里中聖一

北海道大学農学部

Purification of pulp mill effluent with carbonaceous materials.

Seichi Satonaka

Faculty of Agriculture, Hokkaido University

Keywords: activated carbon, KP, SP, NSC. bark, Japanese oak, *Quercus crispula*

1974-215

パルプ漂白排水中の塩素化リグニンの紫外線分解

島田謹爾

林業試験場

Degradation of chlorinated lignin in pulp bleach effluent by ultraviolet light.

Kinji Shimada

Forestry and Forest Product Research Institute

Keywords: red pine, *Pinus densiflora*, KP, COD, gas chromatography

1974-216

$\gamma$ 線照射によるパルプ製造排水の淡色化について

飯塚堯介、中野準三

東京大学農学部

Reduction of color intensity of pulp mill effluent by  $\gamma$ -ray irradiation.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: thioglignin, lignosulfonic acid, lignin model compounds, COD, active oxygen species, conjugated double bonds, air bubbling

## 第 20 回 (1975.10.20-21)名古屋大学農学部

1975-101

バクテリアによるリグニンモデル化合物の分解 (I)

森 義博、福住俊郎、南 享二

東京大学農学部

Degradation of lignin model compounds by bacteria. I.

Yoshihiro Mori, Toshiro Fukuzumi, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: *Pseudomonas putida*, *Pseudomonas fluorescens*, *Pseudomonas dacunhae*, *Pseudomonas ovalis*, *Pseudomonas surfactasimilis*, DHP,

1975-102

木材腐朽菌による $\beta$ -エーテル化合物の分解

松本 久、福住俊郎、南 享二

東京大学農学部

Degradation of  $\beta$ -ether compounds by wood rotting fungi.

Hisashi Matsumoto, Toshio Fukuzumi, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: *Perenniporia subacida*, *Irpex lacteus*, *Trametes sanguineus*

1975-103

リグニン関連合成高分子の生分解

林 英一<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>、原口隆英<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 製品科学研究所

Biodegradation of synthetic polymer related to lignin.

Eiichi Hayashi<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>, Takafusa Haraguchi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Industrial Products Research Institute

Keywords: poly-(*p*-hydroxy styrene), poly-(3-methoxy-4-hydroxy styrene), poly-(3,5-dimethoxy-4-hydroxy styrene), molecular weight distribution, UV spectrometry

1975-104

白色腐朽菌ヒラタケによるリグニンの分解

広居忠量<sup>\*1</sup>, K.E. Eriksson<sup>\*2</sup>

<sup>\*1</sup> 林業試験場, <sup>\*2</sup> STFI

Degradation of lignin by white rot fungus *Pleurotus ostreatus*.

Tadakazu Hiroi<sup>\*1</sup>, K.E. Eriksson<sup>\*2</sup>

<sup>\*1</sup> Government Forest Experiment Station, <sup>\*2</sup> Swedish Pulp and Paper Research Institute

Keywords: MWL, *Chamaecyparis obtuse*, kraft lignin, *Pinus densiflora*, Ca-lignosulfonate, molecular weight distribution

1975-105

ラッカーゼによりシリング酸から生成した  $\sigma$ -キノン誘導体の構造について

石原達夫、石原光朗

林業試験場

Structure of  $\sigma$ -quinone derivatives derived from syringic acid by laccase.

Tatsuo Ishihara, Mitsuro Ishihara

Government Forest Experiment Station

Keywords: *Polyporus versicolor*, UV spectrometry, 2,6-dimethoxy-*p*-benzoquinone

1975-106

木材腐朽菌によるクラフト廃液の脱色

福住俊郎、西田篤實、島崎徹郎、南 享二

東京大学農学部

Decolorization of kraft pulp mill effluent by wood rotting fungi.

Toshio Fukuzumi, Atsumi Nishida, Tetsuro Shimazaki, Kyoji Minami

Faculty of Agriculture, the University of Tokyo

Keywords: *Tinctoporia* sp., *Trametes* sp., *Tryromyces* sp., *Pleurotus* sp., *Pholiota* sp., *Phallinus* sp.

UV spectrometry, gel filtration

1975-107

南洋材リグニンの特性(5) 赤ラワン、ブナ材の着色

荻山絃一、安江保民

山形大学農学部

Characteristics of the tropical wood lignins. V. -Coloration of red lauan and beech wood.

Koichi Ogiyama, Moritami Yasue

Faculty of Agriculture, Yamagata University

Keywords: *Shorea negrosensis*, *Fagus crenata*, reflectance spectrum,

1975-108

ジオキサン-水によるリグニンの加水分解 -モデル化合物の加水分解-

佐野嘉拓、榊原 彰

北海道大学農学部

Hydrolysis of lignin with dioxane-water. -Hydrolysis of model compounds.

Yoshihiro Sano, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: synthesis of model compounds, NMR, mass spectrometry, thin layer chromatography

1975-109

ジオキサン-水によるプロトリグニンの加水分解 -新 3 量体の単離-

大森茂俊\*<sup>1</sup>、榊原 彰\*<sup>2</sup>

\*<sup>1</sup> 岩手大学農学部、\*<sup>2</sup> 北海道大学農学部

Hydrolysis of protolignin with dioxane-water. -Isolation of a new trimer.

Shigetoshi Omori\*<sup>1</sup>, Akira Sakakibara\*<sup>2</sup>

\*<sup>1</sup>Faculty of Agriculture, Iwate University, \*<sup>2</sup>Faculty of Agriculture, Hokkaido University

Keywords: *Fraxinus excelsissima*, IR spectroscopy, UV spectroscopy, Mass spectrometry, NMR

1975-110

広葉樹プロトリグニンの水素化分解 -2量体の単離と構造解析について

須藤賢一\*<sup>1</sup>、岸 政美\*<sup>2</sup>、榊原 彰\*<sup>2</sup>

\*<sup>1</sup> 林業試験場、\*<sup>2</sup> 北海道大学農学部

Hydrogenolysis of hardwood protolignin. -Isolation and structural analysis of a dimer.

Kenichi Sudo\*<sup>1</sup>, Masami Kishi\*<sup>2</sup>, Akira Sakakibara\*<sup>2</sup>

\*<sup>1</sup>Forestry and Forest Product Research Institute,\*<sup>2</sup>Faculty of Agriculture, Hokkaido University

Keywords: *Fraxinus excelsissima*, TLC, Mass spectrometry, <sup>1</sup>H-NMR, dimethoxyariciresinol

1975-111

アテ材リグニンの水素化分解 -縮合型新2量体その他の単離

安田征市、榊原 彰

北海道大学農学部

Hydrogenolysis of lignin in compression wood. Isolation of a new condensed type dimer and other compounds.

Seiichi Yasuda, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: larch, *Larix Kaempferi*, TLC, Mass spectrometry, <sup>1</sup>H-NMR,

1975-112

リグニンの加溶媒分解 (第5報) -トレーサー法による反応の検討 (3)-

可知省吾\*<sup>1</sup>、荒木廣\*<sup>2</sup>、寺島典二\*<sup>2</sup>、神田孝\*<sup>2</sup>

\*<sup>1</sup> 日本紙パルプ研究所、\*<sup>2</sup> 名古屋大学農学部

Solvolysis of lignin (Part 5)

Comparison of solvolysis lignins with other lignins by the radioisotope tracer techniques (3)Shogo Kachi\*<sup>1</sup>, Hiroshi Araki\*<sup>2</sup>, Noritsugu Terashima \*<sup>2</sup>, Takashi Kanda \*<sup>2</sup>

\*<sup>1</sup>Japan Pulp and Paper Research Institute, Inc, \*<sup>2</sup> Faculty of Agriculture, Nagoya University,

Keywords: solvolysis, lignin, radioisotope, carbon-14, tracer

1975-113

Björkman LCC 中のリグニンに結合する糖の結合様式

越島哲夫、夜久富美子、田中龍太郎

大阪工業技術試験所

Linkage type of sugar unit bound to lignin in Björkman LCC.

Tetsuo Koshijima, Kumiko Yaku, Ryutaro Tanaka

Government Industrial Research Institute, Osaka

Keywords: DEAE Sephadex column chromatography, electrophoresis,

1975-114

シラカンバ樹皮のリグニン

三宅基夫、寺沢 実、奥山 寛

帯広畜産大学

Lignin in the bark of birch.

Motoo Miyake, Minoru Terasawa, Hiroshi Okuyama

Obihiro University of Agriculture and Veterinary Medicine

Keywords: *Betula Tauschii*, cork tissue, nitrobenzene oxidation, suberin, pectin

1975-115

3,5-2 置換 *p*-ヒドロキシケイヒアルコールの脱水素重合

棚橋光彦、武内英夫、樋口隆昌

京都大学木材研究所

Dehydrogenative polymerization of 3,5-disubstituted *p*-hydroxycinnamyl alcohol.

Mitsuhiko Tanahashi, Hideo Takeuchi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: 5-iodo-coniferyl alcohol, 3,5-diiodo-*p*-coumaryl alcohol, sinapyl alcohol, <sup>1</sup>H-NMR

1975-116

ヤドリギリグニンの生合成

黒田宏之、樋口隆昌

京都大学木材研究所

Biosynthesis of lignin in *Viscum album*.

Hiroyuki Kuroda, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *O*-methyl transferase, OMT, guaiacyl lignin, syringyl lignin, *Celtis sinensis*, MWL, <sup>13</sup>C-NMR, radio tracer, phenylalanine-U-<sup>14</sup>C

1975-117

傷害、病害に伴うサツマイモ、ウリ類におけるリグニン形成

瓜谷郁三、寺島典二、小島峯雄

名古屋大学農学部

Lignin formation in sweet potato and cucumber caused by injury or blight.

Ikuzo Uritani, Noritsugu Terashima, Mineo Kojima

Faculty of Agriculture, Nagoya University

Keywords: sweet potato, *Ipomea batatas*, cucumber, *Cucumis sativus*, lignification, injury, blight

1975-118

特別講演、植物病態組織でのリグニン生合成

浅田泰次、大口富三、松本勲

愛媛大学農学部

Invited lecture: Biosynthesis of lignin in diseased plant tissue.

Yasuji Asada, Tomizo Ohguchi, Isao Matsumoto

Faculty of Agriculture, Ehime University

Keywords: *Alternaria japonica*, *Peronospora parasitica*, peroxidase, isoperoxidase, lignification inducer

1975-201

ユーカリ材黒液の高分子的性質

岡山隆之、大江礼三郎

東京農工大学農学部

Macromolecular properties of black liquor from eucalyptus wood.

Takayuki Okayama, Reizaburo Ooe

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: kraft lignin, polyphenol, *Eucalyptus marginata*, gel filtration, molecular weight

1975-202

Mg ベース SCP について(4)―廃液の燃焼性と薬品回収―

周 森、住本昌之、近藤民雄

九州大学農学部

On the Mg-base SCP. IV. -Combustibility of waste liquor and recovery of chemicals.

Syu Sin, Masashi Sumimoto, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: magnesium oxide, heat of combustion, semichemical pulp

1975-203

無機吸着剤によるパルプ廃液の処理

猪狩椒将<sup>\*1</sup>、横山正一郎<sup>\*1</sup>、村上達夫<sup>\*2</sup>

<sup>\*1</sup> 東京工業試験所、<sup>\*2</sup> 富士化学工業株式会社

Treatment of pulp waste liquor with inorganic adsorbent.

Yoshimasa Ikari<sup>\*1</sup>, Shoichiro Yokoyama<sup>\*1</sup>, Tatsuo Murakami<sup>\*2</sup>

<sup>\*1</sup>Government Industrial Research Institute, Tokyo, <sup>\*2</sup>Fuji Chemical Co. Ltd.

Keywords: COD, BOD, TOC, gel filtration

1975-204

粘土懸濁液の粘性に与える高分子量リグニンスルホン酸の影響

小山 実

東京工業試験所

Effect of high molecular lignosulfonic acid on the viscosity of clay suspension.

Minoru Koyama  
Government Industrial Research Institute, Tokyo  
Keywords: montmorillonite, kaolinite,

1975-205

リグニン中のフリーラジカルについて

飯塚堯介、中野準三

東京大学農学部

On the free radical in lignin.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: ESR spectrum, pH, EDTA, metal ion, reducing agents

1975-206

KP 蒸解における炭水化物からの色

鮫島一彦、高村憲男

高知大学農学部

Color originated from carbohydrate in kraft cooking.

Kazuhiko Sameshima, Norio Takamura

Faculty of Agriculture, Kochi University

Keywords: *Betula Tauschii*, xylan, xylose, holocellulose, UV and Visible light spectroscopy

1975-207

クラフトパルプ漂白排水中の低分子化合物について

金沢健治、細谷修二、中野準三

東京大学農学部

Low molecular weight compounds in kraft pulp bleach effluent.

Kenji Kanazawa, Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: thiolignin, TLC, gas chromatography, mass spectrometry

1975-208

パルプ漂白廃液中の低分子有機成分について

島田謹爾

林業試験場

Low molecular organic compounds in pulp bleach effluent

Kinji Shimada

Government Forest Experiment Station

Keywords: Japanese red pine, *Pinus densiflora*, BKP, GC/MS,

1975-209

高収率パルプ白色度向上について—亜塩素酸塩利用の効果—

加納直、岩見田糺、角祐一郎

山陽国策パルプ株式会社

Peroxide bleaching of chemimechanical pulps – Effect of pretreatment with sodium chlorite.

Tadashi Kano, Tadashi Iwamida, Yuichiro Sumi

Sanyo Kokusaku Pulp Co., Ltd.

Keywords: chemimechanical pulp, peroxide bleaching, pretreatment, sodium chlorite, brightness

1975-210

パルプのオゾン漂白におけるセルロース保護剤の効果

上嶋 洋、藤井利郎、赤松 勲

四国工業技術試験所

Effect of cellulose protector in ozone bleaching of pulp.

Hiroshi Kamishima, Toshio Fujii, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords: *Pseudotsuga taxifolia*, iron, copper, zinc, cobalt, manganese, organic protector

1975-211

酸素・アルカリ蒸解におけるリグニンの挙動について - $\alpha$ -カルボニル基に基づく新しい反応サイト

青柳哲夫、細谷修二、中野準三

東京大学農学部

Behavior of lignin during oxygen-alkali cooking. -New reaction site based on  $\alpha$ -carbonyl group.

Tetsuo Aoyagi, Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compounds, reaction mechanism, benzyl alcohol, benzyl ether

1975-212

Guaiacylglycerol- $\beta$ -guajacyl ether の酸素・アルカリ酸化分解

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Oxygen-alkali degradation of guaiacylglycerol- $\beta$ -guajacyl ether.

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: UV spectrometry, quinone, pH dependence

1975-213

亜硫酸ソーダ-酸素・アルカリ2段蒸解試験並びに蒸解時におけるリグニンの挙動について

林 忠和、幡 克美、十河村男、山崎 徹

香川大学農学部

Two stage sodium sulfite-oxygen alkali cooking test and behavior of lignin during the cooking.

JongHer Lin, Katsumi Hata, Murao Sogo, Toru Yamasaki

Faculty of Agriculture, Kagawa University

Keywords: Japanese red pine, *Pinus densiflora*, beech, *Fagus crenata*, IR spectrometry

1975-214

酸素・アルカリ処理に関する研究 -廃液の濃縮過程で生ずる沈殿について-

浅野 勲、坂井克己、近藤民雄

九州大学農学部

Studies on the oxygen alkali treatment. -On the precipitant formed in the concentration process of waste liquor.

Isao Asano, Kokki Sakai, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: birch, *Betula tauschii*, scaling problem,

1975-215

アルカリ、酸素漂白におけるプロテクターの保護機構(第3報)

山田紹良、小森重男、林 治助、戸坂圀夫

北海道大学工学部

Protection mechanism by protectors during alkali oxygen bleaching.

Akira Yamada, Shigeo Komori, Jisuke Hayashi, Kunio Tosaka

Faculty of Engineering, Hokkaido University

Keywords: softwood UKP, hydroxyl radical, reducing sugar, glucose

1975-216

アルカリ-酸素蒸解に関する研究(第3報)ふりかけ法による稲わらからのパルプ製造について  
戸坂圀夫<sup>\*1</sup>、渡辺貞良<sup>\*1</sup>、林 治助<sup>\*1</sup>、山田邦重<sup>\*2</sup>、小川文人<sup>\*3</sup>

<sup>\*1</sup>北海道大学工学部、<sup>\*2</sup>株式会社ほくさん、<sup>\*3</sup>王子製紙株式会社

Studies on the oxygen alkali cooking. III. Pulp production from rice straw by sprinkling process.

Kunio Tosaka <sup>\*1</sup>, Sadayoshi Watanabe<sup>\*1</sup>, Jisuke Hayashi<sup>\*1</sup>, Kunishige Yamada<sup>\*2</sup>, Fumito Ogawa<sup>\*3</sup>

<sup>\*1</sup>Faculty of Engineering, Hokkaido University, <sup>\*2</sup>Hokusan Co. Ltd., <sup>\*3</sup>Oji Paper Co. Ltd

Keywords: tensile strength, burst factor, breaking length,

1975-217

非木材パルプに関する研究

御田昭雄<sup>\*1</sup>、山本登久男<sup>\*2</sup>、勝地光雄<sup>\*2</sup>、山崎恒夫<sup>\*2</sup>、勝山敦弘<sup>\*2</sup>、

赤羽利昭<sup>\*3</sup>、梅木一義<sup>\*3</sup>

<sup>\*1</sup>東京工業試験所、<sup>\*2</sup>静岡県製紙工業試験所、<sup>\*3</sup>チッソエンジニアリング株式会社

Studies on non-woody pulp.

Akio Mita<sup>\*1</sup>, Tokuo Yamamoto<sup>\*2</sup>, Mitsuo Katsuji<sup>\*2</sup>, Tsuneo Yamazaki<sup>\*2</sup>, Atsuhiro Katsuyama<sup>\*2</sup>, Toshiaki Akabane<sup>\*3</sup>, Kazuyoshi Umeki<sup>\*3</sup>

<sup>\*1</sup>Government Industrial Research Institute, Tokyo, <sup>\*2</sup>Paper Research Institute of Shizuoka Prefecture, <sup>\*3</sup>Chisso Engineering Co. Ltd.

Keywords: straw, bagasse, silica, SOX chemimechanical pulp, tensile strength

1975-218

特別講演、

これからのウッドケミカスおよび無公害パルプ化に関する最近の海外の研究の動向

中野準三

東京大学農学部

Invited lecture:

Recent research trends in wood chemicals and pollution-free pulping in foreign countries.

Junzo Nakano

Faculty of Agriculture, the University of Tokyo

## 第 21 回 (1976.10.18-19) 東京大学農学部

1976-101

成育時の光質とリグニン

田中治郎

林業試験場

Relation between light quality and lignin structure during growth.

Jiro Tanaka

Government Forest Products Research Institute

Keywords: *Platanus occidentalis*, environmental factor, S/V ratio, wave length,

1976-102

木材腐朽菌によるリグニンモデル化合物の代謝

西田篤実、福住俊郎

東京大学農学部

Metabolism of lignin model compounds by wood rotting fungi.

Atsumi Nishida, Toshio Fukuzumi

Faculty of Agriculture, the University of Tokyo

Keywords: white-rot fungi, *Trametes* sp., ferulic acid, *p*-coumaric acid, UV spectrometry

1976-103

バクテリアによるリグニンモデル化合物の分解(III)

片山義博、福住俊郎

東京大学農学部

Degradation of lignin model compounds by bacteria. III.

Yoshihiro Katayama, Toshio Fukuzumi

Faculty of Agriculture, the University of Tokyo

Keywords: *Pseudomonas* sp., dehydrodiconiferyl alcohol, pinosresinol, guaiacylglycerol- $\beta$ -coniferyl ether, <sup>1</sup>H-NMR, UV spectrometry

1976-104

Betulachrysoquinone hemiketal, A *p*-benzoquinone hemiketal type macrocyclic compound produced by *Phanerochaete chrysosporium*.

C.-L. Chen<sup>\*1</sup>, H.-M. Chang<sup>\*1</sup>, T.K. Kirk<sup>\*2</sup>

<sup>\*1</sup>North Carolina State University, <sup>\*2</sup>Forest Products Laboratory, USDA

Keywords: *Betula lutea*, fungal metabolite, <sup>1</sup>H-NMR, UV spectroscopy

1976-105

アミノベンゼンスルホン酸塩リグニンについて(V)

黒田健一<sup>\*1</sup>、坂井克己<sup>\*2</sup>、近藤民雄<sup>\*2</sup>

<sup>\*1</sup>東京教育大学農学部、<sup>\*2</sup>九州大学農学部

On aminobenzenesulfonate lignin. V.

Ken-ichi Kuroda<sup>\*1</sup>, Kokki Sakai<sup>\*2</sup>, Tamio Kondo<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Education, <sup>\*2</sup> Faculty of Agriculture, Kyushu University

Keywords: vanillyl alcohol, sodium metanilate, <sup>1</sup>H-NMR, UV spectroscopy, IR spectroscopy

1976-106

クラフト蒸解時のイオウの挙動 第1報 蒸解条件とイオウの配分

近藤隆一郎、近藤民雄

九州大学農学部

Behavior of sulfur during kraft pulping. I. On the distribution of sulfur into vapor-, liquid- and

solid-phases during cooking.

Ryuichiro Kondo, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: white birch, *Betula Tauschii*, sulfidity, gas chromatography, methyl mercapthane, dimethyl sulfide, dimethyl disulfide,

1976-107

ゲル浸透クロマトグラフィーによるカラマツアルカリリグニンの分子量分布測定(その2)

香川詔士、小室益広

関東学院大学工学部

Determination of molecular weight distribution of larch alkali lignin by gel permeation chromatography. II.

Shoji Kagawa, Masuhiro Komuro

College of Engineering, Kanto Gakuin University

Keywords: larch, *Larix Kaempferi*, mass spectrometry,

1976-108

竹リグニンのエステル構造 -Coniferyl *p*-Coumarate の脱水素重合-

中村吉紀<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup>山陽国策パルプ株式会社、<sup>\*2</sup>京都大学木材研究所

Ester structure in bamboo lignin. Dehydrogenative polymerization of coniferyl *p*-coumarate.

Yoshiki Nakamura<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Sanyo-Kokusaku Pulp Co. Ltd., <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: UV spectrometry, IR spectrometry, Zutropfverfahren, Zulaufverfahren

1976-109

ネズコ材のリグニンおよびリグナン

久津木英俊、塩 徹、樋口隆昌

京都大学木材研究所

Lignin and lignan in *Thuja Standishii*.

Hidetoshi Kutsuki, Toru Shio, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Thuja plicata*, *O*-methyl transferase, dihydroxythujaplicatin, dihydroxythujaplicatin methyl ether, *S*-adenosylmethionine-<sup>14</sup>CH<sub>3</sub>,

1976-110

ユリノキ中のレジノール型リグナン類

藤本英人、樋口隆昌

京都大学木材研究所

Resinol type lignans in *Liriodendron tulipifera*.

Hideto Fujimoto, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: pinoresinol, medioresinol, syringaresinol, Iriodendrin, TLC, <sup>1</sup>H-NMR,

1976-111

ジオキサン・水によるリグニンの加水分解 –アルデヒド型フェニルクマラン2量体の単離

青山政和、榊原 彰

北海道大学農学部

Hydrolysis of lignin in dioxane–water. –Isolation of aldehyde type phenylcoumaran dimer.

Masakazu Aoyama, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Japanese oak, *Quercus crispula*, TLC, UV spectroscopy, IR spectroscopy, <sup>1</sup>H-NMR,

1976-112

圧縮あて材プロトリグニンの水素化分解 – 縮合型二量体の単離

安田征市、榊原 彰

北海道大学農学部

Hydrogenolysis of protolignin in compression wood. –Isolation of condensed type dimers.

Seiichi Yasuda, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: larch, *Larix leptolepis*, mass spectrometry, IR spectroscopy, <sup>1</sup>H-NMR,

1976-113

リグニン水素化分解物の <sup>13</sup>C-NMR による検討

武山浩武、佐藤哲夫、榊原 彰

北海道大学農学部

Examination of lignin hydrogenolysis products by <sup>13</sup>C-NMR.

Hirotake Takeyama, Tetsuo Sato, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Yezo spruce, *Picea jezoensis*,

1976-114

*Arundo donax*, *Welwitschia bainesii* 及び関連物質の酸化分解

安田征市<sup>\*1</sup>、G. E. Miksche<sup>\*2</sup>

<sup>\*1</sup>北海道大学農学部、<sup>\*2</sup>Lund Institute of Technology, Sweden

Oxidative degradation of *Arundo donax*, *Welwitschia bainesii* and related materials.

Seiichi Yasuda<sup>\*1</sup>, G. E. Miksche<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Lund Institute of Technology, Sweden

Keywords: leaf lamina, petiole, permanganate oxidation, gas chromatography,

1976-115

シリングル核リッチリグニンの単離

山崎 徹<sup>\*1</sup>、幡 克美<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup>香川大学農学部、<sup>\*2</sup>京都大学木材研究所

Isolation of syringyl nucleus-rich lignin.

Toru Yamasaki<sup>\*1</sup>, Katsumi Hata<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: mercury acetate, mercuration, MWL, nitrobenzene oxidation,

11976-116

総合討論:リグニン化学構造

座長: 寺島典二 (名古屋大学農学部)

General discussion: Structure of lignin.

Moderator: Noritsugu Terashima (Faculty of Agriculture, Nagoya University)

Keywords:

1976-201

パルプの酸素酸化反応機構 反応速度論的研究

山田紹良、戸坂罔夫、林 治助

北海道大学工学部

Reaction mechanism of oxygen oxidation of pulp. -Kinetic study.

Akira Yamada, Kunio Tosaka, Jisuke Hayashi

Faculty of Engineering, Hokkaido University

Keywords: cellulose protectant, glucose, triethanolamine, magnesium sulfate, Mg-EDTA

1976-202

放射性同位元素標識リグニンの反応 -リグニンを構成する各炭素の酸素・アルカリ蒸解中の挙動 (2)

荒木 広、寺島典二

名古屋大学農学部

Radiotracer experiments on lignin reactions. -The behavior of lignin carbons in oxygen-alkali pulping process. II.

Hiroshi Araki, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: oxygen-alkali pulping, radiotracer, radioisotope, carbon 14, pine, lignin, gel filtration,

1976-203

Dihydrodehydrodiisoeugenol の酸素・アルカリ酸化

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Oxygen alkali oxidation of dihydrodehydrodiisoeugenol.

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: UV spectrometry, difference spectrum,  $\sigma$ -quinone

1976-204

非木材植物の酸化的脱リグニンについて

Tran van Ai、坂井克己、近藤民雄

九州大学農学部

On the oxidative delignification of certain non-woody plants.

Tran van Ai, Kokki Sakai, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Oryza sativa*, *Hordeum vulgare*, *Phyllostachys pubescens*, *Saccharum officinarum*, sodium chlorite, Wise method

1976-205

クラフトパルプの酸素-オゾン漂白について

藤井利郎、上嶋 洋、赤松 勲

#### 四国工業技術試験所

Oxygen-ozone bleaching of kraft pulp.

Tosiro Fujii, Hiroshi Kamishima, Isao Akamatsu

National Industrial Research Institute of Shikoku

Keywords: Douglas fir, *Pseudotsuga taxifolia*, brightness, pH

1976-206

クラフトパルプのメタノール添加オゾン漂白

上嶋 洋、藤井利郎、赤松 勲

四国工業試験所

Bleaching of kraft pulp by ozone with addition of methanol.

Hiroshi Kamishima, Tosiro Fujii, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords: cellulose protectant, brightness, breaking length, tear factor

1976-207

総合討論: 酸化的脱リグニン

座長 近藤民雄 (九州大学農学部)

General discussion: Oxidative delignification.

Moderator: Tamio Kondo (Faculty of Agriculture, Kyushu University)

1976-208

サルファイト系高歩留パルプの製造に関する研究 第5報 ディスクリファイニングによって露出する繊維表面

岩見田 紘<sup>\*1</sup>, 角 祐一郎<sup>\*1</sup>, 中野準三<sup>\*2</sup>

<sup>\*1</sup> 山陽国策パルプ株式会社, <sup>\*2</sup> 東京大学農学部

Studies on production of sulfite chemimechanical pulps, Part 5: Fiber surface exposed by disk-refining.

Tadashi Iwamida<sup>\*1</sup>, Yuichiro Sumi<sup>\*1</sup>, Junzo Nakano<sup>\*2</sup>

<sup>1</sup>Sanyo Kokusaku Pulp Co., Ltd., <sup>2</sup> Faculty of Agriculture, the University of Tokyo,

Keywords: sulfite chemimechanical pulp, disk-refining, fiber surface, compound middle lamella, secondary wall, *Abies Mayriana*, *Betula Tauschii*, scanning electron microscopy,

1976-209

リグニンの塩素化アルカリ抽出 (IX) 塩素化ジオキサンリグニン (CL) の 2, 3 の物理化学的性質  
河内進策

宮崎大学農学部

Chlorination of lignin followed by alkali extraction. IX. Physicochemical properties of chlorinated dioxane lignin.

Sinsaku Kawachi

Faculty of Agriculture, Miyazaki University

Keywords: Japanese red pine, *Pinus densiflora*, dioxane lignin, viscosity, heat of wetting

1976-210

アカマツ材クラフト漂白廃液中の有機成分

島田謹爾

林業試験場

Organic components in bleaching effluent of red pine kraft pulp.

Kinji Shimada

Government Forest Experiment Station

Keywords: *Pinus densiflora*, gas chromatography, mass spectrometry, alkali-copper dioxide oxidation,

1976-211

パルプ廃液の浄化に関する研究 一活性汚泥法による処理一

八重樫稔、三浦 清

北海道大学農学部

Studies on the purification of pulp mill effluent. -Treatment with activated sludge.

Minoru Yaegashi, Kiyoshi Miura

Faculty of Agriculture, Hokkaido University

Keywords: *Betula Tauschii*, Glehn's spruce, *Picea Glehnii*. chromaticity, COD, BOD, TOC

1976-212

パルプスラッジから粒状活性炭の製造

品部義秋, 国正秀昭

東洋パルプ株式会社

Manufacturing of granular activated carbon from pulp and paper sludge.

Yoshiaki Shinabe, Hideaki Kunimasa

Toyo Pulp Co., Ltd.

Keywords: pulp and paper mills, organic sludges, granular activated carbon, adsorption, dry distillation

1976-213

紙パルプ排水水質モニタリングについての一方法

中村孝一, 佐藤坦, 福島正輝, 秦邦男

十條製紙

A monitoring method of pulp and paper effluents.

Koichi Nakamura, Taira Sato, Masateru Fukushima, Kunio Hata

Jujo Paper Co., Ltd.

Keywords: pulp and paper effluents, COD, BOD, continuous monitoring system, ultraviolet absorption method

1976-214

特別講演、紙・パルプ産業の現状と問題点

松井康博

十條製紙株式会社

Invited lecture:

Present state and future problems in pulp and paper industry.

Yasuhiro Matsui

Jujo Paper Co. Ltd.

## 第 22 回 (1977.10.8-9)北海道大学農学部

1977-101

DHP 合成に対する新しい試み

棚橋光彦、樋口隆昌

京都大学木材研究所

A new trial of synthesis of DHP.

Mitsuhiko Tanahashi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: dialysis membrane, cellulose tube, coniferyl alcohol, sinapyl alcohol, Zulaufverfahren, Zutropfverfahren

1977-102

グワヤシルグリセロール- $\beta$ -グワヤシルエーテルと糖類の反応(第2報)

田中憲次、中坪文明、樋口隆昌

京都大学木材研究所

Reaction of guaiacylglycerol- $\beta$ -guaiacyl ether and sugar. II.

Kenji Tanaka, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: LCC, lignin carbohydrate complex, quinone methide, gel filtration,  $^1\text{H-NMR}$

1977-103

コニフェリルアルコールと  $\alpha$ -カテキンの脱水素共重合

小寺 学、棚橋光彦、樋口隆昌

京都大学木材研究所

Dehydrogenative copolymerization of coniferyl alcohol and  $\alpha$ -catechin.

Manabu Kodera, Mitsuhiko Tanahashi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: molecular weight, UV spectroscopy, permanganate oxidation,

1977-104

リグニン生合成と側鎖飽和型フェノール成分

寺沢 実、三宅基夫

帯広畜産大学

Biosynthesis of lignin and phenolic components with saturated side chain.

Minoru Terasawa, Motoo Miyake

Obihiro University of Agriculture and Veterinary Medicine

Keywords: *Betula platyphylla*, beturoside- $^{14}\text{C(U)}$ , platypylloside- $^{14}\text{C(U)}$ , phenylalanine- $^{14}\text{C(U)}$ , radio-tracer

1977-105

アメリカデイコリグニン生合成の特異性

久津木英俊、樋口隆昌

京都大学木材研究所

Specificity in lignin biosynthesis in *Erythrina crista-galli*.

Hidetoshi Kutsuki, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: radio-tracer, ferulic acid-2- $^{14}\text{C}$ , sinapic acid-2- $^{14}\text{C}$ , acidolysis, TLC, poplar, *Pinus Thunbergii*

1977-106

デヒドロジコニフェリルアルコールの微生物分解

大田雅彦<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、岩原章二郎<sup>\*2</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>香川大学農学部

Degradation of dehydrodiconiferyl alcohol by microorganisms.

Masahiko Ohta<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, Shojiro Iwahara<sup>\*2</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup> Faculty of Agriculture, Kagawa University

Keywords: biodegradation, *Fusarium* sp., phenylcoumaran substructures, <sup>1</sup>H-NMR,

1977-107

微生物によるコニフェリルアルコール脱水素重合体(DHP)の分解について

岩原章二郎<sup>\*1</sup>、桑原正章<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup>香川大学農学部、<sup>\*2</sup>京都大学木材研究所

Degradation of dehydrogenative polymer of coniferyl alcohol (DHP) by microorganisms.

Shojiro Iwahara<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: biodegradation, *Fusarium* sp., gel filtration, pinosresinol, dehydrodiconiferyl alcohol

1977-108

微生物によるリグニン関連芳香族化合物の代謝

桑原正章、岩原章二郎

香川大学農学部

Metabolism of lignin related aromatic compounds by microorganisms.

Masaaki Kuwahara, Shojiro Iwahara

Faculty of Agriculture, Kagawa University

Keywords: biodegradation, *Pseudomonas* sp., *Rhodotorula* sp., *Corynebacterium glutamicum*, demethoxylation

1977-109

木材腐朽菌の Benzoic acids, Cinnamic acids の還元酵素、及び Ferulic acid から Vanillic acid の生成酵素系について

西田篤実、福住俊郎

東京大学農学部

Reducing enzymes of benzoic acids and cinnamic acids in wood rotting fungi, and enzyme system converting ferulic acid to vanillic acid.

Atsumi Nishida, Toshio Fukuzumi

Faculty of Agriculture, the University of Tokyo

Keywords: *Trametes* sp., 3,4,5-trimethoxybenzoic acid, gas chromatography

1977-110

アテ材化学成分の研究 -主として圧縮アテ材のリグニンについて-

榊原 彰<sup>\*1</sup>、諸星紀幸<sup>\*2</sup>、安田征市<sup>\*3</sup>

<sup>\*1</sup>北海道大学農学部、<sup>\*2</sup>東京農工大学農学部、<sup>\*3</sup>名古屋大学農学部

Studies on the chemical components of reaction wood. -Lignin in compression wood.

Akira Sakakibara<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*2</sup>, Seiichi Yasuda<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of

Agriculture and Technology, <sup>\*3</sup>Faculty of Agriculture, Nagoya University

Keywords: *Abies sachalinensis*, *Larix leptolepis*, *Fraxinus mandshurica*, lariciresinol *p*-coumarate, *p*-hydroxyphenyl unit

1977-111

Mäule 反応の呈色機構(第 8 報)

飯塚堯介、中野準三

東京大学農学部

Mechanism of Mäule color reaction. VIII.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compound, ESR spectroscopy, visible light absorption spectroscopy  
chlorinated *o*-quinone,

1977-112

トレーサー法によるリグニンの諸反応の解析 -パルプ化過程におけるフェニルプロパン側鎖末端基の挙動-

荒木 広、富村洋一、寺島典二

名古屋大学農学部

Radiotracer experiments on lignin reactions. -The behaviour of phenylpropane side-chain carbons during pulping process-

Hiroshi Araki, Yoichi Tomimura, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords; radiotracer, radioisotope, carbon 14, pine, lignin, kraft pulping, soda pulping, oxygen-alkali pulping, gel filtration,

1977-113

三弗化硼素、フェノール系におけるリグニン及びリグニンモデル化合物の反応

船岡正光、阿部 勲

三重大学農学部

Reaction of lignin and lignin model compounds in boron trifluoride and phenol system.

Masamitsu Funaoka, Isao Abe

Faculty of Agriculture, Mie University

Keywords; diphenylmethane, catechol, nucleus exchange reaction

1977-114

中性での H<sub>2</sub>O<sub>2</sub> 酸化によるリグニンの淡色化について

石川久雄、沖 妙、大久保克美

愛媛大学農学部

Lignin color reduction by H<sub>2</sub>O<sub>2</sub> oxidation in neutral condition.

Hisao Ishikawa, Tae Oki, Katsumi Okubo

Faculty of Agriculture, Ehime University

Keywords; lignosulfonic acid, thioglignin, dioxane lignin, MWL, reductive bleaching, zinc dithionite, *o*-quinone, *p*-quinone

1977-115

過酸化物および酸素・アルカリによるリグニン酸化分解の特徴

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Specificity in oxidative degradation of lignin by peroxide and oxygen alkali.

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords; lignin model compounds, dioxane lignin, peracetic acid, hydrogen peroxide

1977-116

総合討論:

座長: 樋口隆昌(京都大学木材研究所)

General discussion:

Moderator: Takayoshi Higuchi (Wood Research Institute, Kyoto University)

1977-201

リグニン及びリグニンモデル化合物のオゾン分解

金子英信、細谷修二、中野準三

東京大学農学部

Degradation of lignin and lignin model compounds by ozone.

Hidenobu Kaneko, Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords; guaiacylglycerol- $\beta$ -guaiacyl ether, TLC, HPLC,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$

1977-202

針葉樹リグニンモデル化合物のオゾン分解

小島康夫、三浦 清、香山 彊

北海道大学農学部

Degradation of softwood lignin model compounds by ozone.

Yasuo Kojima, Kiyoshi Miura, Tsutomu Kayama

Faculty of Agriculture, Hokkaido University

Keywords; UV spectrometry, IR spectrometry, TLC,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$

1977-203

液相法によるパルプのオゾン漂白

藤井利郎、上嶋 洋、赤松 勲

四国工業技術試験所

Ozone bleaching of pulp in liquid phase.

Toshiro Fujii, Hiroshi Kamishima, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords; Douglas fir, *Pseudotsuga taxifolia*, cellulose protectant, gas phase bleaching

1977-204

クラフトパルプのオゾン漂白におけるメタノールのセルロース保護機構に関する研究

上嶋 洋、藤井利郎、赤松 勲

四国工業技術試験所

Mechanism of protection of cellulose by methanol during ozone bleaching of kraft pulp.

Hiroshi Kamishima, Toshiro Fujii, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords; Douglas fir, *Pseudotsuga taxifolia*, *n*-hexane, ethyl acetate, acetone methyl oxalate, pyridine, methyl cellosolve

1977-205

RGP のオゾン及びアルカリによる後処理

小林 武、細川 純、久保隆昌、木村 裕

四国工業技術試験所

Posttreatment of RGP with ozone and alkali.

Takeshi Kobayashi, Jun Hosokawa, Takamasa Kubo, Yutaka Kimura

Government Industrial Research Institute, Shikoku

Keywords;

1977-206

酸素・アルカリ蒸解におけるリグニンの挙動について

青柳哲夫、細谷修二、中野準三

東京大学農学部

Behavior of lignin during oxygen alkali pulping.

Tetsuo Aoyagi, Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords; lignin model compounds, TLC, mass spectrometry, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR

1977-207

亜硫酸ソーダー酸素・アルカリ蒸解について

幡 克美、林 忠和、十河村男、山崎 徹

香川大学農学部

On the sodium sulfite-oxygen/alkali pulping.

Katsumi Hata, JongHer Lin, Murao Sogo, Toru Yamasaki

Faculty of Agriculture, Kagawa University

Keywords; beech, *Fagus crenata*, *Eucalyptus* sp. physical properties of NS-OA pulp

1977-208

クラフト蒸解におけるリグニン中へのイオウの取り込み

石野良明、近藤隆一郎、近藤民雄

九州大学農学部

Introduction of sulfur into lignin during kraft pulping.

Yoshiaki Ishino, Ryuichiro Kondo, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords; Japanese red pine, *Pinus densiflora*, hydrogen sulfide, sulfidation of wood, wood sulfide

1977-209

クラフト蒸解時のイオウの挙動(III)―揮発性有機イオウ化合物の生成について―

近藤隆一郎、近藤民雄

九州大学農学部

Behavior of sulfur during kraft pulping. III. On the formation of volatile organic sulfur compounds.

Ryuichiro Kondo, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords; *Betula Tauschii*, *Pinus densiflora*, dioxane lignin, lignin model compound, methyl mercaptane, dimethyl sulfide, dimethyl disulfide, demethylation reaction

1977-210

SOX 法によるバガスのパルプ化

御田昭雄<sup>\*1</sup>、佐伯 剛<sup>\*2</sup>

<sup>\*1</sup> 東京工業試験所、<sup>\*2</sup> 工学院大学

Pulping of bagasse by SOX process.

Akio Mita<sup>\*1</sup>, Tsuyoshi Saiki<sup>\*2</sup>

<sup>\*1</sup>Government Chemical Industrial Research Institute, Tokyo, <sup>\*2</sup>Kogakuin University

Keywords; cooking with ( $\text{Na}_2\text{SO}_4 + \text{SO}_2$ ), soda pulping, electron microscopy

1977-211

$\text{SO}_2 + \text{MgSO}_4$  2 成分蒸解法に関する研究 「広葉樹の木材細胞壁の porous 構造と溶出リグニンの分子量特性」

鈴木 勉、戸坂 圀夫、林 治助

北海道大学工学部

Studies on two component pulping with  $\text{SO}_2 + \text{MgSO}_4$ . "Relation between porous structure of hardwood cell wall and molecular weight characteristics of dissolved lignin".

Tsutomu Suzuki, Kunio Tosaka, Jisuke Hayashi

Faculty of Engineering, Hokkaido University

Keywords; *Betula Ermanii*, pore volume, gel filtration, cell wall morphology

1977-212

マグネシヤ系吸着剤を中心にした NSCP 廃水の処理

猪狩淑将<sup>\*1</sup>、横山正一郎<sup>\*1</sup>、板矢柳太郎<sup>\*2</sup>、池田恵一<sup>\*2</sup>、大熊恒雄<sup>\*2</sup>、

加藤啓介<sup>\*3</sup>、深川和幸<sup>\*3</sup>

<sup>\*1</sup> 東京工業試験所、<sup>\*2</sup> 北曹、<sup>\*3</sup> 住重エンバイロ

Processing of NSCP effluent with magnesia adsorbent.

Yoshimasa Ikari<sup>\*1</sup>, Shoichiro Yokoyama<sup>\*1</sup>, Ryutaro Itaya<sup>\*2</sup>, Kei-ichi Ikeda<sup>\*2</sup>, Tsuneo Okuma<sup>\*2</sup>, Keisuke Kato<sup>\*3</sup>, Kazuyuki Fukagawa<sup>\*3</sup>

<sup>\*1</sup>Government Chemical Industrial Research Institute, Tokyo, <sup>\*2</sup>Hokuso Co. Ltd., <sup>\*3</sup>Sumijyu

Environmental Engineering Co. Ltd.

Keywords; COD, chromaticity, TOC, activated sludge

1977-213

クラフトパルプ廃水、アルカリチオリグニン、リグニンモデル物質の石灰による凝集処理

赤松 勲、上嶋 洋、藤井利郎、細川 純

四国工業技術試験所

Coagulation treatments with lime of effluent from kraft pulp mill, alkali thiolignin, and lignin model compounds.

Isao Akamatsu, Hiroshi Kamishima, Toshiro Fujii, Jun Hosokawa

Government Industrial Research Institute, Shikoku

Keywords; curcumin, tin, zinc, dehydrodiisoeugenol

1977-214

総合討論:

座長: 中野準三  
東京大学農学部  
General discussion:  
Moderator: Junzo Nakano  
Faculty of Agriculture, the University of Tokyo

1977-215

特別講演:  
フラインケミカルスを中心としたリグニン利用の将来  
岡部次郎  
山陽国策パルプ株式会社

Invited lecture:  
Future aspects of utilization of lignin as fine chemicals.  
Jiro Okabe  
Sanyo-Kokusaku Pulp Co. Ltd.

Keywords: water-reducing admixtures, granulation agent for ore powder, cement detergent,

## 第 23 回 (1978.11.1-2) 愛媛大学農学部

1978-101

シナップ酸形成能の高いコノテガシワ *O*-メチル基転位酵素について  
久津木英俊、島田幹夫、樋口隆昌  
京都大学木材研究所

*O*-Methyl transferase in *Thuja orientalis* having high sinapic acid forming ability.

Hidetoshi Kutsuki, Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: substrate specificity, metal ion demand, optimum pH, Michaelis constant

1978-102

透析膜法による DHP の合成

棚橋光彦、樋口隆昌

京都大学木材研究所

Synthesis of DHP by the dialysis membrane method.

Mitsuhiko Tanahashi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: Zulaufverfahren, Zutropfverfahren, coniferyl alcohol, sinapyl alcohol, LCC, cell wall model

1978-103

木材腐朽菌による針葉樹、広葉樹型リグニンの分解に見られるシリンギル核劣化の優先性

野口明雄<sup>\*1</sup>、島田幹夫<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、青島清雄<sup>\*2</sup>

<sup>\*1</sup> 京都大学木材研究所、<sup>\*2</sup> 林業試験場

Preferential degradation of syringyl nucleus in decay of softwood and hardwood lignin by wood-rotting fungi.

Akio Noguchi<sup>\*1</sup>, Mikio Shimada<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, Kiyoo Aoshima<sup>\*2</sup>

\*<sup>1</sup>Wood Research Institute, Kyoto University, \*<sup>2</sup>Forestry and Forest Products Research Institute  
Keywords: *Coriolus versicolor*, *Poria subacida*, *Tyromyces palustris*, host specificity, radio-labeled lignin model compounds,

1978-104

リグニン生分解への立体生化学的アプローチ:ラッカーゼのリグニン側鎖不斉構造に及ぼす非立体特異的酸化反応の意義

島田幹夫、野口明雄、樋口隆昌

京都大学木材研究所

Biostereochemical approaches to lignin biodegradation: Meaning of non-stereo specific oxidation reaction on asymmetric side chain structure of lignin by laccase.

Mikio Shimada, Akio Noguchi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Coriolus versicolor*, <sup>3</sup>H-coniferyl alcohol, <sup>3</sup>H/<sup>14</sup>C-coniferyl alcohol, <sup>3</sup>H/<sup>14</sup>C-DHP,

1978-105

グアヤシルグリセロール-β-コニフェリルエーテルの微生物分解(第2報)

片山健至、中坪文明、樋口隆昌

京都大学木材研究所

Microbial degradation of guaiacylglycerol-β-coniferyl ether. II.

Takeshi Katayama, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Fusarium solani*, TLC, <sup>1</sup>H-NMR, UV spectrometry

1978-106

デヒドロジコニフェリールアルコールの酵素的酸化について

岩原章二郎<sup>\*1</sup>、西平 強<sup>\*1</sup>、城森孝仁<sup>\*1</sup>、桑原正章<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup>香川大学農学部, <sup>\*2</sup>京都大学木材研究所

Enzymatic oxidation of dehydrodiconiferyl alcohol.

Shojiro Iwahara<sup>\*1</sup>, Tsuyoshi Nishihira<sup>\*1</sup>, Takahito Jomori<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: *Fusarium* spp. gel filtration, TLC,

1978-107

糸状菌および細菌によるリグニン関連芳香族化合物の代謝

桑原 正章、登林浩司、佐藤哲雄、岩原章二郎

香川大学農学部

Metabolism of lignin related aromatic compounds by fungi and bacteria.

Masaaki Kuwahara, Koji Noboribayashi, Tetsuo Sato, Shojiro Iwahara

Faculty of Agriculture, Kagawa University

Keywords: *Pseudomonas* sp., *Fusarium solani*, *Fusarium oxysporum*, *Phanerochaete chrysosporium*,

differential respirometer,

1978-108

カラマツの phenylpropane 誘導体および関連物質

三木啓司、笹谷宜志、榊原 彰

北海道大学農学部

Phenylpropane derivatives and related compounds from *Larix Kaempferi*.

Keiji Miki, Takashi Sasaya, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: larch, *Larix Kaempferi*, inner bark, UV spectroscopy, <sup>1</sup>H-NMR,

1978-109

ジオキサン・水によるリグニンの加水分解 —ラクトン環を有する化合物の単離—

青山政和、榊原 彰

北海道大学農学部

Hydrolysis of lignin by dioxane-water. —Isolation of compounds having lactone ring.

Masakazu Aoyama, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: Japanese oak, *Quercus crispula*, IR spectroscopy, mass spectrometry, <sup>1</sup>H-NMR,

1978-110

プロトリグニンの水素化分解に関する研究 —新 3 量体の単離—

保田智之、榊原 彰

北海道大学農学部

Studies on the hydrogenolysis of protolignin.—Isolation of a new trimer.

Yasuda Tomoyuki, Ajira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: larch, *Larix Kaempferi*, compression wood, matairesinol, IR spectroscopy, mass spectrometry, <sup>1</sup>H-NMR,

1978-111

リグニンの化学構造の不均質性に関する研究

富村洋一、横井達明、寺島典二

名古屋大学農学部

Studies on the heterogeneity of lignin structure.

Yooichi Tomimura, Tatsuaki Yokoi, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: *Pinus Thunbergii*, Kamabuchi poplar (*Populus nigra* X *Populus Maximowiczii*), radiotracer, <sup>3</sup>H, <sup>14</sup>C, double labeling

1978-112

MWL より分離した LCC 中のリグニンと糖の結合様式について

榎 章郎、有国 尚、越島哲夫

京都大学木材研究所

Linkages between lignin and carbohydrates in LCC isolated from MWL.

Akio Enoki, Hisashi Arikuni, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, enzymatic degradation, Seruroshin, boron tribromide,

1978-113

β-アルコキシ脱離反応を用いたアリアルグリセロール-β-アリアルエーテル結合の選択的開裂

松本雄二、石津 敦、中野準三

東京大学農学部

Selective cleavage of arylglycerol- $\beta$ -aryl ether bond by  $\beta$ -alkoxy elimination reaction.

Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *erythro* and *threo* isomers,  $^{13}\text{C}$ -NMR, mass spectrometry, TLC

1978-114

三弗化硼素・フェノール系におけるリグニンの反応 -ジフェニルメタン構造の形成について

船岡正光、阿部 勲

三重大学農学部

Reaction of lignin in borontrifluoride-phenol system. -Formation of diphenylmethane structure.

Masamitsu Funaoka, Isao Abe

Faculty of Agriculture, Mie University

Keywords: Yezo spruce, *Picea jezoensis*, TLC, quinone methide, quinhydrone, visible light absorption spectrometry

1978-115

過マンガン酸カリ酸化分解によるリグニン化学構造の分析

諸星紀幸<sup>\*1</sup>、W. G. Glasser<sup>\*2</sup>

東京農工大学農学部

Analysis of lignin structure by oxidative degradation with potassium permanganate.

Noriyuki Morohoshi<sup>\*1</sup>, W.G. Glasser<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Virginia Polytechnic Institute and State University

Keywords: Loblolly pine, *Pinus taeda*, red alder, *Alnus rubra*, gel filtration, gas chromatography

1978-116

アルカリリグニンの着色構造 -バニリルアルコール縮合物の着色構造について-

安田征市、藤井和美、尹 炳虎、寺島典二

名古屋大学農学部

Chromophoric structures of alkali lignin. Chromophoric structures of condensation products from vanillyl alcohol.

Seiichi Yasuda, Kazumi Fujii, Byung-Ho Yoon, Noritsugu Terashima.

Faculty of Agriculture, Nagoya University

Keywords:  $^{13}\text{C}$ -enrichment,  $^{13}\text{C}$ -NMR, diguaiacyl methane, quinone methide,

1978-117

核共役二重結合を有する化合物の過酸化水素に対する挙動

小島康夫、香山 彊

北海道大学農学部

Behavior of aromatic compounds carrying conjugated double bonds in the reaction with hydrogen peroxide.

Yasuo Kojima, Tsutomu Kayama

Faculty of Agriculture, Hokkaido University

Keywords: isoeugenol, dehydrodiisoeugenol, vanillin, *o*-methoxy-*p*-hydroquinone, mass spectrometry,  $^1\text{H}$ -NMR,

1978-201

高濃度オゾン水によるクラフトパルプの漂白

藤井利郎\*<sup>1</sup>、上嶋 洋\*<sup>1</sup>、赤松 勲\*<sup>1</sup>、中山繁樹\*<sup>2</sup>、難波敬典\*<sup>2</sup>

\*<sup>1</sup> 四国工業技術試験所、\*<sup>2</sup> 三菱電機株式会社

Bleaching of kraft pulp with water containing high concentration of ozone.

Toshiro Fujii\*<sup>1</sup>, Hiroshi Kamishima\*<sup>1</sup>, Isao Akamatsu\*<sup>1</sup>, Shigeki Nakayama\*<sup>2</sup>, Takanori Nanba\*<sup>2</sup>

\*<sup>1</sup>Government Industrial Research Institute, Shikoku, \*<sup>2</sup>Mitsubishi Electric Corporation

Keywords: Douglas fir, *Pseudotsuga taxifolia*, brightness, viscosity, pH

1978-202

高収率パルプの製造に関する研究(第3報)TMP のオゾン処理に及ぼすリファイニング温度の影響  
久保隆昌、細川 純、小林 武、赤松 勲、木村 裕

四国工業技術試験所

Studies on the high yield pulp production. III. Effect of refining temperature on ozone treatment of TMP.

Takamasa Kubo, Jun Hosokawa, Takeshi Kobayashi, Isao Akamatsu, Yutaka Kimura

Government Industrial Research Institute, Shikoku

Keywords: Japanese red pine, *Pinus densiflora*, freeness, fiber length distribution, breaking length

1978-203

酸素酸化精製パルプのオゾン漂白について(第2報)

萱場 基、戸坂罔夫、林 治助

北海道大学工学部

Ozone bleaching of oxygen treated pulp. II.

Motoi Kayaba, Kunio Tosaka, Jisuke Hayashi

Faculty of Engineering, Hokkaido University

Keywords: *Betula Tauschii*, brightness,

1978-204

チオリグニンのオゾン分解について

金子英信、細谷修二、中野準三

東京大学農学部

Degradation of thiolignin by ozone.

Hidenobu Kaneko, Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: ESR spectroscopy, double bond content, GPC, IR spectroscopy, <sup>1</sup>H-NMR,

1978-205

クラフト蒸解時のイオウの挙動(IV) 揮発性有機イオウ化合物の生成について

近藤隆一郎、近藤民雄

九州大学農学部

Behavior of sulfur during kraft pulping. IV. On the formation of volatile organic sulfur compounds.

Ryuichiro Kondo, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Betula Tauschii*, *Pinus densiflora*, labile methoxyl group, dioxane lignin

1978-206

放射線前照射チップのクラフト蒸解に関する研究

稲葉政満、飯塚堯介、中野準三

東京大学農学部

Studies on the kraft pulping of wood chips pretreated by  $\gamma$ -ray.

Masamitsu Inaba, Gyosuke Mashitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: beech, *Fagus crenata*,  $\alpha$ -hydroxylalkyl radical

1978-207

アルカリ蒸解助剤テトラヒドロアントラキノンの脱リグニン促進機構

矢口時也<sup>\*1</sup>、佐藤惇夫<sup>\*1</sup>、野村芳禾<sup>\*1</sup>、中村正人<sup>\*1</sup>、細谷修二<sup>\*2</sup>、中野準三<sup>\*2</sup>

<sup>\*1</sup> 本州製紙株式会社、<sup>\*2</sup> 東京大学農学部

Promotion mechanism of delignification by alkaline cooking aids, tetrahydroanthraquinone.

Tokiya Yaguchi<sup>\*1</sup>, Atsuo Satoh<sup>\*1</sup>, Yoshika Nomura<sup>\*1</sup>, Masato Nakamura<sup>\*1</sup>, Shuji Hosoya<sup>\*2</sup>, Junzo Nakano<sup>\*2</sup>

<sup>\*1</sup>Honshu Paper Co. Ltd. <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: guaiacylglycerol- $\beta$ -guaiacyl ether, oxygen-free cooking, carbohydrate

1978-208

ユーカリ材の抽出成分量とパルプ収率

亀井基和<sup>\*1</sup>、大江礼三郎<sup>\*2</sup>

<sup>\*1</sup> 北越製紙株式会社、<sup>\*2</sup> 東京農工大学農学部

Content of extractives and yield of pulp from eucalyptus wood.

Motokazu Kamei<sup>\*1</sup>, Raysaburo Oye<sup>\*2</sup>

<sup>\*1</sup>Hokuetsu Paper Co. Ltd., <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Eucalyptus calophylla*, *Eucalyptus diversicolor*, Klason lignin

1978-209

酸素・アルカリ蒸解の蒸解要因(II)界面活性剤添加の効果

日黒貞利、近藤民雄

九州大学農学部

Cooking factor in oxygen alkali pulping. II. Effect of addition of surface active agents.

Sadatoshi Meguro, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Betula Tauschii*, Asplund pulp, sodium laurylbenzene sulfonate, Tween 20

1978-210

マグネファイト-酸素・Mg(OH)<sub>2</sub> 蒸解について

十河村男、幡 克美、山崎 徹

香川大学農学部

On the magnefite-O<sub>2</sub>+Mg(OH)<sub>2</sub> pulping.

Murao Sogo, Katsumi Hata, Toru Yamasaki

Faculty of Agriculture, Kagawa University

Keywords: *Betula Tauschii*, *Eucalyptus* sp., gel filtration, MWL

1978-211

非木材繊維の叩解について(第2報)

ラム・チ・パクチュエト<sup>\*1</sup>、原 啓志<sup>\*2</sup>、大江礼三郎<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 三島製紙株式会社

Beating of non-woody fiber. II.

Lam T. B. T<sup>\*1</sup>, Keishi Hara<sup>\*2</sup>, Raysabro Oye<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Mishima Paper Co., Ltd.

Keywords: *Linum usitatissimum*, *Hibiscus cannabinus*, mercury penetration, monosaccharide composition

1978-212

バガスから新聞紙パルプの調製について

御田昭雄<sup>\*1</sup>、佐伯 剛<sup>\*2</sup>

東京工業試験所、工学院大学

Production of newspaper pulp from bagasse.

Akio Mita<sup>\*1</sup>, Tsuyoshi Saiki<sup>\*2</sup>

<sup>\*1</sup> Government Chemical Industrial Research Institute, Tokyo, <sup>\*2</sup> Kogakuin University

Keywords: bleaching, brightness, breaking length, tear factor, percent Elmendorf tear factor, folding endurance

1978-213

TMP 法によるバガスのパルプ化

西山昌史<sup>\*1</sup>、松尾隆吉<sup>\*1</sup>、小林良生<sup>\*1</sup>、佐藤隆士<sup>\*2</sup>、Naiyana Niyomwan<sup>\*3</sup>

<sup>\*1</sup> 四国工業技術試験所、<sup>\*2</sup> 日立造船株式会社、<sup>\*3</sup> ASRCT

Pulping of bagasse by TMP process.

Masashi Nishiyama<sup>\*1</sup>, Ryukichi Matsuo<sup>\*1</sup>, Yoshinari Kobayashi<sup>\*1</sup>, Takashi Sato<sup>\*2</sup>, Naiyana Niyomwan<sup>\*3</sup>

<sup>\*1</sup> Government Industrial Research Institute, Shikoku, <sup>\*2</sup> Hitachi Zosen Corporation, <sup>\*3</sup> ASRCT

Keywords: freeness, breaking length, tear factor,

1978-2014

KP 晒廃液中の毒性物質の分画とキャラクタリゼーション

鮫島一彦<sup>\*1</sup>、B. Simson<sup>\*2</sup>、C. W. Dence<sup>\*2</sup>

<sup>\*1</sup> 高知大学農学部、<sup>\*2</sup> ニューヨーク州立大学

Fractionation and characterization of toxic substances in effluent from KP bleaching process.

Kazuhiko Sameshima<sup>\*1</sup>, B. Simon<sup>\*2</sup>, C.W. Dence<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Kochi University, <sup>\*2</sup> State University of New York.

Keywords: southern pine, *Daphnia magna*, *Aspergillus fumigatus*, TOC, molecular weight, VPO

1978-215

KP 蒸解廃液の活性汚泥処理と限外口過特性について

三浦 清、平田裕浩

北海道大学農学部

Active sludge treatment of KP waste liquor and its ultrafiltration characteristics.

Kiyoshi Miura, Yasuhiro Hirata

Faculty of Agriculture, Hokkaido University

Keywords: *Betula platyphylla*, *Picea Glehnii*, BOD, COD, UV and visible light absorption,

1978-216

Mg 系吸着剤のパルプ廃液成分吸着能

猪狩俣将、横山正一郎

東京工業試験所

Adsorption capacity of Mg containing adsorbents for components in pulp mill effluent.

Yoshimasa Ikari, Shoichiro Yokoyama

Government Chemical Industrial Research Institute, Tokyo

Keywords: COD, adsorption isotherm,

1978-217

活性炭吸着機構に及ぼすパルプ製造排水成分の物理化学的性状の影響

飯山賢治、中野準三

東京大学農学部

Effect of physicochemical properties of pulp mill effluent on the mechanism of adsorption by activated carbon.

Kenji Iiyama, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: softwood lignin sulfonic acid, molecular size, intrinsic viscosity, adsorption isotherm

1978-218

特別講演、高収率パルプの現状と問嘩点

角祐一郎

山陽国策パルプ株式会社

Invited lecture:

Present state and problems in high yield pulp production.

Yuichiro Sumi

Sanyo-Kokusaku Pulp Co. Ltd.

Keywords: SCP, TMP, NSSC, brightness, Tampella process, SCA-Billerud process, Ebara process

## 第 24 回 (1979.11.1-2) 京都大学、生産開発科学研究所

1979-101

$\beta$ -O-4 及びシリングレジノール構造からなる三量体リグニンモデル化合物の合成

釜谷保志、中坪文明、樋口隆昌

京都大学木材研究所

Synthesis of a trimeric lignin model compound composed of  $\beta$ -O-4 and syringaresinol substructures.

Yasushi Kamaya, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: stereochemistry, *erythro* and *threo* isomers, IR spectroscopy,  $^1\text{H-NMR}$

1979-102

$\beta$ -O-4 及び  $\beta$ -1 構造からなる三量体リグニンモデル化合物の合成

難波宏彰、中坪文明、樋口隆昌

京都大学木材研究所

Synthesis of a trimeric lignin model compound composed of  $\beta$ -O-4 and  $\beta$ -1 substructures.  
Hiroaki Namba, Fumiaki Nakatsubo, Takayoshi Higuchi  
Wood Research Institute, Kyoto University  
Keywords: IR spectroscopy, UV spectroscopy,  $^1\text{H-NMR}$ ,

1979-103

フェニルクマラン及び  $\beta$ -1 構造からなる三量体リグニンモデル化合物の合成並びにリグニン  
モデル化合物の合成に関するまとめ

中坪文明、樋口隆昌  
京都大学木材研究所

Synthesis of trimeric lignin model compounds composed of phenylcoumaran and  $\beta$ -1 substructures,  
and summary of synthetic method for lignin model compounds.

Fumiaki Nakatsubo, Takayoshi Higuchi  
Wood Research Institute, Kyoto University  
Keywords: IR spectroscopy,  $^1\text{H-NMR}$ , diastereomers,

1979-104

広葉樹プロトリグニンの水素化分解に関する研究 -新 2 量体( $\gamma$ -O-4)の単離  
黄 炳浩、榊原 彰

北海道大学農学部

Studies on the hydrogenolysis of hardwood protolignin. -Isolation of a new dimeric product with  
 $\gamma$ -O-4 linkage.

Byung Ho Hwang, Akira Sakakibara  
Faculty of Agriculture, Hokkaido University  
Keywords: *Fraxinus excelsissima*, TLC, UV spectrum, IR spectrum, MS spectrum,  $^1\text{H-NMR}$ ,

1979-105

リグナン類の  $^{13}\text{C-NMR}$  スペクトル

三木啓司、笹谷宣志、榊原 彰  
北海道大学農学部

$^{13}\text{C-NMR}$  spectroscopy of lignans.

Keiji Miki, Takashi Sasaya, Akira Sakakibara  
Faculty of Agriculture, Hokkaido University  
Keywords: larch, *Larix Kaempferi*, diastereomer, *erythro* and *threo* isomers, chemical shift

1979-106

ユウガオ及びヒョータン硬化果皮のリグニンについて

川上日出国、福田忠徳  
名古屋大学農学部

On the lignin in hardened rind of *Lagenaria siceraria* Standley var. *hispida* Hara and *Lagenaria*  
*siceraria* Standley var. *gourd* Hara.

Hidekuni Kawakami, Tadanori Fukuda  
Faculty of Agriculture, Nagoya University  
Keywords: phenylalanine ammonia-lyase, nitrobenzene oxidation, permanganate oxidation,  
ethanolysis,  $^{13}\text{C-NMR}$ , lignin structure

1979-107

### 出土木材リグニンの化学構造

玉井 篤、井上嘉幸、南 享二

筑波大学農林工学系

Chemical structure of lignin in excavated wood.

Atsushi Tamai, Yoshiyuki Inoue, Kyoji Minami

Institute of Agricultural and Forest Engineering, University of Tsukuba

Keywords: *Aesculus turbinata*, MWL, permanganate oxidation, <sup>1</sup>H-NMR, nitrobenzene oxidation

1979-108

### 透析膜法による LCC の合成と植物細胞壁のモデル化

棚橋光彦、樋口隆昌

京都大学木材研究所

Synthesis of LCC by dialysis membrane method and modeling of plant cell wall.

Mitsuhiko Tanahashi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phyllostachys pubescens*, thermal softening property, hydrophobic chromatography,

1979-109

### リグニン・糖結合体に関する研究(その2)リグニン・糖結合体に及ぼす界面活性剤の効果

東 順一、高橋信義、越島哲夫

京都大学木材研究所

Studies on lignin-carbohydrate complex. II. Effect of surface active agents on lignin-carbohydrate complex.

Junichi Azuma, Nobuyoshi Takahashi, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: Japanese red pine, *Pinus densiflora*, gel filtration, non-ionic detergent, anionic detergent, cationic detergent

1979-110

### 二量体に相当するリグニンモデル化合物の酸化分解

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Oxidative degradation of lignin model compounds corresponding to dimer.

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: guaiacylglycerol- $\beta$ -guaiacyl ether, dihydrodehydrodiisoeugenol, symprocosigenol, oxygen-alkali oxidation, alkaline H<sub>2</sub>O<sub>2</sub> oxidation, peracetic acid oxidation

1979-111

### リグニンの主分散及びローカルモード緩和

畠山兵衛<sup>\*1</sup>、中村邦雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

<sup>\*1</sup>製品科学研究所、<sup>\*2</sup>神奈川県工業試験所、<sup>\*3</sup>繊維高分子材料研究所

Main dispersion and local mode relaxation of lignin.

Hyo Hatakeyama<sup>\*1</sup>, Kunio Nakamura<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Industrial Products Research Institute, <sup>\*2</sup>Industrial Research Institute of Kanagawa Prefecture,

<sup>\*3</sup>Research Institute for Polymers and Textiles.

Keywords: lignin related polystyrenes, MWL, GPC, broad-line NMR, DSC, glass transition

temperature

1979-112

細胞間層リグニンの性状について

趙 南爽、飯塚堯介、中野準三

東京大学農学部

On the characteristics of compound middle lamella lignin.

Nam Seok Cho, Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Betula Ermanii*, MWL, nitrobenzene oxidation, S/V ratio,

1979-113

リグニンのオゾン分解

金子英信、細谷修二、中野準三

東京大学農学部

Degradation of lignin with ozone.

Hidenobu Kaneko, Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: dehydrodivanillyl alcohol, thiolignin, *Picea jezoensis*, soda lignin, TLC, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR

1979-114

リグニンの親水性化に関する研究(2)

飯塚堯介、中野準三

東京大学農学部

Studies on introducing hydrophilicity to lignin. II.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: softwood kraft lignin, sulfonation, surface tension, metal complex formation

1979-115

クラフトリグニンの調製について - 失敗の記録から

中野準三、高塚千代子

東京大学農学部

Preparation of kraft lignin. -Problems in purification procedure.

Junzo Nakano, Chiyoko Takatsuka

Faculty of Agriculture, the University of Tokyo

Keywords: methoxyl content, dioxane, freeze drying

1979-116

特別講演、

Invited lecture:

Speculative pathways for the fungal metabolism of lignin substructures.

T. K. Kirk

Forest Products Laboratory, Madison, U.S.A

Keywords: white-rot fungi, *Phanerochaete chrysosporium*, *Fusarium* sp.,

1979-201

針葉樹リグニンと広葉樹リグニンの担子菌による分解

広居忠量

林業試験場

Degradation of softwood lignin and hardwood lignin by *Basidiomycetes*.

Tadakazu Hiroi,

Forestry and Forest Products Research Institute

Keywords: *Chamaecyparis obtuse*, *Betula Tauschii*, *Pinus densiflora*, *Fagus crenata*, MWL, *Phanerochaete chrysosporium*,

1979-202

カタウロコタケ粗酵素によるリグニンの分解

福田 滋、原口隆英、諸星紀幸

東京農工大学農学部

Degradation of lignin by crude enzyme of *Stereum flustulosum*.

Shigeru Fukuda, Takafusa Haraguchi, Noriyuki Morohoshi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Picea jezoensis*, *Ulmus davidiana*, MWL, Bavendamm's reaction, vanillic acid, ferulic acid

1979-203

*Fusarium* spp. によるリグニン関連芳香族化合物の側鎖の分解について

岩原章二郎<sup>\*1</sup>、城森孝仁<sup>\*1</sup>、一色健二<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

香川大学農学部、京都大学木材研究所

Degradation of side chain of lignin related aromatic compounds by *Fusarium* spp.

Shojiro Iwahara<sup>\*1</sup>, Takahito Jomori<sup>\*1</sup>, Kenji Isshiki<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: biodegradation, 3,4-dimethoxycinnamaldehyde, 3,4-dimethoxycinnamic acid, pinoresinol, UV spectroscopy

1979-204

リグニンの酸化分解反応(II). H<sub>2</sub>O<sub>2</sub>によるクラフトパルプ廃液の酸化分解処理

辰己憲司<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup>公害資源研究所、<sup>\*2</sup>名古屋大学農学部

Oxidative degradation of lignin. II. Oxidative degradation treatment of kraft pulp mill effluent with hydrogen peroxide.

Kenji Tatsumi<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>National Research Institute for Pollution and Resources, <sup>\*2</sup>Faculty of Agriculture, Nagoya University

Keywords: *Pinus densiflora*, Fenton reagent, hydroxyl radical, degradation by UV-H<sub>2</sub>O<sub>2</sub>, COD, TOC

1979-205

クラフト蒸解時のイオウの挙動(VI)蒸解時のメチルメルカプタンについて

近藤隆一郎、近藤民雄

九州大学農学部

Behavior of sulfur during kraft pulping. VI. Methyl mercaptan generated during cooking.

Ryuichiro Kondo, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Betula Tauschii*, *Pinus densiflora*, volatile organic sulfur, kraft cooking

1979-206

処理木粉によるクラフト臭気成分の吸着処理

池田耕作、近藤隆一郎、近藤民雄

九州大学農学部

Adsorption treatment of kraft smell components with pretreated wood powder.

Kosaku Ikeda, Ryuichiro Kondo, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Betula Tauschii*, hydrogen sulfide, methyl mercaptan

1979-207

多段オゾン漂白効果の要因について

小林 武、細川 純、久保隆昌、木村 裕

四国工業技術試験所

Factors affecting multistage ozone bleaching.

Takeshi Kobayashi, Jun Hosokawa, Takamasa Kubo, Yutaka Kimura

Government Industrial Research Institute, Shikoku

Keywords: ash content, resin content, brightness, viscosity,

1979-208

パルプのオゾン漂白廃水の性状

三浦 清、佐藤礼人

北海道大学農学部

Properties of effluent from ozone bleaching of pulp.

Kiyoshi Miura, Ayato Sato

Faculty of Agriculture, Hokkaido University

Keywords: *Betula Tauschii*, kraft pulping, ultrafiltration, UV absorption, BOD, COD

1979-209

針葉樹材 CTMP のオゾン処理

細川 純、久保隆昌、小林 武、赤松 勲

四国工業技術試験所

Ozone treatment of softwood CTMP.

Jun Hosokawa, Takamasa Kubo, Takeshi Kobayashi, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords: *Pinus densiflora*, sulfur dioxide, folding endurance, breaking length, brightness

1979-210

イピルイピルの SOX 法によるパルプ化

御田昭雄<sup>\*1</sup>、佐伯 剛<sup>\*2</sup>

<sup>\*1</sup> 化学技術研究所, <sup>\*2</sup> 工学院大学

Pulping of *Leucaena leucocephala* by SOX process.

Akio Mita<sup>\*1</sup>, Tsuyoshi Saiki<sup>\*2</sup>

<sup>\*1</sup>The Government Chemical Industrial Research Institute, Tokyo, <sup>\*2</sup>Kogakuin University

Keywords: neutral sulfite semichemical pulp, kraft pulp, brightness, ring crush test

1979-211

酸素・アルカリ蒸解の蒸解要因(IV)界面活性剤による脱リグニン促進について

目黒貞利、近藤民雄

九州大学農学部

Cooking factors in oxygen alkali pulping. IV. Promotion of lignin removal by surfactant.

Sadatoshi Meguro, Tamio Kondo

Faculty of Agriculture, Kyushu University

Keywords: *Betula Tauschii*, *Pinus densiflora*, sodium laurylbenzene sulfonate, Asplund process, dioxane lignin

1979-212

TMP 法によるパラゴム廃材のパルプ化

久保隆昌、細川 純、小林 武、赤松 勲、小林良生

四国工業技術試験所

Pulping of Para rubber waste wood by TMP process.

Takamasa Kubo, Jun Hosokawa, Takeshi Kobayashi, Isao Akamatsu, Yoshio Kobayashi

Government Industrial Research Institute, Shikoku

Keywords: *Hevea brasiliensis*, TMP, freeness, breaking length, tear factor, brightness

1979-213

TMP 法によるバガスパルプの漂白特性

松尾隆吉、西山昌史、小林良生

四国工業技術試験所

Bleaching characteristics of bagasse pulp produced by TMP process.

Ryukichi Matsuo, Masashi Nishiyama, Yoshinari Kobayashi

Government Industrial Research Institute, Shikoku

Keywords: sugar cane, *Saccharum* sp, brightness,

1979-214

活性汚泥処におけるクラフトリグニンの挙動

鮫島一彦、高村憲男、瀬戸辰彦

高知大学農学部

Behavior of kraft lignin during treatment with activated sludge.

Kazuhiko Sameshima, Norio Takamura, Tatsuhiko Seto

Faculty of Agriculture, Kochi University

Keywords: *Pinus densiflora*, *Betula Tauschii*, BOD, COD, gel filtration, UV absorption spectroscopy

1979-215

パルプ蒸解廃液からの活性炭製造に関する研究 第4報

戸坂圀夫、鈴木英次、林治助

北海道大学工学部

Studies on the production of activated carbon from pulp waste liquor. IV.

Kunio Tosaka, Eiji Suzuki, Jisuke Hayashi

Faculty of Engineering, Hokkaido University

Keywords: *Abies Mayriana*, steam activation

1979-216

特別講演、リグニン利用の現状と問題点

町原 晃

山陽国策パルプ株式会社

Invited lecture: Present state and problems in utilization of lignin.

Akira Machihara

Sanyo-Kokusaku Pulp Co. Ltd.

Keywords: cement dispersant, binder of ore powder, detergent

## 第 25 回 (1980.10.17-18)九州大学農学部

1980-101

1,2-ジアリールプロパン-1,3-ジオール化合物の *Fusarium solani* による分解

難波宏彰、中坪文明、樋口隆昌

京都大学木材研究所

Degradation of 1,2-diarylpropane-1,3-diol compounds by *Fusarium solani*.

Hiroaki Namba, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: mass spectrometry, <sup>1</sup>H-NMR, UV absorption spectroscopy, phenol oxidase, aldorase

1980-102

シリングル核を含む  $\beta$ -O-4 および  $\beta$ -5 型ジリグノールの *Fusarium solani* による分解

片山健至、中坪文明、樋口隆昌

京都大学木材研究所

Degradation of  $\beta$ -O-4 and  $\beta$ -5 dilignols containing syringyl nucleus by *Fusarium solani*.

Takeshi Katayama, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: biodegradation, syringylglycerol- $\beta$ -vanillin ether, oxygenase, phenol oxidase

1980-103

*Fusarium solani* による *d,t*-シリングレジノールの分解

釜谷保志、中坪文明、樋口隆昌

京都大学木材研究所

Degradation of *d,t*-syringaresinol by *Fusarium solani*.

Yasushi Kamaya, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: UV absorption spectroscopy, mass spectrometry, <sup>1</sup>H-NMR, HPLC, phenol oxidase

1980-104

リグニンの微生物分解に関与する酵素系について

沖 妙、渡部広行、石川久雄

愛媛大学農学部

Enzyme systems participating in microbial degradation of lignin.

Tae Oki, Hiroyuki Watanabe, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Lentinus edodes*, *Fagus crenata*, dioxane lignin, guaiacylglycerol- $\beta$ -guaiacyl ether, UV absorption spectroscopy, gel filtration, phenol oxidase, laccase, peroxidase

1980-105

カタウロコタケ粗酵素によるリグニンの分解(第2報)

—菌体内粗酵素によるミズナラ MWL の分解—

福田 滋、諸星紀幸、原口隆英

東京農工大学農学部

Degradation of lignin by crude enzyme of *Stereum flustulosum*. II. Degradation of Japanese oak MWL by intracellular crude enzyme.

Shigeru Fukuda, Noriyuki Morohoshi, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: syringic acid, 2,6-dimethoxy-1,4-benzoquinone, IR spectrum

1980-106

リグニン生分解と酸化還元酵素

石原達夫

林業試験場

Biodegradation of lignin and oxidoreductase.

Tatsuo Ishihara

Forestry and Forest Products Research Institute

Keywords: *Pleurotus ostreatus*, *Betula Tauschii*, laccase, cellobiose oxidase, redox potential,

1980-107

木材腐朽菌(カワラタケ)によるリグニンモデル化合物の代謝

片山義博

筑波大学農林工学系

Metabolism of lignin model compounds by wood rotting fungi *Coridus versicolor*.

Yoshihiro Katayama

Institute of Agricultural and Forest Engineering, University of Tsukuba

Keywords: syringaresinol, pinosresinol, UV absorption spectroscopy,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ,

1980-108

*Phanerochaete chrysosporium* によるフェニルクマラン型二量体の分解機構の研究

梅澤俊明<sup>\*1</sup>、中坪文明<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、T.K. Kirk<sup>\*2</sup>

<sup>\*1</sup> 京都大学木材研究所、<sup>\*2</sup> マジソン林産物研究所

Degradation mechanism of phenylcoumaran type dimer by *Phanerochaete chrysosporium*.

Toshiaki Umezawa<sup>\*1</sup>, Fumiaki Nakatsubo<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, T.K. Kirk<sup>\*2</sup>

<sup>\*1</sup> Wood Research Institute, Kyoto University, <sup>\*2</sup> Forest Products Laboratory, Madison, U.S.A

Keywords:

2-(4-hydroxy-3,5-dimethoxyphenyl)-3-hydroxymethyl-5-formyl-7-methoxycoumaran, phenol oxidase

1980-109

硫酸リグニンの化学構造

—アリアルグリセロール-β-アリアルエーテル型構造からの縮合物の化学構造—

安田征市、寺島典二、伊東 健

名古屋大学農学部

Chemical structures of sulfuric acid lignin. —Chemical structures of condensation products from arylglycerol-β-aryl ether type structures—

Seiichi Yasuda, Noritsugu Terashima, Takeshi Ito

Faculty of Agriculture, Nagoya University

Keywords: <sup>13</sup>C-NMR, creosol, phenylcoumaran, Hibbert's ketone, diphenylpropane compounds

1980-110

木酢液について

黒田健一

筑波大学農林工学系

On the wood vinegar.

Kenichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Keywords: *Pinus densiflora*, dioxane lignin, nitrobenzene oxidation, permanganate oxidation, HPLC, guaiacol, creosol, 4-ethylguaiacol

1980-111

カキシブの硬化機構

田中治郎

林業試験場

Hardening mechanism of persimmon juice.

Jiro Tanaka

Forestry and Forest Products Research Institute

Keywords: UV spectroscopy, IR spectroscopy, carbonyl group

1980-112

ビーズ状リグニン樹脂の製造に関する研究

飯塚堯介、中野準三

東京大学農学部

Studies on production of beads type resin from lignin.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: hardwood lignosulfonic acid, two-step resinification, one-step resinification

1980-113

リグニンの酸化分解(III) —H<sub>2</sub>O<sub>2</sub>によるリグニンモデル化合物の酸化分解—

辰己憲司\*<sup>1</sup>、寺島典二\*<sup>2</sup>

\*<sup>1</sup> 公害資源研究所、\*<sup>2</sup> 名古屋大学農学部

Oxidative degradation of lignin. III. Oxidative degradation of lignin model compounds with hydrogen peroxide.

Kenji Tatsumi\*<sup>1</sup>, Noritsugu Terashima\*<sup>2</sup>

\*<sup>1</sup>National Research Institute for Pollution and Resources, \*<sup>2</sup>Faculty of Agriculture, Nagoya University

Keywords: UV radiation, pH dependence, veratric acid, vanillic acid, protocatechuic acid

1980-114

リグニンのオゾン分解について

金子英信、中野準三

東京大学農学部

Degradation of lignin with ozone.

Hidenobu Kaneko, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compound, thioglignin, surface tension, dispersion effect, dispersion number, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR,

1980-115

クラフト蒸解廃液中の生物活性物質

重松章彦、鮫島一彦、高村憲男

高知大学農学部

Bioactive substances in kraft pulp waste liquor.

Akihiko Shigematsu, Kazuhiko Sameshima, Norio Takamura

Faculty of Agriculture, Kochi University

Keywords: *Pinus densiflora*, *Betula Tauschii*, *Oryzias latipes*, medaka bioassay, toxicity,

1980-116

パルプ廃液中の有機塩素化合物の毒性および分解性

島田謹爾

林業試験場

Toxicity and degradability of organic chlorine compounds in pulp waste liquor.

Kinji Shimada

Forestry and Forest Products Research Institute

Keywords: bioassay, *Oryzias latipes*, trichloroguaiacol, trichlorosyringol

1980-117

特別講演、石炭の液化と炭化

竹下健次郎

九州大学生産科学研究所

Invited lecture: Liquefaction and carbonization of coal.

Kenjiro Takeshita

Kyushu University Research Institute for Production Science

Keywords: model compounds of coal, coal pitch, mesophase, microphotograph

1980-201

不斉場におけるコニフェリルアルコールの脱水素重合

三木啓司、榊原 彰

北海道大学農学部

Dehydrogenative polymerization of coniferyl alcohol in chiral environment.

Keiji Miki, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Quercus mongolica*, *Larix leptorepis*, holocellulose, hemicellulose, gel filtration

1980-202

シナポイル CoA リガーゼの植物間分布及び性質について

久津木英俊、島田幹夫、樋口隆昌

京都大学木材研究所

Occurrence of synapoyl Co-A ligase among plants and its properties.

Hidetoshi Kutsuki, Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Erythrina crista-galli*, feruloyl Co-A ligase, 5-hydroxyferulic acid

1980-203

広葉樹プロトリグニンの水素化分解物に関する研究

黄 炳浩、榊原 彰

北海道大学農学部

Studies on the hydrogenolysis products from hardwood protolignin.

Byung Ho Hwang, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Fraxinus mandshurica var. japonica*, mass spectrometry, <sup>1</sup>H-NMR, diarylpropane derivative

1980-204

カラマツアテ材リグニンの水素化分解に関する研究

小林千益、安田征市、榊原 彰

北海道大学農学部

Studies on the hydrogenolysis of lignin in compression wood of larch.

Seneki Kobayashi, Seiichi Yasuda, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Larix leptolepis*, phenylisochromane, diarylpropane, lignaloid, lappaol A,B,C,D

1980-205

アリアルグリセロール-β-アリアルエーテル型構造の選択的解裂について

松本雄二、石津 敦、中野準三

東京大学農学部

Selective cleavage of arylglycerol-β-aryl ether type structure.

Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, γ-p-toluenesulfinyl veratrylglycerol-β-guaiacyl ether, MWL, gel filtration

1980-206

エゾマツブラウングリグニン(BL)の性質について

高橋秀敏、青山政和、榊原 彰

北海道大学農学部

On the properties of Brauns' s lignin (BL) from Yezo spruce.

Hidetoshi Takahashi, Masakazu Aoyama, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Picea jezoensis*, lignan, western hemlock, *Tsuga heterophylla*, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR

1980-207

磨碎時間を異にして段階的に単離した広葉樹 MWL の性状について

李 忠正、飯塚堯介、中野準三

東京大学農学部

Characteristics of hardwood MWL isolated with different milling times.

Zhong Zheng Lee, Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: birch, *Betula* sp., cell wall layers, nitrobenzene oxidation, non-conjugated phenolic hydroxyl group,

1980-208

ヘミセルロース・リグニン結合体に関する研究(その4)-アカマツあて材 MWL 画分よりのヘミセルロース・リグニン結合体の性質

向吉俊一郎、東 順一、越島哲夫

京都大学木材研究所

Studies on the hemicellulose-lignin complex. IV. Characteristics of hemicellulose-lignin complex obtained from MWL fraction of red pine compression wood.

Shunichiro Mukoyoshi, Junichi Azuma, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, gel filtration, methylation analysis, Smith degradation, galactose

1980-209

ユーカリ材チップの劣化

岡山隆之、蔵本 敬、屋部雅夫、大江礼三郎

東京農工大学農学部

Biodegradation of eucalyptus wood chip.

Takayuki Okayama, Takashi Kuramoto, Masao Yabe, Raysabro Oye

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: thermal degradation, Klason lignin, holocellulose

1980-210

硝酸法蒸解におけるリグニンの挙動について -モデル実験-

Huynh Van Ba、石津 敦、中野準三

東京大学農学部

Behavior of lignin during nitric acid pulping. -Model experiments.

Huynh Van Ba, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: apocynol, guaiacylglycerol- $\beta$ -guaiacyl ether, veratrylglycerol- $\beta$ -guaiacyl ether, TLC

1980-211

クラフト蒸解における木材成分の溶出挙動と黒液成分の変化

玉生征人、炭村栄一、高橋 武、上埜武夫

山陽国策パルプ株式会社

Dissolution of wood components and change of black liquor composition during kraft cooking.

Masato Tamao, Eiichi Sumimura, Takeshi Takahashi, Takeo Ueno

Sanyo Kokusaku Pulp Co., Ltd.

Keywords: lignin, carbohydrate, low molecular fraction, high molecular fraction, active alkali,

1980-212

バガスの過酸化水素アルカリ蒸解について

御田昭雄、柏原 進、河村英司

化学技術研究所

Pulping of bagasse with hydrogenperoxide and alkali.

Akio Mita, Susumu Kashiwabara, Eishi Kawamura

The Government Chemical Industrial Research Institute, Tokyo

Keywords: energy consumption, pulp yield, Kappa number, pentosan content

1980-213

KP の酸素-オゾン-過酸化水素漂白

藤井利郎、上嶋 洋、赤松 勲

四国工業技術試験所

Bleaching of KP with oxygen-ozone-hydrogen peroxide.

Toshiro Fujii, Hiroshi Kamishima, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords: *Pseudotsuga taxifolia*, viscosity, brightness

1980-214

パルプのオゾン漂白に関する研究

三浦 清、香山 疆

北海道大学農学部

Studies on the ozone bleaching of pulp.

Kiyoshi Miura, Tsutomu Kayama

Faculty of Agriculture, Hokkaido University

Keywords: *Abies Mayriana*, SEM (scanning electron microscopy), ESR (electron spin resonance spectroscopy)

1980-215

薬液添加TMPの製造とその品質について

加地隆男、菊池春朗、河村道雄

大王製紙株式会社

Manufacturing and properties of TMP with chemicals.

Takao Kaji, Shunro Kikuchi, Michio Kawamura

Daio Paper Corporation

Keywords: *Picea* sp., *Eucalyptus*, high yield pulp, resource saving, specific energy consumption, domestic pine,

1980-216

針葉樹 CTMP に関する研究 -収率差における物性と漂白性について-

小島康夫、香山 疆

北海道大学農学部

Studies on the softwood CTMP. -Relation between pulp yield and physical properties, and bleachability.

Yasuo Kojima, Tsutomu Kayama

Faculty of Agriculture, Hokkaido University

Keywords: *Picea Glehnii*, freeness, density, printing opacity, brightness,

1980-217

総合討論、これからのリグニン研究 –若手研究者の立場から–

飯山賢治(東京大学農学部 司会)、安田征市(名古屋大学農学部)、鮫島一彦(高知大学農学部)、  
飯塚堯介(東京大学農学部)、中坪文明(京都大学木質科学研究所)

General discussion on “Future prospects of lignin research”. – From young researchers.

Moderator: Kenji Iiyama (Faculty of Agriculture, the University of Tokyo)

Seiichi Yasuda (Faculty of Agriculture, Nagoya University)

Kazuhiko Sameshima (Faculty of Agriculture, Kochi University)

Gyosuke Meshitsuka (Faculty of Agriculture, the University of Tokyo)

Fumiaki Nakatsubo (Faculty of Agriculture, Kyoto University)

## 第 26 回 (1981.10.29-30)工業技術院筑波研究センター

1981-101

*Fusarium solani*によるグリセロール-2-バニリン酸エーテルおよびフェニルクマラン型二量体の分解  
片山健至、中坪文明、樋口隆昌

京都大学木材研究所

Degradation of glycerol-2-vanilic acid ether and phenylcoumaran-type dimer by *Fusarium solani*.

Takeshi Katayama, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: biodegradation, *Fusarium solani*, arylglycerol- $\beta$ -aryl ether, phenylcoumaran

1981-102

*Fusarium solani*による *d,l*-シリングレジンノールの分解(その 2)

釜谷保志、中坪文明、樋口隆昌

京都大学木材研究所

Degradation of *d,l*-syringaresinol by *Fusarium solani*. II.

Yasushi Kamaya, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: biodegradation, *Fusarium solani*, syringaresinol

1981-103

カワラタケ・ラッカーゼの分別と精製及び 2, 3 の性質  
村磯知採、割石博之、永井 享、諸星紀幸、原口隆英  
東京農工大学農学部

Fractionation and purification of laccase from *Coriolus versicolor* and its properties.

Chidori Muraishi, Hiroyuki Wariishi, Tooru Nagai, Noriyuki Morohoshi, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: Laccase, *Coriolus versicolor*

1981-104

カワラタケ・ラッカーゼによるリグニンの変化(第 2 報)–BNL, MWL, LCC, 残渣木粉中のリグニンの  
定量的変化量について–

諸星紀幸、原口隆英

東京農工大学農学部

Changes of lignin by laccase from *Coriolus versicolor*. II. Quantitative evaluation of changes of lignin in BNL, MWL, LCC, residual wood meal.

Noriyuki Morohoshi, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: laccase, *Coriolus versicolor*

1981-105

*Lentinus edodes* 体外酵素による guaiacylglycerol- $\beta$ -guaiacyl ether の分解

沖 妙、仙波裕子、石川久雄

愛媛大学農学部

Degradation of guaiacylglycerol- $\beta$ -guaiacyl ether by the extracellular enzyme of *Lentinus edodes*.

Tae Oki, Yuko Sennami, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Lentinus edodes*, guaiacylglycerol- $\beta$ -guaiacyl ether

1981-106

*Phanerochaete chrysosporium* によるフェノール性水酸基をもつフェニルクマラン型二量体の分解

梅澤俊明、中坪文明、樋口隆昌

京都大学木材研究所

Degradation of a phenolic phenylcoumaran-type dimer by *Phanerochaete chrysosporium*.

Toshiaki Umezawa, Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: phenylcoumaran, dimer, *Phanerochaete chrysosporium*

1981-107

担子菌の変異株を用いたベラトリルアルコール代謝とリグニンの『生合成』的生分解に関する研究  
島田幹夫<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、M.H. Gold<sup>\*2</sup>

<sup>\*1</sup> 京都大学木材研究所、<sup>\*2</sup> OGC

Studies on the metabolism of veratryl alcohol by the mutant of basidiomycete and the biosynthetic degradation of lignin.

Mikio Shimada<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, M.H. Gold<sup>\*2</sup>

<sup>\*1</sup> Wood Research Institute, Kyoto University, <sup>\*2</sup> Oregon Graduate Center

Keywords: Biosynthetic degradation, mutant, basidiomycetes, veratryl alcohol

1981-108

キノンメチド中間体を経る LCC モデルの形成に関する研究

棚橋光彦、樋口隆昌

京都大学木材研究所

Studies on the formation of LCC model compounds through quinone methide intermediate.

Mitsuhiko Tanahashi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: LCC model, quinone methide, glucose, xylose

1981-109

リグニンの KMnO<sub>4</sub> 酸化分解

佐野嘉拓<sup>\*1</sup>、W.G. Glasser<sup>\*2</sup>

北海道大学農学部

Oxidative degradation of lignin with  $\text{KMnO}_4$ .

Yoshihiro Sano<sup>\*1</sup>, W.G.Glasser<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Virginia Polytechnic Institute and State University

Keywords:  $\text{KMnO}_4$  oxidation, MWL

1981-110

オゾノリシスによるリグニン中の glyceraldehyde-2-aryl ether 構造の定量

松本雄二、石津 敦、中野準三

東京大学農学部

Quantitative determination of glyceraldehyde-2-aryl ether in lignin by ozonolysis.

Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: glyceraldehydes-2-aryl ether, ozonolysis, glycerol

1981-111

広葉樹プロトリグニンの水素化分解物に関する研究 一新 2 量体の単離

黄 柄浩、榊原 彰

北海道大学農学部

Hydrogenolysis of hardwood protolignin. -Isolation of a new dimer.

Byung Ho Hwang, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: hydrogenolysis, hardwood lignin, new dimer

1981-112

クラフトパルプ中の残留リグニンの性状

山崎 岳、細谷修二、Chen C. L., Gratzl J.S., Chang H.-m.

ノースカロライナ州立大学

Properties of residual lignin in kraft pulp.

Takeshi Yamasaki, Shuji Hosoya, C. L. Chen, J.S. Gratzl, H.-m. Chang

North Carolina State University

Keywords: residual lignin, kraft pulp, enzymatic treatment, lignin-carbohydrate linkage in pulp

1981-113

硫酸リグニンの化学構造 -アリアルグリセロール- $\beta$ -アリアルエーテルと 72%硫酸との反応-

安田征市、寺島典二、伊東 健

名古屋大学農学部

Structures of sulfuric acid lignin. -Reactions of arylglycerol- $\beta$ -aryl ether in 72% sulfuric acid.

Seiichi Yasuda, Noritsugu Terashima, Takeshi Ito

Faculty of Agriculture, Nagoya University

Keywords: sulfuric acid lignin, arylglycerol- $\beta$ -ary ether, acid condensation

1981-114

水分及び熱処理によるリグニン主分散の変化

矢野彰一郎、品川俊一、畠山兵衛

製品科学研究所

Changes in the main dispersion of dynamic viscoelasticity curves of lignin by water and heat

treatment.

Shoichiro Yano, Shunichi Shinagawa, Hyoe Hatakeyama

Industrial Products Research Institute

Keywords: T<sub>g</sub>, polystyrene, dynamic viscoelasticity

1981-115

ヘミセルロース・リグニン結合体(LCC)に関する研究(その5)ーアカマツ圧縮アテ材よりの Björkman LCC の性質ー

東 順一<sup>\*1</sup>、向吉俊一郎<sup>\*1\*2</sup>、越島哲夫<sup>\*1</sup>

<sup>\*1</sup> 京都大学木材研究所, <sup>\*2</sup> 神崎製紙株式会社

Studies on lignin hemicellulose complex (LCC). V. Characterization of Björkman LCC from red pine compression wood.

Junichi Azuma<sup>\*1</sup>, Shunichiro Mukoyoshi<sup>\*1\*2</sup>, Tetsuo Koshijima<sup>\*1</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University; <sup>\*2</sup>Kanzaki Paper Co. Ltd.

Keywords: *Pinus densiflora*, hemicellulose, GPC

1981-116

リグニンー糖結合体の性状について

飯塚堯介<sup>\*1</sup>、李 忠正<sup>\*1</sup>、中野準三<sup>\*1</sup>、江田 茂<sup>\*2</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*2</sup> 日本専売公社中央研究所

Characterization of lignin-carbohydrate complex.

Gyosuke Meshitsuka<sup>\*1</sup>, Zhong Zheng Lee<sup>\*1</sup>, Junzo Nakano<sup>\*1</sup>, Shigeru Eda<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup> Central Research Institute, Japan Tobacco and Salt Public Corporation

Keywords: LCC, pectinase, GPC

1981-117

特別講演、C<sub>1</sub> 化学について

阪東憲一郎

化学技術研究所

Invited Lecture ; C-1 Chemistry.

Kenichiro Bando

National Chemical Laboratory for Industry

1981-201

亜塩素酸塩法及び過酢酸法によるホロセルロースの調製過程で溶出する多糖成分について

前川英一、越島哲夫

京都大学木材研究所

Dissolution of polysaccharides during the hollocellulose preparation with sodium chlorite and peracetic acid methods.

Eiichi Maekawa, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, *Fagus crenata*, degree of delignification, UV absorption spectroscopy

1981-202

高収率パルプを用いるカルボキシメチルセルロースの調製(II)ーカルボキシメチル化リグニンの加熱処理に対する挙動ー

ラム・チ・バック・チュエット、石津 敦、中野準三  
東京大学農学部

Preparation of carboxymethyl cellulose from high-yield pulp. II, Behavior of carboxymethyl lignin on heating.

Thi Bach Tuyet Lam, Atsushi Ishizu, Junzo Nakano  
Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, MWL, carboxymethyl cellulose, high-yield pulp, carboxymethyl lignin

1981-203

リグニン存在下でのセルロース質の酵素分解

夜久富美子<sup>\*1</sup>、田中龍太郎<sup>\*1</sup>、村木永之介<sup>\*1</sup>、足立公洋<sup>\*1</sup>、越島哲夫<sup>\*2</sup>

<sup>\*1</sup> 大阪工業技術試験所、<sup>\*2</sup> 京都大学木材研究所

Enzymatic hydrolysis of cellulosic materials in the presence of lignin.

Fumiko Yaku<sup>\*1</sup>, Ryutarō Tanaka<sup>\*1</sup>, Einosuke Muraki<sup>\*1</sup>, Kimihiro Adachi<sup>\*1</sup>, Tetsuo Koshijima<sup>\*2</sup>

<sup>\*1</sup>Government Industrial Research Institute, Osaka, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, vibration ball mill, roll mill, cellulase

1981-204

リグニンおよび関連物質の熱分解(第1報)

佐々木坤彪、鈴木正人、佐方克彦、長沢武夫

日本紙パルプ研究所

Pyrolysis of lignin and related materials. I.

Nobutake Sasaki, Masato Suzuki, Katsuhiko Sakata, Takeo Nagasawa  
Japan Pulp & Paper Research Institute, Inc.

Keywords: *Fagus crenata*, chlorinated compound, chlorinated lignin

1981-205

4-n-アルコキシ-3-メトキシ安息香酸誘導体の液晶性

春日和行、畠山兵衛

製品科学研究所

Properties of 4-n-alkoxy-3-methoxybenzoic acid derivatives as liquid crystal.

Kazuyuki Kasuga, Hyoe Hatakeyama

Industrial Products Research Institute

Keywords: vanillin, alkyl chain length, transition temperature,

1981-206

リグニンの酸化分解(IV)紫外線照射下での H<sub>2</sub>O<sub>2</sub> とリグニンモデル化合物の芳香核との反応

辰巳憲司<sup>\*1</sup>、寺島典二<sup>\*1</sup>

<sup>\*1</sup> 公害資源研究所、<sup>\*2</sup> 名古屋大学農学部

Oxidative degradation of lignin. IV. Reactions of aromatic rings of lignin model compounds with hydrogen peroxide under UV irradiation.

Kenji Tatsumi<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>National Research Institute for Pollution and Resources, <sup>\*2</sup>Faculty of Agriculture, Nagoya University

Keywords: HPLC, vanillic acid, protocatechuic acid

1981-207

木材の液化に関する研究 (I) -アルカリ-アルコール法による樹皮の液化-

須藤賢一

林業試験場

Liquefaction of wood. I. -Liquefaction of bark by alkali-alcohol system.

Kenichi Sudo

Forestry and Forest Products Research Institute

Keywords: GPC, IR absorption spectroscopy, <sup>1</sup>H-NMR

1981-208

水素化によるパルプ製造に関する研究

榊原 彰、枝重有祐、植松敏夫、武山浩武

北海道大学農学部

Hydrogenolysis pulping.

Akira Sakakibara, Yusuke Edasige, Toshio Uematsu, Hirotake Takeyama

Faculty of Agriculture, Hokkaido University

Keywords: *Betula platyphylla*, phenol, cresols, xylenols, guaiacol

1981-209

高収率パルプに関する研究 -化学前処理とリファイニングエネルギー-

坂井克己

九州大学農学部

Studies on high yield pulp. -Chemical pretreatment and refining energy.

Kokki Sakai

Faculty of Agriculture, Kyushu University

Keywords: *Pinus Thunbergii*, sodium sulfite, sodium chlorite, refining energy

1981-210

CMP のリファイニング条件について

大森隆志、坂井克己

九州大学農学部

Refining conditions of chemi-mechanical pulp.

Takashi Ohmori, Kokki Sakai

Faculty of Agriculture, Kyushu University

Keywords: CGP, RGP, TMP, sodium sulfite

1981-211

ジャイアント・レウカエナ材の CTMP 法による新聞紙級パルプ

久保隆昌<sup>\*1</sup> 細川 純<sup>\*1</sup>、小林 武<sup>\*1</sup>、赤松 勲<sup>\*1</sup>、小林良生<sup>\*1</sup>、Supasuri Janesuthiwechakul<sup>\*2</sup>

四国工業技術試験所

Production of newspaper grade CTMP from Giant leucaena.

Takamasa Kubo<sup>\*1</sup>, Jun Hosokawa<sup>\*1</sup>, Takeshi Kobayashi<sup>\*1</sup>, Isao Akamatsu<sup>\*1</sup>, Yoshinari Kobayashi<sup>\*1</sup>,

Supasri Janesuthiwechakul<sup>\*2</sup>

<sup>\*1</sup>Government Industrial Research Institute, Sikoku, <sup>\*2</sup>Royal Forest Dept. Thailand

Keywords: Giant leucaena, *Leucaena glauca*, sodium sulfite, pulp properties, refining energy

1981-212

高歩留パルプの改質 -ラジカル的スルホン化反応による TMP の改質-

大井 洋、飯塚堯介、中野準三  
東京大学農学部

Improvement of high yield pulp.-Improvement of TMP by radical sulfonation.

Hiroshi Ohi, Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, sodium sulfite, potassium permanganate, manganese dioxide,

1981-213

木材チップの圧縮と蒸解性

岡山隆之、木下卓麻、大江礼三郎

東京農工大学農学部

Effect of roll-pressing of wood chips on pulping.

Takayuki Okayama, Takuma Kinoshita, Reisabro Oye

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Eucalyptus marginata*, *Pinus densiflora*, roll pressing, shear, kraft pulping

1981-214

ネマガリダケのパルプ化に関する研究

戸坂圀夫\*<sup>1</sup>、望月 明\*<sup>1</sup>、林 治助\*<sup>1</sup>、ヌエ・ニイ・ウェイ\*<sup>2</sup>

\*<sup>1</sup> 北海道大学工学部、\*<sup>2</sup> 京都大学農学部

Studies on pulping of *Sasa kurilensis*.

Kunio Tosaka\*<sup>1</sup>, Akira Mochizuki\*<sup>1</sup>, Jisuke Hayashi\*<sup>1</sup>, \*????????\*<sup>2</sup>

\*<sup>1</sup> Faculty of Engineering, Hokkaido University, \*<sup>2</sup> Faculty of Agriculture, Kyoto University

Keywords: *Sasa kurilensis*, kraft pulping, soda pulping, oxygen alkali pulping

1981-2015

酸素・アルカリ蒸解の蒸解要因 -グアヤコールの酸素酸化に及ぼす酸素担体添加の効果-  
目黒貞利

九州大学農学部

Factors influencing oxygen-alkali cooking. -Effects of oxygen carrier on the oxidation of guaiacol.

Sadatoshi Meguro

Faculty of Agriculture, Kyushu University

Keywords: oxygen carrier, Co-salen, Co-salpr

1981-2016

シュウ酸添加オゾン漂白におけるシュウ酸の回収と再使用

藤井利郎、上嶋 洋、赤松 勲

四国工業技術試験所

Recovery and reuse of oxalic acid from effluent of ozone bleaching with oxalic acid.

Toshio Fujii, Hiroshi Kamishima, Isao Akamatsu

Government Industrial Research Institute, Shikoku

Keywords: *Pseudotsuga taxifolia*, cellulose protectant, calcium oxalate

1981-2017

特別講演、今後のリグニン化学工業の展望

秦 邦男

十條製紙株式会社中央研究所

Invited lecture ; Future prospects of industrial utilization of lignin.

Kunio Hata

Central Research Institute, Jujo Paper Co. Ltd.

## 第 27 回 (1982.10.21-22)名古屋大学農学部

1982-101

オゾノリシスを用いたリグニン側鎖構造の研究 -各種単離リグニンへの適用-

松本雄二、石津 敦、中野準三

東京大学農学部

Studies on the structure of lignin side chain by ozonolysis. -Application to various isolated lignins.

Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, MWL, erythronic acid, threonic acid, glyceraldehydes-2-aryl ether, <sup>13</sup>C-NMR

1982-102

針葉樹リグニンへのシリングル核の導入

飯山賢治、R. Pant、中野準三

東京大学農学部

Introduction of syringyl nuclei to softwood lignin.

Kenji Iiyama, R. Pant, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, *Fagus crenata*, MWL, Mäule color reaction, Fremy' s salt oxidation

1982-103

スギ心材の色とリグニン

黒田宏之、島地 謙

京都大学木材研究所

Color and lignin of Japanese cedar heartwood.

Hiroyuki Kuroda, Ken Shimaji

Wood Research Institute, Kyoto University

Keywords: Japanese cedar, *Cryptomeria japonica*, MWL, LCC, microspectroscopy, morphology

1982-104

逐次アシドリシスにより溶出するリグニンの分子構造

船岡正光、阿部 勲

三重大学農学部

Structure of lignin dissolved by stepwise acidolysis.

Masamitsu Funaoka, Isao Abe

Faculty of Agriculture, Mie University

Keywords: condensed structure, nuclear exchange reaction, nitrobenzene oxidation

1982-105

リグニンおよびリグニン関連型ポリスチレン誘導体の水素結合と吸着水

畠山兵衛\*<sup>1</sup>、広瀬重雄\*<sup>1</sup>、中村邦雄\*<sup>2</sup>、畠山立子\*<sup>3</sup>

\*<sup>1</sup> 製品科学研究所、\*<sup>2</sup> 神奈川県工業試験所、\*<sup>3</sup> 繊維高分子材料研究所

Hydrogen bond and adsorbed water of lignin and lignin-like polystyrene derivatives.

Hyoe Hatakeyama\*<sup>1</sup>, Shigeo Hirose\*<sup>1</sup>, Kunio Nakamura\*<sup>2</sup>, Tatsuko Hatakeyama\*<sup>3</sup>

\*<sup>1</sup>Industrial Products Research Institute, \*<sup>2</sup>Kanagawa Industrial Technology Center, \*<sup>3</sup>Research Institute for Polymers and Textiles

Keywords: *Libocedrus decurrens*, dioxane lignin, lignin-like polystyrene derivatives, thermal analysis, glass transition temperature

1982-106

リグニン-糖間結合に対するペクチン質の寄与

飯塚堯介、中野準三

東京大学農学部

Contribution of pectic substances to lignin carbohydrate bond.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: birch, *Betula* sp., endo-pectin lyase, endo-polygalacturonase, pectin esterase, LCC

1982-107

リファイナーメカニカルパルプを用いるカルボキシメチルセルロースの調製(第3報) カルボキシメチル炭水化物の溶出に及ぼすリグニンの影響

ラム・チ・バック・チュエット、飯山賢治、石津 敦、中野準三

東京大学農学部

Preparation of carboxymethyl cellulose from refiner mechanical pulp. III. Effect of lignin on the dissolution of carboxymethylated carbohydrates.

Thi Bach Tuyet Lam, Kenji Iiyama, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, *Fagus crenata*, mannan, xylan, <sup>1</sup>H-NMR,

1982-108

針葉樹仮道管の壁形成における多糖類とリグニンの堆積

高部圭司、藤田 稔、佐伯 浩、原田 浩

京都大学農学部

Deposition of polysaccharides and lignin during the cell wall formation of softwood tracheids.

Keiji Takabe, Minoru Fujita, Hiroshi Saiki, Hiroshi Harada

Faculty of Agriculture, Kyoto University

Keywords: *Cryptomeria japonica*, UV microscopy, autoradiography, <sup>3</sup>H-glucose, <sup>14</sup>C-glucose, <sup>3</sup>H-phenylalanine

1982-109

アカマツ圧縮アテ材の脱リグニン液中に溶出してくる多糖の性質

東 順一\*<sup>1</sup>、向吉俊一郎\*<sup>1\*2</sup>、越島哲夫\*<sup>1</sup>

\*<sup>1</sup> 京都大学木材研究所、\*<sup>2</sup> 神崎製紙株式会社

Characterization of polysaccharides dissolving out during the delignification of red pine compression wood.

Junichi Azuma\*<sup>1</sup>, Mukoyoshi Shunichiro\*<sup>1\*2</sup>, Tetsuo Koshijima\*<sup>2</sup>

\*<sup>1</sup>Wood Research Institute, Kyoto University, \*<sup>2</sup>Kanzaki Paper Co. Ltd.

Keywords: *Pinus densiflora*, LCC, sodium chlorite, galactoglucomannan

1982-110

リグニンの酸化分解(V)酸素およびヒドロキシラジカルとリグニンの芳香核との反応

辰己憲司\*<sup>1</sup>、寺島典二\*<sup>2</sup>

\*<sup>1</sup> 公害資源研究所、\*<sup>2</sup> 名古屋大学農学部

Oxidative degradation of lignin. V. Reactions of lignin aromatic nuclei with oxygen and hydroxyl radical.

Kenji Tatsumi\*<sup>1</sup>, Noritsugu Terashima\*<sup>2</sup>

\*<sup>1</sup> National Research Institute for Pollution and Resources, \*<sup>2</sup> Faculty of Agriculture, Nagoya University

Keywords: UV radiation, pH dependence, vanillic acid, protocatechuic acid, gallic acid

1982-111

求核性試薬添加ソーダ蒸解

大原誠資、飯塚堯介、R. Pant、中野準三

東京大学農学部

Soda pulping with addition of nucleophilic reagents.

Seiji Ohara, Gyosuke Meshitsuka, R. Pant, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: soda pulping, nucleophilic reagent, methyl mercaptan, thiophenol

1982-112

酸素・アルカリ蒸解の蒸解要因。Co-Salen 触媒活性に及ぼす蒸解因子の影響

目黒貞利、今村博之

九州大学農学部

Cooking factors influencing oxygen-alkali pulping. -Factors influencing the catalytic activity of Co-salen.

Sadatoshi Meguro, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: cobalt (II) bis(salicylidene)ethylenediamine, oxidation of guaiacol,

1982-113

クレゾール・水によるパルプ化法について

榊原 彰、技重有祐、武山浩武

北海道大学農学部

Pulping with cresol and water.

Akira Sakakibara, Yusuke Edashige, Hirotake Takeyama

Faculty of Agriculture, Hokkaido University

Keywords: *Picea Glehnii*, organosolv pulping,

1982-114

オルガノソルブパルプ化に関する研究

佐野嘉拓、榊原 彰、笹谷宜志

北海道大学農学部

Studies on organosolv pulping.

Yoshihiro Sano, Akira Sakakibara, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Keywords: *Quercus crispula*, *Betula Tauschii*, *Picea Glehnii*, *Larix Kaempferi*, *Abies Mayriana*, phenol, cresol,

1982-115

有機溶媒とサルファイトによるパルプ化 (I) スギ SCP 蒸解におけるイソプロピルアルコール添加の効果 (その 1)

文 星筆、坂井克己、今村博之

九州大学農学部

Pulping with organic solvents and sulfite. I. Effects of the addition of isopropyl alcohol on SCP cooking of Japanese cedar.

Sung-Phil Mun, Kokki Sakai, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: *Cryptomeria japonica*, neutral sulfite, monosulfite, bisulfite, isopropyl alcohol, Japanese cedar

1982-116

広葉樹 (GL 材) CTMP の強度と繊維特性

久保隆昌、細川 純、小林 武、赤松 勲

四国工業技術試験所

Strength properties and fiber characteristics of hardwood CTMP.

Government Industrial Research Institute, Shikoku

Takamasa Kubo, Jun Hosokawa, Takeshi Kobayashi, Isao Akamatsu

Keywords: Giant leucaena, *Leucaena leucocephala*, TMP,

1982-117

リグニンおよび関連物質の熱分解 (第 3 報)

佐々木坤彪、荒木 廣、鈴木正人、長沢武夫

日本紙パルプ研究所

Pyrolysis of lignin and related materials. III.

Nobutake Sasaki, Hiroshi Araki, Masato Suzuki, Takeo Nagasawa

Japan Pulp & Paper Research Institute, Inc.

Keywords: *Fagus crenata*, thiolignin, pyrolysis, chlorinated lignin, TG, DSC

1982-118

特別講演、木材の細胞壁の構造と形成

原田 浩

京都大学農学部

Invited lecture ; Structure and formation of wood cell wall.

Hiroshi Harada

Faculty of Agriculture, Kyoto University

Keywords: vascular cambium, chemical composition, cell wall layers

1982-201

大気汚染地域で見られたスギ葉中のタンニン生合成阻害について

加藤輝隆\*<sup>1</sup>、加須屋実\*<sup>1</sup>、鏡森定信\*<sup>1</sup>、河野昭一\*<sup>2</sup>

富山医科薬科大学医学部、富山大学生物学科

Inhibition of tannin biosynthesis in the leaves of Japanese cedar in the air polluted area.

Terutaka Kato<sup>\*1</sup>, Minoru Kasuya<sup>\*1</sup>, Sadanobu Kagamimori<sup>\*1</sup>, Shoichi Kawano<sup>\*2</sup>

<sup>\*1</sup>Faculty of Medicine, Toyama Medical and Pharmaceutical University, <sup>\*2</sup>Department of Biology, Toyama University

Keywords: *Cryptomeria japonica*, glucose content, shikimic acid

1982-202

リグニン存在下でのセルロース質の酵素分解(2)

夜久富美子<sup>\*1</sup>、田中龍太郎<sup>\*1</sup>、村木永之介<sup>\*1</sup>、田中文男<sup>\*2</sup>、越島哲夫<sup>\*2</sup>

<sup>\*1</sup>大阪工業技術試験所、<sup>\*2</sup>京都大学木材研究所

Enzymatic hydrolysis of cellulosic substance in the presence of lignin. II.

Fumiko Yaku<sup>\*1</sup>, Ryutarō Tanaka<sup>\*1</sup>, Einosuke Muraki<sup>\*1</sup>, Fumio Tanaka<sup>\*2</sup>, Tetsuo Koshijima<sup>\*2</sup>

<sup>\*1</sup>Government Industrial Research Institute, Osaka, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, *Shorea negrosensis*, *Pentacme contorta*, vibration ball mill, MWL, LCC,

1982-203

爆砕木材の特性とその酵素糖化

棚橋光彦<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、高田信輔<sup>\*2</sup>、花井四郎<sup>\*3</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>近畿大学農学部、<sup>\*3</sup>宝酒造株式会社

Characterization of steam-exploded wood and its enzymatic hydrolysis.

Mitsuhiko Tanahashi, Takayoshi Higuchi, Shinsuke Takada, Shiro Hanai

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Faculty of Agriculture, Kinki University, <sup>\*3</sup>Takara Shuzo Co. Ltd.

Keywords: *Betula Tauschii*, *Larix Kaempferi*, SEM, TEM, pulping

1982-204

*Fusarium* 属菌の生産するリグニン関連芳香族化合物の分解に関与する酵素系について

岩原章二郎

香川大学農学部

On the enzymes produced by *Fusarium* species that participate in degradation of lignin-related aromatic compounds.

Shojiro Iwahara

Faculty of Agriculture, Kagawa University

Keywords: laccase, pinosresinol, syringaresinol, UV absorption spectroscopy

1982-205

*Phanerochaete chrysosporium* のピリジン補酵素代謝 -リグニン分解との関連性について

桑原正章、麻田恭彦、石田 豊、河上智栄美、赤池嘉彦

香川大学農学部

Metabolism of pyridine coenzymes in *Phanerochaete chrysosporium*. -In relation to lignin degradation.

Masaaki Kuwahara, Yasuhiko Asada, Yutaka Ishida, Chiemi Kawakami, Yoshihiko Akaike

Faculty of Agriculture, Kagawa University

Keywords: *Aspergillus* sp., radiotracer, NAD, NADP

1982-206

Guaiacylglycerol- $\beta$ -guaiacyl ether の分解に関与する酵素系について

沖 妙、新本美智枝、石川久雄

愛媛大学農学部

Enzymes involved in the degradation of guaiacylglycerol- $\beta$ -guaiacyl ether.

Tae Oki, Michie Shinmoto, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Pinus densiflora*, *Phanerochaete chrysosporium*, *Lentinus edodes*, peroxidase, laccase

1982-207

木材腐朽菌によるリグニンモデル化合物の代謝について

榎 章郎<sup>\*1</sup>、田中裕美<sup>\*1</sup>、高橋旨象<sup>\*2</sup>、布施五郎<sup>\*1</sup>

<sup>\*1</sup> 近畿大学農学部、<sup>\*1</sup> 京都大学木材研究所

Metabolism of lignin model compounds by wood rotting fungi

Akio Enoki<sup>\*1</sup>, Hiromi Tanaka<sup>\*1</sup>, Munezoh Takahashi<sup>\*2</sup>, Goro Fuse<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Kinki University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: white rot fungi, brown rot fungi

1982-208

*Phanerochaete chrysosporium* による 5-carboxyprotocatechuic acid の分解

梅澤俊明、樋口隆昌

京都大学木材研究所

Degradation of 5-carboxyprotocatechuic acid by *Phanerochaete chrysosporium*.

Toshiaki Umezawa, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: 5,5'-dehydrodivanillic acid, phenylcoumaran

1982-209

*Phanerochaete chrysosporium* によるシリンガレジノールの分解

釜谷保志、樋口隆昌

京都大学木材研究所

Degradation of syringaresinol by *Phanerochaete chrysosporium*.

Yasushi Kamaya, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: <sup>1</sup>H-NMR, <sup>13</sup>C-NMR,

1982-210

リグニンとリグニンモデル化合物の光増感剤及びヒドロキシルラジカルによる分解

久津木英俊<sup>\*1\*2</sup>、M. H. Gold<sup>\*2</sup>

<sup>\*1</sup> 京都大学木材研究所、<sup>\*2</sup> オレゴン大学院センター

Degradation of lignin and lignin model compounds by photosensitizer and hydroxyl radical.

Hidetoshi Kutsuki<sup>\*1\*2</sup>, Michael H. Gold<sup>\*2</sup>

<sup>\*1\*2</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Oregon Graduate Center

Keywords: *Phanerochaete chrysosporium*, nonphenolic lignin model compounds, singlet oxygen, <sup>14</sup>C-DHP

1982-211

カワラタケ生育時に分泌される酵素類について

諸星紀幸、中村 剛、村磯知採、原口隆英  
東京農工大学農学部

Characterization of enzymes secreted during the growth of *Coriolus versicolor*.  
Noriyuki Morohoshi, Tuyoshi Nakamura, Chidori Muraiso, Takafusa Haraguchi  
Faculty of Agriculture, Tokyo University of Agriculture and Technology  
Keywords: tyrosinase, laccase, cellulase, pectinase, protease, gel filtration

1982-212

カワラタケラッカーゼによるリグニンの変化(第3報)―精製ラッカーゼのリグニンに対する反応性―  
割石博之、藤田佳代、諸星紀幸、原口隆英  
東京農工大学農学部

Changes of lignin by the treatment with laccase from *Coriolus versicolor*. III. Reactivity of purified laccase with lignin.

Hiroyuki Wariishi, Kayo Fujita, Noriyuki Morohoshi, Takafusa Haraguchi  
Faculty of Agriculture, Tokyo University of Agriculture and Technology  
Keywords: Yezo spruce, *Picea jezoensis*, BNL, MWL, LCC, ESR

1982-213

白腐れ菌菌体内の酸素添加酵素について  
田部眞哉、野中久美雄、原口隆英  
東京農工大学農学部

Characterization of intracellular oxygenation enzyme of white rot fungi.

Shinya Tabe, Kumio Nonaka, Takafusa Haraguchi  
Faculty of Agriculture, Tokyo University of Agriculture and Technology  
Keywords: *Pycnoporus coccineus*, *Stereum frustulosum*, catechol, protocatechuic acid, vanillic acid

1982-214

*Lentinus edodes* の広葉樹材への作用とそのクラフトパルプ化  
赤松 勲、上嶋 洋、藤井利郎、小林 武  
四国工業技術試験所

Treatment of hardwood with *Lentinus edodes* and its kraft pulping.

Isao Akamatsu, Hiroshi Kamishima, Toshiro Fujii, Takeshi Kobayashi  
Government Industrial Research Institute, Shikoku  
Keywords: *Quercus acutissima*, *Quercus serrata*, X-ray diffraction, cellulose crystallinity, MWL

1982-215

*Erwinia carotovora* を用いた発酵精練によるコウゾのパルプ化  
小林良生、松尾隆吉  
四国工業技術試験所

Pulping of Kozo bast by retting with *Erwinia carotovora*.

Yoshio Kobayashi, Ryukichi Matsuo  
Government Industrial Research Institute, Shikoku  
Keywords: *Broussonetia kazinoki* × *B. papyrifera*, retting, *Erwinia carotovora*, brightness

1982-216

パルプ廃液の新しい微生物処理法へのアプローチ

鮫島一彦、高村憲男

高知大学農学部

Approach to the new microbiological treatment of pulping effluent.

Kazuhiko Sameshima, Norio Takamura

Faculty of Agriculture, Kochi University

Keywords: BOD, wood rotting fungi,

1982-217

特別講演、バイオマス特にリグニン経由化学製品開発の世界的動向

鈴木 明

野口研究所

Invited lecture ; World trend of research and development of chemicals from biomass and especially from lignin

Akira Suzuki

Noguchi Institute

Keywords: hydrocracking, ethanol production,

## 第 28 回 (1983.10.7-8) 北海道大学農学部

1983-101

オートラジオグラフィーからみた細胞間層と二次壁の木化

高部圭司、藤田 稔、佐伯 浩、原田 浩

京都大学農学部

Lignification of middle lamella and secondary wall investigated by autoradiography.

Keiji Takabe, Minoru Fujita, Hiroshi Saiki, Hiroshi Harada

Faculty of Agriculture, Kyoto University

Keywords: *Cryptomeria japonica*, UV microscopy, fluorescent microscopy, <sup>3</sup>H-phenylalanine

1983-102

細胞壁形成、とくに木化の細胞学的検討

藤田 稔、高部圭司、佐伯 浩、原田 浩

京都大学農学部

Cytological studies on cell wall formation especially on lignification.

Minoru Fujita, Keiji Takabe, Hiroshi Saiki, Hiroshi Harada

Faculty of Agriculture, Kyoto University

Keywords: *Populus euramericana*, *Cryptomeria japonica*, reaction wood, microautoradiography,

1983-103

オートラジオグラフィーからみたマツ属放射柔細胞壁の木化

山本幸一<sup>\*1</sup>、深沢和三<sup>\*2</sup>、石田茂雄<sup>\*2</sup>

<sup>\*1</sup> 林業試験場、<sup>\*2</sup> 北海道大学農学部

Studies on lignification of ray parenchyma wall of pine by microautoradiography.

Koichi Yamamoto<sup>\*1</sup>, Kazumi Fukazawa<sup>\*2</sup>, Shigeo Ishida<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Faculty of Agriculture Hokkaido University

Keywords: *Pinus strobes*, *Pinus densiflora*, *Pinus banksiana*, <sup>3</sup>H-phenylalanine, <sup>14</sup>C-glucose

1983-104

カラマツ 2 次師部の厚壁細胞の木化経過

今川一志、深沢和三、石田茂雄

北海道大学農学部

Lignification process of sclerenchyma cell of larch secondary phloem.

Kazushi Imagawa, Kazumi Fukazawa, Shigeo Ishida

Faculty of Agriculture, Hokkaido University

Keywords: *Larix leptolepis*, sclerenchyma fiber, UV microscope

1983-105

紫外及び電子顕微鏡による細胞壁中のリグニン分布の観察

広居忠量、藤井智之

林業試験場

Observation of lignin distribution across cell wall by UV microscopy and electron microscopy.

Tadakazu Hiroi, Tomoyuki Fujii

Forestry and Forest Products Research Institute

Keywords: *Fagus crenata*, guaiacyl lignin, syringyl lignin, electron microphotography, UV microphotography

1983-106

広葉樹材複合細胞間層リグニンの性状について

飯塚堯介、中野準三

東京大学農学部

Characterization of lignin in compound middle lamella of hardwood.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Betula maximowiczii*, nitrobenzene oxidation, Klason lignin, condensed structure

1983-107

ソルボリシスリグニン -低分子量フラクションについて-

佐野嘉拓、遠藤博之、榊原 彰

北海道大学農学部

Solvolytic lignin. -Characterization of low molecular weight fraction.

Yoshihiro Sano, Hiroyuki Endo, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Quercus crispula*, *p*-cresol, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR,

1983-108

硫酸リグニンの化学構造

安田征市、寺島典二、浜中 篤

名古屋大学農学部

Chemical structures of sulfuric acid lignin.

Seiichi Yasuda, Noritsugu Terashima, Atsushi Hamanaka.

Faculty of Agriculture, Nagoya University

Keywords: *Pinus densiflora*, carbohydrates, arylglycerol- $\beta$ -aryl ether, <sup>1</sup>H-NMR, nitrobenzene oxidation, permanganate oxidation, condensation reaction

1983-109

トリメチルクロロシラン／ヨウ化ナトリウムによるリグニン中のエーテル結合の選択的開裂

近藤哲男、飯塚堯介、中野準三

東京大学農学部

Selective cleavage of ether linkage in lignin by trimethylchlorosilane/sodium iodide.

Tetsuo Kondo, Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, MWL, guaiacylglycerol- $\beta$ -guaiacyl ether, gel filtration chromatography

1983-110

アルカリ蒸解時のリグニンの縮合反応について -特にコニフェリルアルコールの蒸解時の役割-

近藤隆一郎<sup>\*1</sup>、J.F. McCarthy<sup>\*2</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>ワシントン大学

Condensation reactions of lignin during alkaline pulping. -Role of coniferyl alcohol during cooking.

Ryuichiro Kondo<sup>\*1</sup>, J. F. McCarthy<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>University of Washington

Keywords: western hemlock, *Thuja heterophylla*, soda cooking, soda AQ cooking, kraft cooking, gel filtration chromatography

1983-111

リグニンの酸化分解(VI) -ヒドロキシラジカルとリグニンの芳香核との反応-

辰巳憲司<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup>公害資源研究所、<sup>\*2</sup>名古屋大学農学部

Oxidative degradation of lignin. VI. -Reaction of aromatic ring in lignin with a hydroxyl radical.

Kenji Tatsumi<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>National Research Institute for Pollution and Resources, <sup>\*2</sup>Faculty of Agriculture, Nagoya University

Keywords: veratric acid, UV irradiation, gas chromatography, mass spectrometry

1983-112

分子軌道法によるリグニンの反応性の検討

飯山賢治

東京大学農学部

Studies on reactivity of lignin by molecular orbital method.

Kenji Iiyama

Faculty of Agriculture, the University of Tokyo

Keywords: biphenyl, apocynol, cooking with nucleophilic additives

1983-113

リグニン吸着水の<sup>1</sup>H核磁気緩和

畠山兵衛<sup>\*1</sup>、岩田ひろ<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup>製品科学研究所、<sup>\*2</sup>繊維高分子材料研究所

Proton nuclear magnetic relaxation of adsorbed water in lignin.

Hyo Hatakeyama<sup>\*1</sup>, Hiro Iwata<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Industrial Products Research Institute, <sup>\*2</sup>Research Institute for Polymers and Textiles

Keywords: *Hyderia decuurens*, dioxane lignin, DSC

1983-114

リグノスルホン酸塩の吸湿と粘弾性

矢野彰一郎<sup>\*1</sup>、Mikael Rigdahl<sup>\*2</sup>、Petter Kolseth<sup>\*2</sup>、Alf de Ruvo<sup>\*2</sup>

<sup>\*1</sup>製品科学研究所、<sup>\*2</sup>STFI (Sweden)

Moisture adsorption and viscoelasticity of lignosulfonate.

Shoichiro Yano<sup>\*1</sup>、Mikael Rigdahl<sup>\*2</sup>、Petter Kolseth<sup>\*2</sup>、Alf de Ruvo<sup>\*2</sup>

<sup>\*1</sup>Industrial Products Research Institute, <sup>\*2</sup>STFI (Sweden)

Keywords: *Picea abies*, adsorption isotherm

1983-115

特別講演、Biomass の加水分解工程

小林達吉

東京教育大学名誉教授

Invited lecture ; Hydrolysis process of biomass.

Tatsukichi Kobayashi

Professor emeritus, Tokyo University of Education

1983-201

カワラタケ菌体外分泌蛋白の 2 次元電気泳動

諸星紀幸、割石博之、原口隆英

東京農工大学農学部

Two dimensional electrophoresis of the proteins secreted by *Coriolus versicolor*.

Noriyuki Morohoshi, Hiroyuki Wariishi, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: laccase, cellulase,  $\beta$ -glucosidase, xylanase, affinity chromatography

1983-202

Guaiacylglycerol- $\beta$ -guaiacyl ether の生分解に関する酵素系について

沖 妙、新本美智枝、石川久雄

愛媛大学農学部

Studies on the enzymes involved in the biodegradation of guaiacylglycerol- $\beta$ -guaiacyl ether.

Tae Oki, Michie Shinmoto, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Coprinus aff ellisii*, *Phanerochaete chrysosporium*, *Coriolus versicolor*, *Irpex lacteus*, *Schizophyllum commune*

1983-203

*Phanerochaete chrysosporium* による  $\beta$ -O-4 及び  $\beta$ -1 型二量体の分解における  $^{18}\text{O}_2$  の取り込み  
梅澤俊明<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、中坪文明<sup>\*2</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>京都大学農学部

Incorporation of  $^{18}\text{O}_2$  during the degradation of  $\beta$ -O-4 and  $\beta$ -1 type dimers by *Phanerochaete chrysosporium*.

Toshiaki Umezawa<sup>\*1</sup>、Takayoshi Higuchi<sup>\*1</sup>、Fumiaki Nakatsubo<sup>\*2</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Faculty of Agriculture, Kyoto University

Keywords:  $^1\text{H-NMR}$ , mass spectrometry

1983-204

カンバ材リグニンの生分解

寺沢 実<sup>\*1</sup>、D. Tai<sup>\*2</sup>、C. L. Chen<sup>\*3</sup>、H-m. Chang<sup>\*3</sup>、T. K. Kirk<sup>\*4</sup>

<sup>\*1</sup>帯広畜産大学、<sup>\*2</sup>南京林産工業学院、<sup>\*3</sup>ノースカロライナ州立大学、<sup>\*4</sup>USDA 林産物研究所

Biodegradation of birch lignin.

Minoru Terasawa<sup>\*1</sup>, D. Tai<sup>\*2</sup>, C.L. Chen<sup>\*3</sup>, H-m. Chang<sup>\*3</sup>, T. K. Kirk<sup>\*4</sup>

<sup>\*1</sup>Obihiro University of Agriculture and Veterinary Medicine, <sup>\*2</sup>Nanjing University of Forest Industry,

<sup>\*3</sup>North Carolina State University, <sup>\*4</sup>Forest Products Laboratory Madison

Keywords: *Betula platyphylla*, *Phanerochaete chrysosporium*, degradation products

1983-205

木材の酵素による加水分解 –無機塩存在下での蒸煮・爆砕処理の効果–

須藤賢一、石井 忠、志水一允、藤井智之、長沢定男

林業試験場

Enzymatic hydrolysis of wood. –Effects of steam-explosion under the presence of inorganic salts.

Kenichi Sudo, Tadashi Ishii, Kazumasa Shimizu, Tomoyuki Fujii, Sadao Nagasawa

Forestry and Forest Products Research Institute

Keywords: *Betula platyphylla*, *Fagus crenata*, *Aesculus turbinata*, *Larix Kaempferi*, aluminium chloride, ammonium chloride,

1983-206

リグニン–糖間の物理および化学的結合について

Lam Thi Bach Tuyet、飯山賢治、中野準三

東京大学農学部

Studies on the physical and chemical associations between lignin and carbohydrate.

Lam Thi Bach Tuyet, Kenji Iiyama, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: refiner mechanical pulp, carboxymethylation, gel filtration, <sup>1</sup>H-NMR,

1983-207

ヘミセルロース・リグニン結合体に関する研究(その 10)–バガス Björkman LCC の性質–

加藤 厚、東 順一、越島哲夫

京都大学木材研究所

Studies on hemicellulose–lignin bond. X. Characterization of bagasse Björkman LCC.

Atsushi Kato, Junichi Azuma, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Saccharum* sp., ferulic acid, coumaric acid, gel filtration, <sup>13</sup>C-NMR

1983-208

Klason Lignin に残存する炭水化物について

松本雄二、寺澤一雄、石津 敦、中野準三

東京大学農学部

Studies on the carbohydrate remaining in Klason lignin.

Yuji Matsumoto, Kazuo Terasawa, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, *Betula* sp., ozone degradation,

1983-209

白色腐朽菌のポプラチップへの作用と同菌による部分分解材のTMP化

赤松 勲、吉原一年、上嶋 洋、藤井利郎

四国工業技術試験所

Treatment of poplar chips with white rot fungi and production of TMP from the treated chips.

Isao Akamatsu, Kazutoshi Yoshihara, Hiroshi Kamishima, Toshiro Fujii

Government Industrial Research Institute, Shikoku

Keywords: *Populus* sp., defibration energy, pulp properties

1983-210

前加水分解処理(アスプルンド法)残渣パルプの性質

島田謹爾、高野 勲、宇佐見国典、長沢定男、須藤賢一、志水一允

林業試験場

Characterization of prehydrolysis (Asplund) pulp.

Kinji Shimada, Isao Takano, Kuninori Usami, Sadao Nagasawa, Kenichi Sudo, Kazumasa Shimizu

Forestry and Forest Products Research Institute

Keywords: *Betula Tauschii*, *Pinus densiflora*, *Fagus crenata*, *Larix Kaempferi*, chlorine, chlorine dioxide, sodium hypochlorite, strength properties

1983-211

過酸化水素-アルカリ法(PA法)による沖縄産ギンネムのパルプ化

金沢健治<sup>\*1</sup>、御田昭雄<sup>\*1</sup>、柏原 進<sup>\*1</sup>、原 信治<sup>\*2</sup>、浅見明彦<sup>\*2</sup>

<sup>\*1</sup> 化学技術研究所、<sup>\*2</sup> 東海パルプ株式会社

Peroxide-alkali pulping (PA process) of lead tree (*Leucaena leucocephala*).

Kenji Kanazawa<sup>\*1</sup>, Akio Mita<sup>\*1</sup>, Susumu Kashiwabara<sup>\*1</sup>, Shinji Hara<sup>\*2</sup>, Akihiko Asami<sup>\*2</sup>

<sup>\*1</sup>National Chemical Laboratory for Industry, <sup>\*2</sup>Tokai pulp Co. Ltd.

Keywords: bleachability, EDTA, anthraquinone

1983-212

アルカリ酸素蒸解に関する研究(第7報)-稲わらパルプの酸化漂白-

戸坂圀夫、林 治助

北海道大学工学部

Studies on alkali-oxygen pulping. VII. -Oxidative bleaching of rice straw pulp.

Kunio Tosaka, Jisuke Hayashi

Faculty of Engineering, Hokkaido University

Keywords: *Oryza sativa*, ozone bleaching, alkaline hydrogen peroxide bleaching, brightness

1983-213

ネマガリタケのソルボリシスパルプ化

中村敏也、榊原 彰

北海道大学農学部

Solvolytic pulping of *Sasa kurilensis*.

Toshiya Nakamura, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: cresol, brightness, biomass refinery

1983-214

高歩留 SP 廃液を利用した耐水性接着剤の製造

境 一男、佐藤 裕、成田 升、下田 優

王子建材工業株式会社

Preparation of waterproof adhesives from high yield sulfite pulp effluent.

Kazuo Sakai, Hiroshi Sato, Masu Narita, Suguru Shimoda

Oji Kenzai Co. Ltd.

Keywords: phenol, lauan plywood, birch plywood, larch plywood, particleboard,

1983-215

カラマツ樹皮の水酸化ナトリウム抽出物を利用した接着剤の製造

窪田 実、平田三郎、斉藤 勝、駒沢克己、青山政和

北海道立林産試験場

Preparation of adhesives from sodium hydroxide extracts of larch bark.

Minoru Kubota, Saburo Hirata, Masaru Saito, Katsumi Komazawa, Masakazu Aoyama

Hokkaido Forest Products Research Institute

Keywords: *Larix Kaempferi*, polyphenol,

1983-216

紙・パルプ廃液からの活性炭の製造

里中聖一、磯部泰佐、香山 疆

北海道大学農学部

Production of activated carbon from pulp and paper mill effluent.

Seiichi Satonaka, Taisuke Isobe, Tsutomu Kayama

Faculty of Agriculture, Hokkaido University

Keywords: *Picea Glehnii*, *Betula Tauschii*, *Quercus crispula*,

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1984-101

広葉樹複合細胞間層リグニンの性状について(第 2 報)

飯塚堯介、中野準三

東京大学農学部

Characterization of lignin in compound middle lamella of hardwood. II.

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Betula maximowicziana*, *Betula Tauschii*, fiber, soft xylem, permanganate oxidation, nitrobenzene oxidation

1984-102

針葉樹プロトリグニンの芳香核縮合度について

船岡正光、阿部 勲

三重大学農学部

Degree of condensation of aromatic rings in softwood protolignin.

Masamitsu Funaoka, Isao Abe

Faculty of Agriculture, Mie University

Keywords: *Chamaecyparis obtuse*, nuclear exchange method, condensation degree

1984-103

スギ穿孔性害虫被害材リグニンの化学的特性  
島田謹爾、西田篤実、高野 勲、宇佐美国典  
林業試験場

Chemical characteristics of lignin in the wood damaged by boring insect.

Kinji Shimada, Atsumi Nishida, Isao Takano, Kuninori Usami

Forestry and Forest Products Research Institute

Keywords: *Anaglyptus subfasciatus*, *Resseliella odai*, *Epi-notia granitalis*, permanganate oxidation

1984-104

硫酸リグニンの化学構造 – 1,2-ジアリール-1,3-プロパンジオールと硫酸との反応  
安田征市、足立久美子、寺島典二、太田勝人  
名古屋大学農学部

Chemical structures of sulfuric acid lignin. –Reactions of 1,2-diaryl- 1,3-propanediol with sulfuric acid.

Seiichi Yasuda, Kumiko Adachi, Noritsugu Terashima, Katsuhito Oota

Faculty of Agriculture, Nagoya University

Keywords: pinosresinol,

1984-105

リグニン・ヘミセルロース結合体の簡便な調製法とその構造  
東 順一<sup>\*1</sup>、渡辺隆司<sup>\*1\*2</sup>、越島哲夫<sup>\*1</sup>

<sup>\*1</sup> 京都大学木材研究所、<sup>\*2</sup> 山陽国策パルプ株式会社

Simple preparation of lignin hemicellulose complex and its chemical structure.

Junichi Azuma<sup>\*1</sup>, Takashi Watanabe<sup>\*1\*2</sup>, Tetsuo Koshijima<sup>\*1</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Sanyo Kokusaku Pulp Co. Ltd.

Keywords: *Pinus densiflora*, Björkman LCC, ion exchange chromatography, <sup>13</sup>C-NMR

1984-106

クラフトパルプにおけるリグニンと炭水化物の結合  
磯貝 明、石津 敦、中野準三  
東京大学農学部

Linkages between lignin and carbohydrate in kraft pulp.

Akira Isogai, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: gel permeation chromatography, lignin cellulose linkage, lignin hemicellulose linkage

1984-107

リグニンの酸化分解(VII)ヒドロキシラジカルによるリグニンの分解  
辰巳憲司<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup> 公害資源研究所、<sup>\*2</sup> 名古屋大学農学部

Oxidative degradation of lignin. VII. Degradation of lignin with a hydroxyl radical.

Kenji Tatsumi<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>National Research Institute for Pollution and Resources, <sup>\*2</sup>Faculty of Agriculture, Nagoya University

Keywords: aromatic ring, UV irradiation, lignin model compounds, mass spectrometry,

1984-108

好アルカリ性細菌によるリグニンモデル化合物の分解

川上日出国、近藤規子

名古屋大学農学部

Degradation of lignin model compounds by alkalophilic bacteria.

Hidekuni Kawakami, Noriko Kondo

Faculty of Agriculture, Nagoya University

Keywords:  $\beta$ -O-4 dimer, biphenyl compounds, mass spectrometry, *Pseudomonas ovalis*

1984-109

菌体外酵素による Guaiacylglycerol- $\beta$ -guaiacyl ether の生分解

沖 妙、新本美智枝、石川久雄

愛媛大学農学部

Biodegradation of guaiacylglycerol- $\beta$ -guaiacyl ether by extracellular enzyme.

Tae Oki, Michie Shinmoto, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Coriolus versicolor*, *Irpex lacteus*, *Phanerochaete chrysosporium*, *Coprinus off ellisii*, dioxane lignin

1984-110

カワラタケ菌体外酵素によるリグニンモデル化合物の分解

諸星紀幸、原口隆英

東京農工大学農学部

Degradation of lignin model compounds by the extracellular enzyme of *Coriolus versicolor*

Noriyuki Morohoshi, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Coriolus versicolor*, laccase III, syringylglycerol- $\beta$ -(2,6-dimethoxyphenyl) ether

1984-111

$\alpha$ -O-4 型及び  $\alpha$  位にケトンを有する  $\beta$ -O-4 型リグノールの *Fusarium solani* M-13-1 による分解  
片山健至<sup>\*1</sup>、山田康博<sup>\*1</sup>、十河村男<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup> 香川大学農学部、<sup>\*2</sup> 京都大学木材研究所

Degradation of an  $\alpha$ -O-4 type lignol and  $\beta$ -O-4 type lignol with  $\alpha$ -ketone by *Fusarium solani* M-13-1.

Takeshi Katayama<sup>\*1</sup>, Yasuhiro Yamada<sup>\*1</sup>, Murao Sogo<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Kagawa University, <sup>\*2</sup> Wood Research Institute, Kyoto University

Keywords: dilignols, non-cyclic benzyl ether, trilignols, mass spectrometry, <sup>13</sup>C-NMR,

1984-112

4-エトキシ-3-メキシフェニルグリセロール- $\beta$ -シリンガアルデヒドエーテルのカワラタケによる分解

河合真吾、梅沢俊明、樋口隆昌

京都大学木材研究所

Degradation of 4-ethoxy-3-methoxyphenylglycerol- $\beta$ -syringaldehyde ether by *Coriolus versicolor*.

Shingo Kawai, Toshiaki Umezawa, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: biodegradation, lignin substructure model compound, *Phanerochaete chrysosporium*, *Pseudomonas putida*, TLC, NMR, GC-MS,

1984-113

*Phanerochaete chrysosporium*による  $\beta$ -O-4 結合の開裂とアリールグリセロールの生成機構について

梅澤俊明、樋口隆昌

京都大学木材研究所

Cleavage of  $\beta$ -O-4 bond and formation of arylglycerol by *Phanerochaete chrysosporium*.

Toshiaki Umezawa, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords:  $^{18}\text{O}$  tracer, TLC, GC-MS

1984-114

リグニン分解へのバイオミメティックアプローチ(I) -リグニンモデル化合物の分解反応に及ぼすヘミンの触媒効果

島田幹夫<sup>\*1</sup>、波部 豪<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、岡本 忠<sup>\*2</sup>

<sup>\*1</sup> 京都大学木材研究所、<sup>\*2</sup> 京大化学研究所

Biomimetic approach to the degradation of lignin. I. Catalytic effect of hemin on the degradation of lignin model compounds.

Mikio Shimada<sup>\*1</sup>, Tsuyoshi Habe<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, Tadashi Okamoto<sup>\*2</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Institute for Chemical Research, Kyoto University

Keywords: iron porphyrin, cytochrome, peroxidase, catalase

1984-115

リグニン分解へのバイオミメティックアプローチ(II) -リグニン分解酵素及び酵素モデル触媒による重水素化リグニンモデル化合物の分解

波部 豪、島田幹夫、樋口隆昌

京都大学木材研究所

Biomimetic approach to the degradation of lignin. II. -Degradation of deuterated lignin model compounds by lignin degrading enzyme and enzyme model catalyst.

Tsuyoshi Habe, Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phanerochaete chrysosporium*, hemin

1984-116

特別講演、リグニン化学構造研究の回顧

榊原 彰

北海道大学農学部

Invited lecture; Retrospection on the research of lignin chemical structure.

Akira Sakakibara

Faculty of Agriculture, Hokkaido University

1984-201

爆砕処理による木質系物質の利用

志水一允<sup>\*1</sup>、須藤賢一<sup>\*1</sup>、長沢定男<sup>\*1</sup>、島田規男<sup>\*2</sup>、菅原一晃<sup>\*3</sup>

<sup>\*1</sup> 林業試験場、<sup>\*2</sup> 東和化成、<sup>\*3</sup> 三菱重工

Utilization of woody biomass by steam explosion.

Kazumasa Shimizu<sup>\*1</sup>, Kenichi Sudo<sup>\*1</sup>, Sadao Nagasawa<sup>\*1</sup>, \*Norio Shimada<sup>\*2</sup>, Kazuaki Sugawara<sup>\*3</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Towa-Kasei Co. Ltd., <sup>\*3</sup>Mitsubishi Heavy Industries Co. Ltd.

Keywords: *Betula Tauschii*, *Fagus crenata*, *Quercus serrata*, *Castanopsis cuspidate*, GPC

1984-202

A Solid State CP/MAS NMR-Study of a Product Synthesized from Lignin and Sulphur.

K. Levon, B. Hortling, J.J. Lindberg

ヘルシンキ大学

A solid state CP/MAS NMR-study of a product synthesized from lignin and sulphur.

K. Levon, B. Hortling, J.J. Lindberg

University of Helsinki

Keywords: sulphur lignin, poly(phenylene)sulphides, lignosulphonate, solution NMR

1984-203

リグニン関連型構造を有するコレステリルエステルの合成とその液晶性

春日和行、畠山兵衛

製品科学研究所

Synthesis of cholesteryl ester with lignin-related structure and its characteristics as liquid crystal.

Kazuyuki Kasuga, Hyoe Hatakeyama

Industrial Products Research Institute

Keywords: 4-*n*-alkoxybenzoic acid derivative, polarization microscope, DSC

1984-204

水-リグノスルホン酸 Na 塩混合系の DSC 及び <sup>23</sup>Na-NMR

畠山兵衛<sup>\*1</sup>、広瀬重雄<sup>\*1</sup>、中村邦雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

製品科学研究所、神奈川県工業試験所、繊維高分子材料研究所

DSC and <sup>23</sup>Na-NMR studies of the water-sodium lignosulphonate system.

Hyoe Hatakeyama<sup>\*1</sup>, Shigeo Hirose<sup>\*1</sup>, Kunio Nakamura<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Industrial Products Research Institute, <sup>\*2</sup>Kanagawa Industrial Technology Center, <sup>\*3</sup>Institute for Textiles and Polymers

Keywords: non-freezing water, freezing bound water,

1984-205

マニラ麻の Bio-RMP 化について

赤松 勲、上島 洋、藤井利郎、吉原一年

四国工業技術試験所

Preparation of bio-refiner mechanical pulp from Manila hemp.

Susumu Akamatsu, Hiroshi Kamishima, Toshiro Fujii, Kazutoshi Yoshihara

Government Industrial Research Institute, Shikoku

Keywords: Bio-RMP, Manila hemp, white rot fungi, *Coriolus hirstus*

1984-206

ソルボリスパルプの組織化学的研究

枝重有祐、榊原 彰

北海道大学農学部

Histochemical study of solvolysis pulp.

Yusuke Edashige, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: beech, *Fagus crenata*, sapwood, heartwood, UV microscopy

1984-207

加溶媒分解におけるヘミセルロースの挙動

小沢修二、武山浩武、榊原 彰

北海道大学農学部

Behaviors of hemicellulose during solvolysis.

Shuji Ozawa, Hirotake Takeyama, Akira Sakakibara

Faculty of Agriculture, Hokkaido University

Keywords: *Betula Tauschii*, cresol, GPC, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, MS

1984-208

有機溶媒と亜硫酸塩による脱リグニン(Ⅲ) イソプロピルアルコール-亜硫酸塩セミケミカルパルプ化における樹種特性

文 星筆、近藤隆一郎、坂井克己、今村博之

九州大学農学部

Delignification with organic solvents and bisulfite. III. Characteristics of wood species on semichemical pulping with isopropyl alcohol and bisulfite.

Sung-Phil Mung, Ryuichiro Kondo, Kokki Sakai, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: softwood, hardwood, tropical wood,

1984-209

アルカリ蒸解における針葉樹型および広葉樹型リグニンの反応性の差異

近藤隆一郎、堤 祐司、野口浩司、今村博之

九州大学農学部

Differences in reactivity between softwood and hardwood lignins during alkaline pulping.

Ryuichiro Kondo, Yuji Tsutsumi, Koji Noguchi, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: kinetics, guaiacylglycerol- $\beta$ -guaiacyl ether, syringylglycerol- $\beta$ -syringyl ether,  $\beta$ -aryl ether cleavage,

1984-210

Modified Kraft Pulping. A way to decrease lignin content and improve pulp quality.

Peter Sandström

STFI, Swedish Pulp and Paper Research Institute

Keywords: initial phase, bulk delignification, final phase, effective alkali

1984-211

酸素・アルカリ蒸解の蒸解要因(10)コバルト・アミノアルコール錯体の脱リグニン促進効果

目黒貞利、今村博之

九州大学農学部

Factors influencing oxygen-alkali cooking. X. Delignification enhancement by the addition of cobalt-amino alcohol complex.

Sadatoshi Meguro, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: *Betula Tauschii*, Co-salen, Co-triethanolamine complex,

1984-212

GP リグニンのニトロベンゼン酸化について

平島英則<sup>\*1</sup>、住本昌之<sup>\*2</sup>

<sup>\*1</sup>片山化学工業株式会社、<sup>\*2</sup>九州大学農学部

Nitrobenzene oxidation of GP lignin.

Hidenori Hirashima<sup>\*1</sup>, \*Masashi Sumimoto<sup>\*2</sup>

<sup>\*1</sup>Katayama Chemical Industries Co. Ltd, <sup>\*2</sup>Faculty of Agriculture, Kyushu University

Keywords: *Pinus densiflora*, bleaching, brightness

1984-213

脱リグニン反応に及ぼす超音波照射の影響(第2報)超音波照射下におけるリグニンの挙動

譚 国民、安田征市、寺島典二

名古屋大学農学部

Effect of ultrasonic irradiation on delignification reaction. II. Behavior of lignin during delignification under ultrasonic irradiation.

Guo-Min Tan, Seiichi Yasuda, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: *Pinus densiflora*, MWL, guaiacylglycerol- $\beta$ -guaiacyl ether, calcium hypochlorite

1984-214

バガスの UPAP の漂白の無塩素化について

御田昭雄、柏原 進

化学技術研究所

Nonchlorine bleaching of UPAP from bagasse.

Akio Mita, Susumu Kashiwabara

National Chemical Laboratory for Industry

Keywords: AQ, AP, brightness

1984-215

晒排液中の突然変異原性に関する研究(第1報)各種の親核試薬による突然変異原性の解毒機構

橘 燦郎<sup>\*1</sup>、J. Santodonato<sup>\*2</sup>、C. W. Dence<sup>\*3</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>シラキュース大学、<sup>\*3</sup>ニューヨーク州立大学

Studies on the mutagenicity of bleach effluent. I. Mechanism of the detoxication of mutagenicity by nucleophilic reagents.

Sanro Tachibana<sup>\*1</sup>, J. Santodonato<sup>\*2</sup>, C. W. Dence<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>University of Syracuse, <sup>\*3</sup>State University of New York

Keywords: *Pinus virginiana*, *Pinus taeda*, 2-chloropropenal, chloroacetone, chloro- $\sigma$ -benzoquinone,

1984-216

招待講演、

Soda-AQ/Oxygen Pulping Process as an Alternative to Kraft Process for Production of Bleached Pulp from Softwood.

Y. C. Tsai, N. H. Shin, H.-m. Chang, J. S. Gratzl  
ノースカロライナ州立大学

Invited lecture;

Y. C. Tsai, N. H. Shin, H.-m. Chang, J. S. Gratzl  
North Carolina State University

Keywords: viscosity, brightness,

## 第 30 回 (1985.11.6-7) 高知会館

1985-101

スギ細胞壁の木化とペルオキシダーゼ活性の分布

高部圭司、原田 浩

京都大学農学部

Lignification and distribution of peroxidase activity in Japanese cedar cell wall.

Keiji Takabe, Hiroshi Harada

Faculty of Agriculture, Kyoto University

Keywords: *Cryptomeria japonica*, osmium black, electron micrograph, lignin skeleton,

1985-102

カラマツ師部の厚壁細胞の木化(予報)

今川一志、深沢和三

北海道大学農学部

Lignification of fiber sclereid in the phloem of larch. (Preliminary report).

Kazushi Imagawa, Kazumi Fukazawa

Faculty of Agriculture, Hokkaido University

Keywords: *Larix leptolepis*, UV micrograph, lignin distribution, differentiation

1985-103

広葉樹リグニン中のグアヤシルおよびシリングル構造の選択的標識

寺島典二<sup>\*1</sup>、福島和彦<sup>\*1</sup>、高部圭司<sup>\*2</sup>

名古屋大学農学部、京都大学農学部

Selective radio-labeling of guaiacyl and syringyl structures in hardwood lignin

Noritsugu Terashima<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Keiji Takabe<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>Faculty of Agriculture, Kyoto University

Keywords: magnolia, *Magnolia kobus*, oxford poplar, *Populus Maximowiczii* X *Populus belorinensis*, autoradiography, guaiacyl unit, syringyl unit, <sup>3</sup>H-coniferin, <sup>3</sup>H-syringin

1985-104

リグニンモデル化合物の合成とそのニトロベンゼン酸化について

季 典艶、橘 燦郎、住本昌之

九州大学農学部

Synthesis of lignin model compounds and their nitrobenzene oxidation.

Dian Yan Lee, Sanro Tachibana, Masashi Sumimoto

Faculty of Agriculture, Kyushu University

Keywords: guaiacylglycerol- $\beta$ -coniferyl ether, guaiacylglycerol- $\beta$ -guaiacyl ether, nitrobenzene oxidation, <sup>1</sup>H-NMR, mass spectrometry

1985-105

硫酸リグニンの化学構造 —硫酸溶液中におけるシリングルアルコールの反応とグアヤシルおよびシリングル核の反応性

安田征市、太田勝人

名古屋大学農学部

Chemical structures of sulfuric acid lignin. —Reactions of syringyl alcohol and reactivity of guaiacyl and syringyl nucleus in sulfuric acid.

Seiichi Yasuda, Katsuhito Oota

Faculty of Agriculture, Nagoya University

Keywords: condensation, hardwood lignin, guaiacyl nucleus, syringyl nucleus,  $^{13}\text{C}$ -NMR

1985-106

リグニン・ヘミセルロース結合体のマイクロ波加熱

東 順一、土井美紀、越島哲夫

京都大学木材研究所

Microwave heating of lignin hemicellulose complex.

Junichi Azuma, Miki Doi, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, MWL, LCC, furfural, sugars,  $^{13}\text{C}$ -NMR, UV spectroscopy

1985-107

アルカリ蒸解において安定な LCC 結合について

種田英孝<sup>\*1</sup>、細谷修二<sup>\*2</sup>、中野準三<sup>\*1</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*2</sup> 林業試験場

LCC bond stable during alkaline cooking

Hidetaka Taneda<sup>\*1</sup>, Shuji Hosoya<sup>\*2</sup>, Junzo Nakano<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>Forestry and Forest Products Research Institute

Keywords: guaiacylglycerol- $\alpha$ -methylglucoside- $\beta$ -guaiacyl ether, HPLC,  $^{13}\text{C}$ -NMR,

1985-108

アルカリ性処理におけるシリングルグリセロール- $\beta$ -シリングルエーテル型モデル化合物の反応生成物について

堤 祐司、近藤隆一郎、今村博之

九州大学農学部

Reaction products from syringylglycerol- $\beta$ -syringyl ether type model compounds on alkaline treatment.

Yuji Tsutsumi, Ryuichiro Kondo, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: soda cooking, kraft cooking, soda-AQ cooking, HPLC,

1985-109

$\beta$ -O-4 型結合開裂の新反応

竹内寿一、坂井克己、文 星筆、今村博之

九州大学農学部

A new reaction for cleavage of  $\beta$ -O-4 type bonds.

Jyuichi Takeuchi, Kokki Sakai, Sung-Phil Mung, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: methanol, ethanol, isopropanol, *t*-butyl alcohol, magnesium sulfite, lignin

1985-110

有機溶媒と亜硫酸塩による脱リグニン(V) 低分子フェノール類について

文 星筆、坂井克己、今村博之

九州大学農学部

Delignification with organic solvents and sulfite. V. On the low molecular weight phenols.

Sung-Phil Mung, Kokki Sakai, Hiroyuki Imamura

Keywords: *Cryptomeria japonica*, magnesium sulfite, phenols, isopropyl alcohol,

1985-111

フェニルクマラン型構造のオゾン分解について

羽生直人、松本雄二、中野準三

東京大学農学部

Ozonolysis of phenylcoumaran type structure.

Naoto Habu, Yuji Matsumoto, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: dicarboxylic acids, GLC, GC-MS, <sup>1</sup>H-NMR

1985-112

ヨウ素化トリメチルシランによるリグニン・エーテル結合の選択的開裂について

飯塚堯介、近藤哲男、中野準三

東京大学農学部

Selective cleavage of ether linkage in lignin by trimethylsilyliodide.

Gyosuke Meshitsuka, Tetsuo Kondo, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Betula maximowicziana*, MWL, guaiacylglycerol- $\beta$ -guaiacyl ether, <sup>1</sup>H-NMR

1985-113

蒸煮処理材酵素糖化残渣リグニンの性状について

須藤賢一、志水一允、島田謹爾、桜井孝一、藤井智之

林業試験場

Characterization of residual lignin after steaming and enzymatic hydrolysis.

Kenichi Sudo, Kazumasa Shimizu, Kinji Shimada, Koichi Sakurai, Tomoyuki Fujii

Forestry and Forest Products Research Institute

Keywords: *Betula platyphylla*, nitrobenzene oxidation, permanganate oxidation,

1985-114

Guaiacylglycerol- $\beta$ -guaiacyl ether と lignin 生分解に関与する酵素について

沖 妙、石川久雄

愛媛大学農学部

Enzymes involved in the biodegradation of guaiacylglycerol- $\beta$ -guaiacyl ether and lignin.

Tae Oki, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Phanerochaete chrisosporium*, *Coprinus aff ellisii*, UV spectroscopy, GPC

1985-115

リグニン分解へのバイオミメティックアプローチ (IV) -鉄・ポルフィリン錯体と一電子酸化剤によるリグニン関連化合物の分解機構

島田幹夫<sup>\*1</sup>、河波好宏<sup>\*2</sup>、梅澤俊明<sup>\*1</sup>、棚橋光彦<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、岡本 忠<sup>\*3</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>近畿大学農学部、<sup>\*3</sup>京都大学化学研究所

Biomimetic approach to the biodegradation of lignin. IV. -Degradation mechanism of lignin related compounds by ferriporphyrin and one electron oxidant.

Mikio Shimada<sup>\*1</sup>, Yoshihiro Kawanami<sup>\*2</sup>, Toshiaki Umezawa<sup>\*1</sup>, Mitsuhiro Tanahashi<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, Tadashi Okamoto<sup>\*3</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Faculty of Agriculture, Kinki University, <sup>\*3</sup>Institute for Chemical Research, Kyoto University

Keywords: active oxygen species, phenylcoumaran, heme-enzyme, t-butylhydroperoxide, ceric ammonium nitrate

1985-116

カワラタケ菌体外酵素によるリグニンモデル化合物の分解

諸星紀幸、中村雅哉、原口隆英

東京農工大学農学部

Degradation of lignin model compounds by extracellular enzyme of *Coriolus versicolor*.

Noriyuki Morohoshi, Masaya Nakamura, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: laccase III, guaiacylglycerol- $\beta$ -guaiacyl ether, guaiacylglycerol- $\beta$ -syringyl ether

1985-117

カワラタケラッカーゼによる $\beta$ -1型リグニンモデル化合物の分解

河合真吾<sup>\*1</sup>、梅澤俊明<sup>\*1</sup>、島田幹夫<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、小池一雄<sup>\*2</sup>、西田友昭<sup>\*2</sup>、諸星紀幸<sup>\*3</sup>、原口隆英<sup>\*3</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>王子製紙株式会社中央研究所、<sup>\*3</sup>東京農工大学農学部

Degradation of  $\beta$ -1 type lignin model compounds by laccase of *Coriolus versicolor*.

Shingo Kawai<sup>\*1</sup>, Toshiaki Umezawa<sup>\*1</sup>, Mikio Shimada<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, Kazuo Koike<sup>\*2</sup>, Tomoaki Nishida<sup>\*2</sup>, Noriyuki Morohoshi<sup>\*3</sup>, Takafusa Haraguchi<sup>\*3</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Oji Paper Co. Ltd., <sup>\*3</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology.

Keywords: biodegradation, lignin substructure model compound, stable isotope tracer, <sup>18</sup>O<sub>2</sub>, mass spectrometry, 1,2-disyringylpropane-1,3-diol

1985-118

特別講演、酵母細胞壁溶解酵素とその利用

高知大学農学部

長崎 亀

Invited lecture ; Enzymes involved in the dissolution of yeast cell wall and its utilization.

Susumu Nagasaki

Faculty of Agriculture, Kochi University

Keywords:  $\beta$ -1,3 glucanase,

1985-201

*Phanerochaete chrysosporium* による  $\beta$ -O-4 二量体の分解における $\beta$ -アリアル基の転位と C $\alpha$ -C $\beta$  開裂

梅澤俊明、樋口隆昌  
京都大学木材研究所

Rearrangement of  $\beta$ -aryl group and C $\alpha$ -C $\beta$  cleavage in the degradation of  $\beta$ -O-4 dimer by *Phanerochaete chrysosporium*.

Toshiaki Umezawa, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords:  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{18}\text{O}$ , stable isotope tracer method,  $^1\text{H}$ -NMR, mass spectrometry

1985-202

シュードモナス属細菌 TMY1009 株の変異株による  $\beta$ -エーテル型モデル化合物の分解と中間代謝物の生成

安部修一、鮫島正浩、佐分義正、善本知孝

東京大学農学部

Degradation of  $\beta$ -O-4 type lignin model compounds and formation of intermediate metabolites by the mutant of *Pseudomonas* TMY1009.

Shuichi Abe, Masahiro Samejima, Yoshimasa Saburi, Tomotaka Yoshimoto

Faculty of Agriculture, the University of Tokyo

Keywords:  $\beta$ -O-4, TLC, UV spectroscopy

1985-203

好アルカリ性細菌によるリグニンモデル化合物及びリグニンの分解

川上日出国、青井理恵、丹羽 淳

名古屋大学農学部

Degradation of lignin model compounds and lignin by alkalophilic bacteria

Hidekuni Kawakami, Rie Aoi, Makoto Niwa

Faculty of Agriculture, Nagoya University

Keywords: diarylpropane diol, beech, *Fagus crenata*, 1,2-guaiacylpropane-1,3-diol, 1-guaiacyl-2-syringylpropane GPC

1985-204

白色腐朽菌 *Phanerochaete chrysosporium* の生分解によって生成した脱脂シラカンバチップ中の低分子成分

寺沢 実<sup>\*1</sup>、香山 疆<sup>\*1</sup>、C.L. Chen<sup>\*2</sup>、D.-S. Tai<sup>\*3</sup>

北海道大学農学部、ノースカロライナ州立大学、南京林学院

Low molecular weight compounds formed in the degradation of extractive-free birch tips by a white rot fungus *Phanerochaete chrysosporium*.

Minoru Terasawa<sup>\*1</sup>, Tsutomu Kayama<sup>\*1</sup>, C.L. Chen<sup>\*2</sup>, D.-S. Tai<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>North Carolina State University, <sup>\*3</sup>Nanjing Forestry University

Keywords: *Betula platyphylla*, acetophenone derivatives, ligninase

1985-205

ミツマタ韌皮の酵素パルプ化過程におけるリグニン及びヘミセルロースの溶出挙動

田辺寛之、小林良生

四国工業技術試験所

Dissolution behavior of lignin and hemicellulose during enzymatic pulping of mitsumata (oriental paperbush) bast.

Hiroyuki Tanabe, Yoshinari Kobayashi  
Government Industrial Research Institute, Shikoku  
Keywords: *Edgeworthia chrysantha*, carbohydrate composition

1985-206

菌処理マニラ麻の H<sub>2</sub>O<sub>2</sub> 添加 TMP 化  
赤松 勲、上嶋 洋、吉原一年  
四国工業技術試験所

Preparation of thermomechanical pulp with addition of hydrogen peroxide from fungi treated Manila hemp.

Isao Akamatsu, Hiroshi Kamishima, Kazutoshi Yoshihara  
Government Industrial Research Institute, Shikoku

Keywords: *Coriolus hirtus*, Klason lignin, holocellulose, pulp yield, pulp properties

1985-207

GP リグニン中のコニフェリルアルデヒド構造の挙動について  
平嶋英則、住本昌之  
九州大学農学部

Behaviors of coniferyl aldehyde structure in GP lignin.

Hidenori Hirashima, Masashi Sumimoto  
Faculty of Agriculture, Kyushu University

Keywords: red pine, *Pinus densiflora*, H<sub>2</sub>O<sub>2</sub>, NaBH<sub>4</sub>

1985-208

リグノセルロースの HF 糖化 -HF リグニンの構造  
広居忠量、石井 忠  
林業試験場

Saccharification of lignocellulose by HF. -Structure of HF lignin.

Tadakazu Hiroi, Tadashi Ishii

Forestry and Forest Products Research Institute

Keywords: red pine, *Pinus densiflora*, white birch, *Betula platyphylla*, <sup>13</sup>C-NMR, IR spectroscopy, permanganate oxidation

1985-209

広葉樹材蒸煮処理効果の樹種による差  
山口 彰、志水一允、桜井孝一、藤井智之  
林業試験場

Differences in the effectiveness of steaming for saccharification among wood species.

Akira Yamaguchi, Kazumasa Shimizu, Koichi Sakurai, Tomoyuki Fujii

Forestry and Forest Products Research Institute

Keywords: enzymatic susceptibility, nitrobenzene oxidation, S/V ratio, sugar composition

1985-210

リグニンの繊維化について  
須藤賢一、志水一允  
林業試験場

Preparation of fiber from lignin.

Kenichi Sudo, Kazumasa Shimizu

Forestry and Forest Products Research Institute

Keywords: carbon fiber, white birch, *Betula platyphylla*, steaming, methanol extraction

1985-211

The Effect of Modified Lignosulphonate on Beating.

Kalle Levon, Gyosuke Meshitsuka and Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: aminated lignosulphonate, mannich reaction, beating rate, freeness,

1985-212

リグニンの水素化分解 –反応温度および時間の検討–

小山 実、金沢健治、山田谷正子、杉本義一

化学技術研究所

Hydrogenolysis of lignin. –Investigation of reaction time and temperature.

Makoto Koyama, Kenji Kanazawa, Masako Yamadaya, Giichi Sugimoto

National Chemical Laboratory for Industry

Keywords: thiolignin, cresol lignin, molecular weight distribution, monophenols,

1985-213

無機吸着剤に濃縮したバイオマスの熱分解

猪狩俣将<sup>\*1</sup>、横山正一郎<sup>\*1</sup>、井上晴彦<sup>\*2</sup>

<sup>\*1</sup> 化学技術研究所, <sup>\*2</sup> クニミネ工業株式会社

Pyrolysis of biomass adsorbed on inorganic adsorbents.

Yoshimasa Ikari<sup>\*1</sup>, Shoichiro Yokoyama<sup>\*1</sup>, \* Haruhiko Inoue<sup>\*2</sup>

<sup>\*1</sup>National Chemical Laboratory for Industry, <sup>\*2</sup>Kunimine Industries Co. Ltd.

Keywords: gasification, methanol synthesis, recovery of adsorbent

1985-214

ソルボリシスパルプ化による木材の脱リグニン –パルプ化条件とリグニンの性質

佐野 嘉拓、笹谷 宜志

北海道大学農学部

Delignification of wood by solvolysis pulping. –Pulping conditions and the properties of lignin.

Yoshihiro Sano, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Keywords: beech, *Fagus crenata*, white birch, *Betula platyphylla*, cresol, solvolysis lignin

1985-215

ソルボリシスパルプ化による木材の脱リグニン –パルプ残存リグニン

枝重有祐、佐野嘉拓、笹谷宜志

北海道大学農学部

Delignification of wood by solvolysis pulping. –Residual lignin in pulp.

Yusuke Edashige, Yoshihiro Sano, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Keywords: beech, *Fagus crenata*, cresol, gel filtration, MWL, nitrobenzene oxidation, <sup>1</sup>H-NMR

1985-216

クレゾールを含むヘミセルロース水溶液の精製

西山昌史、細川 純、上嶋 洋

四国工業技術試験所

Removal of cresol from aqueous hemicellulose and cresol solution.

Masashi Nishiyama, Jun Hosokawa, Hiroshi Kamishima

Government Industrial Research Institute, Shikoku

Keywords: beech, *Fagus crenata*, solvolysis pulping, cresol, hemicellulose

1985-217

古代紙の打紙について

大川昭典<sup>\*1</sup>、増田勝彦<sup>\*2</sup>

<sup>\*1</sup>高知県紙業試験場、<sup>\*2</sup>東京国立文化財研究所

Beating of ancient paper.

Akinori Ohkawa<sup>\*1</sup>, Katsuhiko Masuda<sup>\*2</sup>

<sup>\*1</sup>Kochi Prefectural Pulp and Paper Experimental Station, <sup>\*2</sup>National Research Institute for Cultural Properties, Tokyo

Keywords: ancient paper, beating, breaking length

1985-218

特別講演、リグニン研究の回顧

中野準三

東京大学農学部

Invited lecture; A review of my lignin research.

Junzo Nakano

Faculty of Agriculture, the University of Tokyo

## 第 31 回 (1986.10.21-22)京大会館

1986-101

トドマツ圧縮あて材仮道管の木化

高部圭司、深沢和三

北海道大学農学部

Lignification of the tracheid of todomatsu compression wood.

Keiji Takabe, Kazumi Fukazawa

Faculty of Agriculture, Hokkaido University

Keywords: *Abies Mayriana*, UV microscope, electron microscope, peroxidase activity

1986-102

カラマツ樹皮のファイバースクレレイドの機械的単離とその化学成分

竹田昌文、寺沢 実、香山 彊

北海道大学農学部

Mechanical isolation and chemical components of Japanese larch fiber sclereid.

Masafumi Takeda, Minoru Terasawa, Tsutomu Kayama

Faculty of Agriculture, Hokkaido University

Keywords: UV microscope, thioacidolysis, MWL,

1986-103

広葉樹新生組織中のリグニンの性状(II)  
巖 泰振、飯塚堯介、石津 敦、中野準三  
東京大学農学部

Characterization of lignin in differentiating xylem of hardwood. II.

Tae Jin Eom, Gyosuke Meshitsuka, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: *Betula maximowicziana*, MWL, LCC, <sup>1</sup>H-NMR, nitrobenzene oxidation

1986-104

アカマツリグニン・糖結合体の糖鎖とリグニンの結合位置について  
渡辺隆司、海津澄子、越島哲夫  
京都大学木材研究所

Bonding position between carbohydrate and lignin in red pine LCC.

Takashi Watanabe, Sumiko Kaizu, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, DDQ oxidation, cellulase,

1986-105

ブナのリグニン・ヘミセルロース結合体におけるリグニンと糖の結合様式について  
東 順一<sup>\*1</sup>、越島哲夫<sup>\*2</sup>

<sup>\*1</sup> 京都大学農学部、<sup>\*2</sup> 京都大学木材研究所

Linkages between lignin and carbohydrate in beech lignin carbohydrate complex.

Junichi Azuma<sup>\*1</sup>, Tetsuo Koshijima<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Kyoto University, <sup>\*2</sup> Wood Research Institute, Kyoto University

Keywords: *Fagus crenata*, DDQ oxidation, <sup>13</sup>C-NMR,

1986-106

木材腐朽菌によるリグニンモデル配糖体の生成について  
近藤隆一郎、今村博之  
九州大学農学部

Formation of glycoside of lignin model compounds by wood rotting fungi.

Ryuichiro Kondo, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: *Polyporus versicolor*, *Tyromyces palustris*,  $\beta$ -glucosidase, laccase

1986-107

好アルカリ性細菌による水溶性リグニンの生成  
川上日出国、丹羽 淳  
名古屋大学農学部

Formation of water-soluble lignin by alkalophilic bacteria.

Hidekuni Kawakami, Makoto Niwa

Faculty of Agriculture, Nagoya University

Keywords: lignin degradation, wheat, *Hordeum vulgare*, poplar, *Populus* sp.,

1986-108

白色腐朽菌マイタケによる木材からの選択的脱リグニン

広居忠量、藤井智之

林業試験場

Selective delignification of wood by white rot fungus *Grifora frondosa*.

Tadakazu Hiroi, Tomoyuki Fujii

Forestry and Forest Products Research Institute

Keywords: *Betula platyphylla*, microscopy, compound middle lamella, secondary wall

1986-109

$\alpha$  位にケトンを有する  $\beta$ -O-4 型ジリグノールの *Fusarium solani* M-13-1 による分解と立体選択的還元(第2報)

片山健至<sup>\*1</sup>、十河村男<sup>\*1</sup>、堀池満子<sup>\*1</sup>、三木敬夫<sup>\*1</sup>、小橋啓志<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup>香川大学農学部、<sup>\*2</sup>京都大学木材研究所

Degradation and stereoselective reduction of  $\beta$ -O-4 dilignol with a-ketone group by *Fusarium solani* M-13-1. II.

Takeshi Katayama<sup>\*1</sup>, Murao Sogo<sup>\*1</sup>, Mitchiko Horiike<sup>\*1</sup>, Takao Miki,<sup>\*1</sup> Keishi Kohashi<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: *erythro/threo* ratio, <sup>1</sup>H-NMR, syringylpropanone, UV spectroscopy

1986-110

カワラタケラッカーゼの単離とその化学的、生化学的特徴

諸星紀幸、吉武彰文、片山義博、原口隆英

東京農工大学農学部

Isolation of laccase from *Coriolus versicolor*, and its chemical and biochemical characteristics.

Noriyuki Morohoshi, Akifumi Yoshitake, Yoshihiro Katayama, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: phenol oxidase, electrophoresis, crystallization, antigen

1986-111

Lignin peroxidase による  $\beta$ -O-4 リグニンモデル化合物の分解

三木啓司<sup>\*1</sup>、Michael H. Gold<sup>\*2</sup>

<sup>\*1</sup>公害資源研究所、<sup>\*2</sup>Oregon Graduate Center

Degradation of  $\beta$ -O-4 type lignin model compounds by lignin peroxidase.

Keiji Miki<sup>\*1</sup>, Michael H. Gold<sup>\*2</sup>

<sup>\*1</sup>National Research Institute for Pollution and Resources, <sup>\*2</sup>Oregon Graduate Center

Keywords: *Phanerochaete chrysosporium*, cation radical, <sup>18</sup>O tracer,

1986-112

酵素によるジオキサンリグニンの生分解

沖 妙、石川久雄

愛媛大学農学部

Biodegradation of dioxane lignin by enzyme.

Tae Oki, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Phanerochaete chrysosporium*, dioxane lignin, nitrobenzene oxidation

1986-113

リグニンモデル化合物分解酵素遺伝子のクローニング (I) 大腸菌-*Pseudomonas* シヤトルベクター pKT230 およびコスミドベクター pVK100 の受動的伝達能力を利用した分解酵素遺伝子のクローニング系の確立

片山義博<sup>\*1</sup>、西川誠司<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、原口隆英<sup>\*1</sup>、山崎眞狩<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京大学農学部

Cloning of the genes related to the enzyme for lignin model compound degradation. I. -Construction of the cloning system using the *Escherichia coli* and *Pseudomonas* spp. shuttle vector pKT230 and cosmid vector pVK100 by transconjugation.

Yoshihiro Katayama<sup>\*1</sup>, Seiji Nishikawa<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Takafusa Haraguchi<sup>\*1</sup>, Makari Yamasaki<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: 5,5-dehydrodivanillic acid, protocatechuic acid, ferulic acid

1986-114

リグニンモデル化合物分解酵素遺伝子のクローニング (II) 受動的伝達能力を有する大腸菌-*Pseudomonas* シヤトルベクター pKT230 を用いた *P. paucimobilis* SYK-6 株のジーンライブラリの構築とクローニング

西川誠司<sup>\*1</sup>、片山義博<sup>\*1</sup>、中村雅哉<sup>\*1</sup>、村山彰啓<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、原口隆英<sup>\*1</sup>、山崎眞狩<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京大学農学部

Cloning of the genes related to the enzyme for lignin model compound degradation. II. -Construction of gene library from *Pseudomonas paucimobilis* SYK-6 with the shuttle vector pKT230 by transconjugation.

Seiji Nishikawa<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Masaya Nakamura<sup>\*1</sup>, Akihiro Murayama<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Takafusa Haraguchi<sup>\*1</sup>, Makari Yamasaki<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Keywords: *Pseudomonas putida*, vanillic acid, protocatechuic acid,

1986-115

Ulin 材 (*Eusideroxylon zwageri*) の耐朽性と化学成分

Wasrin Syafii、善本知孝、鮫島正浩

東京大学農学部

Durability and chemical components of Ulin (*Eusideroxylon zwageri*) wood.

Wasrin Syafii, Tomotaka Yoshimoto, Masahiro Samejima

Faculty of Agriculture, the University of Tokyo

Keywords: *Coriolus versicolor*, *Tyromeces polutris*, decay test, eusiderin, neolignans

1986-116

菌処理マニラ麻の H<sub>2</sub>O<sub>2</sub> 添加 TMP 化 (その 2)

赤松 勲、上嶋 洋、吉原一年

四国工業技術試験所

Thermomechanical pulping of fungi treated Manila hemp by addition of H<sub>2</sub>O<sub>2</sub>. II.

Susumu Akamatsu, Hiroshi Kamishima, Kazutoshi Yoshihara

Government Industrial Research Institute, Shikoku

Keywords: *Coriolus hirstus*, brightness

1986-117

白色腐朽菌によるパルプ漂白排水の脱色・脱塩素

松本雄二<sup>\*1</sup>、Hou-min Chang<sup>\*2</sup>、T. Joyce<sup>\*2</sup>、T. K. Kirk<sup>\*3</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*2</sup> ノースカロライナ州立大学、<sup>\*3</sup> 米国林産物研究所

Decoloration and dechlorination of pulp bleach effluent by white rot fungi.

Yuji Matsumoto<sup>\*1</sup>、Hou-min Chang<sup>\*2</sup>、T. Joyce<sup>\*2</sup>、T. K. Kirk<sup>\*3</sup>

<sup>\*1</sup> Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup> North Carolina State University, <sup>\*3</sup> Forest Products Laboratory, USDA

Keywords: *Phanerochaete chrysosporium*, rotating biological contactor,

1986-118

パルプ廃液処理に関する研究(5) 廃液リグニンおよびフェノールモノマー類の担子菌類による処理性

鮫鳥一彦、谷岡俊彦、高村憲男

高知大学農学部

Studies on treatment of pulp effluent. V. Treatability of effluent lignin and phenol monomer by basidiomycetes.

Kazuhiko Sameshima, Toshihiko Tanioka, Norio Takamura

Keywords: *Polystictus versicolor*, *Pleurotus ostreatus*, vanillyl alcohol, vanillin, vanillic acid

1986-119

特別講演、人工チトクロム P-450 を用いる脂肪族・芳香族化合物の酸化

田伏岩夫

京都大学工学部

Invited lecture ; Oxidation of aliphatic and aromatic compounds by artificial cytochrome P-450.

Iwao Tabushi

Faculty of Engineering, Kyoto University

1986-201

亜硫酸ナトリウム、ホルムアルデヒドおよびキノン化合物を用いた新蒸解法

大井 洋、中野準三、石津 敦

東京大学農学部

New pulping process with sodium sulfite, formaldehyde and quinone compounds.

Hiroshi Ohi, Junzo Nakano, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: jezo spruce, *Picea jezoensis*, beech, *Fagus crenata*, saghalien fir, *Abies Mayriana*,

1986-202

有機溶媒と亜硫酸塩による脱リグニン(VII)パルプ品質の改善について

文 星筆、坂井克己、今村博之

九州大学農学部

Delignification with organic solvents and sulfite. VII. Improvement of pulp properties.

Sung-Phil Mung, Kokki Sakai, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: *Pinus rigida* × *Pinus taeda*, *Betula platyphylla*, isopropyl alcohol, secondary butyl alcohol

1986-203

フェノオルガノソルブパルプ化法(第3報)

高橋昭博、佐野嘉拓、笹谷宜志

北海道大学農学部

Phenorganosolv pulping. III.

Akihiro Takahashi, Yoshihiro Sano, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Keywords: *Fagus crenata*, pulping, *n*-propyl alcohol, phenol, cresol, pyrocatechol, dissolved lignin

1986-204

有機酸蒸解におけるリグニンの挙動

安田征市、伊藤範明

名古屋大学農学部

Behavior of lignin during pulping with organic acids.

Seiichi Yasuda, Noriaki Ito

Faculty of Agriculture, Nagoya University

Keywords: solvolysis pulping, lignin model compound, acetic acid, arylglycerol- $\beta$ -aryl ether

1986-205

酢酸パルプ化における脱リグニン反応

J. L. Davis<sup>\*1</sup>、中坪文明<sup>\*1</sup>、村上浩二<sup>\*1</sup>、R. A. Young<sup>\*2</sup>

<sup>\*1</sup>京都大学農学部、<sup>\*2</sup>University of Wisconsin

Delignification reaction during acetic acid pulping.

J. L. Davis<sup>\*1</sup>, Fumiaki Nakatsubo<sup>\*1</sup>, Koji Murakami<sup>\*1</sup>, R. A. Young<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyoto University, <sup>\*2</sup>University of Wisconsin

Keywords: guaiacylglycerol- $\beta$ -guaiacyl ether, enol ether, Hibbert's ketones

1986-206

オゾン分解によるリグニン化学構造の研究 - $\beta$ -5、 $\beta$ -1型構造に由来する二塩基性酸の検索

羽生直人、松本雄二、石津 敦、中野準三

東京大学農学部

Structural study of lignin by ozonolysis. - Investigation of dicarboxylic acids derived from  $\beta$ -5 and  $\beta$ -1 structures.

Naoto Habu, Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: dihydrodehydrodiconiferyl alcohol, GLC, GC-MS, <sup>13</sup>C-NMR

1986-207

リグニンのメカノケミストリー - モデル化合物のメカノケミカル反応について

李 典艶、橘 燦郎、住本昌之

九州大学農学部

Mechanochemistry of lignin. -Mechanochemical reaction of lignin model compounds.

Dian Yan Lee, Sanro Tachibana, Masashi Sumimoto

Faculty of Agriculture, Kyushu University

Keywords: coniferyl alcohol methyl ether, veratrylglycerol- $\beta$ -aryl ether, GLC, MS

1986-208

A study on mechanism of pyrolyzed lignin.  
Wenda Lu, Jian Li, Sheng Luo Gwei, Yu Koh ming  
Northeast Forestry University, China  
Keywords: *Larix dahurica*, dioxane lignin, DSC, IR

1986-209  
針葉樹材酵素糖化のためのオゾン酸化前処理  
林 徳子、細谷修二、志水一允  
林業試験場  
Ozonation pretreatment for the enzymatic hydrolysis of softwood.  
Noriko Hayashi, Shuji Hosoya, Kazumasa Shimizu  
Forestry and Forest Products Research Institute  
Keywords: *Cryptomeria japonica*, polarization microscope, cell wall morphology

1986-210  
酸糖化リグニンのラジカルスルホン化  
渡辺正介、飯塚堯介、石津 敦、中野準三  
東京大学農学部  
Radical sulphonation of acid hydrolysis lignin.  
Shosuke Watanabe, Gyosuke Meshitsuka, Atsushi Ishizu, Junzo Nakano  
Faculty of Agriculture, The University of Tokyo  
Keywords: *Betula maximowicziana*, sodium sulfite, MWL, IR

1986-211  
リグニン系高分子電解質と水との相互作用  
畠山兵衛<sup>\*1</sup>、岩田ひろ<sup>\*2</sup>、中村邦雄<sup>\*3</sup>、畠山立子<sup>\*4</sup>  
<sup>\*1</sup> 製品科学研究所、<sup>\*2</sup> 日本紙パルプ研究所、<sup>\*3</sup> 神奈川県工業試験所、<sup>\*4</sup> 繊維高分子材料研究所  
Interaction between water and polyelectrolyte derived from lignin.  
Hyo Hatakeyama<sup>\*1</sup>, Hiro Iwata<sup>\*2</sup>, Kunio Nakamura<sup>\*3</sup>, Tatsuko Hatakeyama<sup>\*4</sup>  
<sup>\*1</sup>Industrial Products Research Institute, <sup>\*2</sup>Japan Pulp & Paper Research Institute, Inc., <sup>\*3</sup>Kanagawa  
Industrial Technology Center, <sup>\*4</sup>Institute for Textiles and Polymers  
Keywords: sodium lignosulfonate, DSC, NMR, relaxation time

1986-212  
リグニン分解物を原料とする耐熱性高分子  
広瀬重雄<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、中村邦雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>  
<sup>\*1</sup> 製品科学研究所、<sup>\*2</sup> 神奈川県工業試験所、<sup>\*3</sup> 繊維高分子材料研究所  
Heat resistant polymer prepared from lignin degradation products.  
Shigeo Hirose<sup>\*1</sup>, Hyo Hatakeyama<sup>\*1</sup>, Kunio Nakamura<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>  
<sup>\*1</sup>Industrial Products Research Institute, <sup>\*2</sup>Kanagawa Industrial Technology Center, <sup>\*3</sup>Institute for  
Textiles and Polymers  
Keywords: polyester, DSC, X ray analysis, Tg

1986-213  
リグニンの水素化分解 –高温における反応時間の影響  
小山 実、金沢健治、山田谷正子、杉本義一  
化学技術研究所

Hydrogenolysis of lignin. –Effect of reaction time at high temperature.

Makoto Koyama, Kenji Kanazawa, Masako Yamadaya, Giichi Sugimoto

National Chemical Laboratory for Industry

Keywords: cresol lignin, thiolignin, monophenols

1986-214

リグニン水素化分解生成物の質量分析 –分子イオンスペクトル法および MS-MS によるキャラクタリゼーション

杉本義一、石川啓一郎、丹羽吉夫、山田谷正子、金沢健治、小山 実

化学技術研究所

Mass spectrometric analysis of hydrogenolysis products of lignin. –Molecular ion spectral analysis and characterization by MS-MS analysis.

Giichi Sugimoto, Keiichiro Ishikawa, Yoshio Niwa, Masako Yamadaya, Kenji Kanazawa, Makoto Koyama

National Chemical Laboratory for Industry

Keywords: thiolignin, alkylphenols

1986-215

フェノール類可溶化木材からの木材用接着剤

小野拓邦、須藤賢一、唐沢仁志

林業試験場

Wood adhesives from wood liquefied by phenol.

Hirokuni Ono, Kenichi Sudo, Hitoshi Karasawa

Forestry and Forest Products Research Institute

Keywords: resol formaldehyde resin, GPC, torsional blade analysis

1986-216

リグニン系炭素繊維 –紡糸用リグニンの性状について

須藤賢一、志水一允

林業試験場

Lignin derived carbon fiber. –Properties of lignin suitable for spinning.

Kenichi Sudo, Kazumasa Shimizu

Forestry and Forest Products Research Institute

Keywords: *Betula platyphylla*, hydrocracking, GPC, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, heat treatment, SEM

1986-217

爆砕リグニンの抗変異原性(第2報) –爆砕リグニン成分及び関連化合物について–

矢澤 到<sup>\*1</sup>、野澤美津子<sup>\*1</sup>、柿島 博<sup>\*1</sup>、西島 靖<sup>\*1</sup>、棚橋光彦<sup>\*2</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup> 鐘紡化粧品研究所、<sup>\*2</sup> 京都大学木材研究所

Antimutagenicity of steam explosion lignin. II. –Steam explosion lignin and related compounds.

Toru Yazawa<sup>\*1</sup>, Mitsuko Nozawa<sup>\*1</sup>, Hiroshi Kakishima<sup>\*1</sup>, Yasushi Nishijima<sup>\*1</sup>, Mitsuhiko Tanahashi<sup>\*2</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Research Laboratory, Kanebo Cosmetic Inc., <sup>\*2</sup>Wood Research Institute, Kyoto University

Keywords: *Chamaecyparis obtuse*, *Betula platyphylla*, *Salmonella typhimurium*, coniferyl alcohol, peroxidase

1986-218

特別講演、リグニンの形成と構造の不均一性

寺島典二

名古屋大学農学部

Invited lecture: Heterogeneity in formation and structure of lignin.

Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: protolignin, condensed unit, *p*-hydroxyphenyl lignin, guaiacyl lignin, syringyl lignin, softwood, hardwood, microautoradiography, cell wall layers

## 第 32 回 (1987.10.20-21) 福岡リーセントホテル

1987-101

紫外線顕微分光法による広葉樹木部構成要素の木化過程の検討

高部圭司<sup>\*1</sup>、深沢和三<sup>\*1</sup>、寺島典二<sup>\*2</sup>、福島和彦<sup>\*2</sup>

<sup>\*1</sup> 北海道大学農学部、<sup>\*2</sup> 名古屋大学農学部

Studies on the lignification process of hardwood xylem elements by UV microscope.

Keiji Takabe<sup>\*1</sup>, Kazumi Fukazawa<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Faculty of Agriculture, Nagoya University

Keywords: Oxford poplar, *Populus Maximowiczii* × *Populus berolinensis*, *Magnolia kobus*, cell wall layers

1987-102

木部細胞分化過程における各種成分量の変化 一切片のデンストメトリー解析を中心として

藤田 稔、杉山由美子、佐伯 浩

京都大学農学部

Changes of the amount of chemical components during differentiation of xylem cell. – Observation of sections by densitometry.

Minoru Fujita, Yumiko Sugiyama, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Keywords: *Cryptomeria japonica*, *Chamaecyparis obtuse*, *Pinus Thunbergii*, *Robinia pseudoacacia*, proteins, peroxidase, lignin

1987-103

西洋ワサビペルオキシターゼを用いた免疫電顕観察法のモデル実験

杉山由美子、藤田 稔、佐伯 浩

京都大学農学部

Model experiment for immunoelectron microscopy by use of horseradish peroxidase.

Yumiko Sugiyama, Minoru Fujita, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Keywords: *Armoracia rusticana*, diaminobenzidine, immunostaining, immunohistochemistry

1987-104

マイクロオートラジオグラフ法による広葉樹リグニン形成過程の可視化

福島和彦、寺島典二

名古屋大学農学部

Visualization of formation process of hardwood lignin by microautoradiography.

Kazuhiko Fukushima, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: magnolia, *Magnolia kobus*, lilac, *Syringa vulgaris*, *p*-hydroxyphenyl lignin, guaiacyl lignin, syringyl lignin,

1987-105

強冷摩砕法による MWL, LCC の調製について

福田忠徳、寺島典二

名古屋大学農学部

Preparation of MWL and LCC by milling under super cooling conditions.

Tadanori Fukuda, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: black pine, *Pinus Thunbergii*, liquid nitrogen, UV spectroscopy, IR spectroscopy

1987-106

エポキシ樹脂包埋 MWL の紫外線顕微分光測光

藤井智之

林業試験場

UV microspectroscopic analysis of MWL embedded in epoxy resin.

Tomoyuki Fujii

Forestry and Forest Products Research Institute

Keywords: beech, *Fagus crenata*, cell wall model,

1987-107

硫酸法によるリグニン定量における酸可溶性リグニン量の評価

前川英一、一澤泰三、越島哲夫

京都大学木材研究所

Evaluation of acid soluble lignin in sulfuric acid lignin determination.

Eiichi Maekawa, Taizo Ichizawa, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Fagus crenata*, *Acer pictum*, *Pinus densiflora*, *Phyllostachys pubescens*, Klason lignin

1987-108

リグニンモデル化合物芳香族炭素の化学シフトに及ぼす置換基の影響

青山政和<sup>\*1</sup>、H. Y. Hassi<sup>\*2</sup>、D. Tai<sup>\*3</sup>、C. L. Chen<sup>\*4</sup>、J. S. Gratzl<sup>\*4</sup>

<sup>\*1</sup>北海道立林産試験場、<sup>\*2</sup>Metsaliiton Teollisuus OY、<sup>\*3</sup>南京林業大学、<sup>\*4</sup>ノースカロライナ州立大学

Effect of substituent groups on the <sup>13</sup>C chemical shift of the aromatic carbons of lignin model compounds.

Masakazu Aoyama<sup>\*1</sup>, H.Y. Hassi<sup>\*2</sup>, D. Tai<sup>\*3</sup>, C.L. Chen<sup>\*4</sup>, J.S. Gratzl<sup>\*4</sup>

<sup>\*1</sup>Hokkaido Forest Products Research Institute, <sup>\*2</sup>Metsaliiton Teollisuus OY, <sup>\*3</sup>Nanjing Forestry University, <sup>\*4</sup>North Carolina State University

Keywords: <sup>13</sup>C-NMR, substituent chemical shift

1987-109

微生物によるリグニン分解(第1報)–高活性、高選択性リグニン分解菌の探索

西田友昭、檜野由憲、三村精男、高原義昌

神戸製鋼所生物学研究所

Lignin biodegradation by wood rot fungi. I. –Screening of highly active and highly selective lignin degrading fungi.

Tomoaki Nishida, Yoshinori Kashino, Akio Mimura, Yoshimasa Takahara

Biotechnology Research Laboratory, Kobe Steel. Ltd.

Keywords: *Fagus crenata*, guaiacol, gallic acid, phenoloxidase activity, ligninolytic activity

1987-110

嫌気性バクテリアによるリグニンモデル化合物の分解

川上日出国、陳 巍、大宮邦雄、清水祥一

名古屋大学農学部

Degradation of lignin model compounds by anaerobic bacteria.

Hidekuni Kawakami, Wei Chen, Kunio Oomiya, Shoichi Shimizu

Faculty of Agriculture, Nagoya University

Keywords: *Fusobacterium varium*, *Enterococcus faecium*, biphenyl,  $\beta$ -ether, phenylcoumaran

1987-111

シュードモナス属細菌 TMY1009 株から得られるリグニンモデル化合物脱水素酵素

羽生直人、鮫島正浩、佐分義正、善本知孝

東京大学農学部

Lignin model compound-dehydrogenation enzyme obtained from *Pseudomonas* TMY1009.

Naoto Habu, Masahiro Samejima, Yoshimasa Saburi, Tomotaka Yoshimoto

Faculty of Agriculture, the University of Tokyo

Keywords: phenylcoumaran, NAD, NADH,

1987-112

ヒイロタケによるリグニン関連芳香族化合物の分解

早川敏雄<sup>\*1</sup>、原口隆英<sup>\*1</sup>、樫野由憲<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 神戸製鋼所

Degradation of aromatic compounds related to lignin by *Pycnoporus coccineus*.

Toshio Hayakawa<sup>\*1</sup>, Takafusa Haraguchi<sup>\*2</sup>, Yoshinori Kashino<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Kobe Steel. Ltd.

Keywords: biodegradation, protocatechuic acid, catechol, oxygenase, GC-MS

1987-113

リグニン分解に対する酵素特性

沖 妙、石川久雄

愛媛大学農学部

Characteristics of lignin degrading enzyme.

Tae Oki, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: *Phanerochaete chrysosporium*, dioxane lignin, laccase, peroxidase

1987-114

*Phanerochaete chrysosporium*におけるリグニン分解酵素系 –Manganese peroxidase の作用機構–

割石博之、Micheal H. Gold

Oregon Graduate Center

Ligninolytic enzyme system in *Phanerochaete chrysosporium*. – Reaction mechanism of manganese peroxidase.

Hiroyuki Wariishi, Michael H. Gold

Oregon Graduate Center

Keywords: EPR spectroscopy, <sup>14</sup>NO–MnP, <sup>15</sup>NO–MnP,

1987-115

Lignin peroxidase によるリグニンモデル化合物の芳香環開裂

三木啓司<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>、Michael H. Gold<sup>\*3</sup>

<sup>\*1</sup> 公害資源研究所, <sup>\*2</sup> 九州大学農学部、<sup>\*3</sup> Oregon Graduate Center

Cleavage of aromatic rings of lignin model compounds by lignin peroxidase.

Keiji Miki<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>, Michael H. Gold<sup>\*3</sup>

<sup>\*1</sup> National Research Institute for Pollution and Resources, <sup>\*2</sup> Faculty of Agriculture, Kyushu University, <sup>\*3</sup> Oregon Graduate Center

Keywords: <sup>18</sup>O tracer, arylglycerol- $\beta$ -biphenyl ether,

1987-116

フェノール類を媒介とする非フェノール性リグニンモデル化合物のカワラタケラッカーゼによる分解

河合真吾、梅澤俊明、樋口隆昌

京都大学木材研究所

Degradation of non-phenolic lignin model compounds in the presence of phenols by laccase of *Coriolus versicolor*.

Shingo Kawai, Toshiaki Umezawa, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: biodegradation, lignin substructure model compound,

1,2-bis-(3,4,5-trimethoxyphenyl)- propane-1,3-diol, mediator, syringaldehyde, GC-MS

1987-117

$\beta$ -O-4- $\beta$ -O-4 型リグニンモデル三量体のリグニンペルオキシターゼによる分解

梅澤俊明、樋口隆昌

京都大学木材研究所

Degradation of  $\beta$ -O-4- $\beta$ -O-4 type lignin model trimer by lignin peroxidase.

Toshiaki Umezawa, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phanerochaete chrysosporium*, GC-MS,

1987-118

バイオミメティックポルフィリン触媒によるリグニン芳香環モデル化合物の環開裂反応

服部武文、島田幹夫、梅澤俊明、樋口隆昌

京都大学木材研究所

Ring cleavage reaction of lignin model compound by biomimetic porphyrin catalyzt.

Takefumi Hattori, Mikio Shimada, Toshiaki Umezawa, Takayoshi Higuchi

Wood research Institute, Kyoto University

Keywords: 3,4-dimethoxybenzylalcohol, lignin peroxidase, <sup>18</sup>O tracer,

1987-119

特別講演、最近のタンニンの研究から

西岡五夫

九州大学薬学部

Invited lecture ; Recent advances in research on tannin.

Itsuo Nishioka

Faculty of Pharmaceutical Science, Kyushu University

Keywords: *Quercus salicina*, *Camellia sinensis*, biological activity

1987-201

シュドモナス属細菌 TMY1009 株におけるリグニンモデル化合物分解酵素産生遺伝子のセルフクローニング系について

鮫島正浩、善本知孝

東京大学農学部

Self cloning system of the genes for the production of lignin model compounds degrading enzyme in *Pseudomonas* TMY1009.

Masahiro Samejima, Tomotaka Yoshimoto

Faculty of Agriculture, the University of Tokyo

Keywords: plasmid, gene library

1987-202

カワラタケ酵素遺伝子のクローニング(II)―Laccase III 糖鎖機能解析と cDNA の合成―

中村雅哉<sup>\*1</sup>、吉武彰文<sup>\*1</sup>、片山義博<sup>\*1\*2</sup>、諸星紀幸<sup>\*1</sup>、原口隆英<sup>\*1</sup>、

<sup>\*1</sup>東京農工大学農学部、<sup>\*2</sup>神戸製鋼生物学的研究所

Cloning of the genes for the enzyme of *Coriolus versicolor*. II – Functional analysis of sugar chains of laccase III and the synthesis of cDNA.

Masaya Nakamura<sup>\*1</sup>, Akifumi Yoshitake<sup>\*1</sup>, \* Yoshihiro Katayama<sup>\*2</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Takafusa Haraguchi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Biotechnology Research Laboratory, Kobe Steel, Ltd.

Keywords: sugar chain function

1987-203

リグニンモデル化合物分解酵素遺伝子のクローニング V

西川誠司<sup>\*1</sup>、片山義博<sup>\*1\*2</sup>、政井英二<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、原口隆英<sup>\*1</sup>、山崎真狩<sup>\*3</sup>

<sup>\*1</sup>東京農工大学農学部、<sup>\*2</sup>神戸製鋼生物学的研究所、<sup>\*3</sup>東京大学農学部

Cloning of the genes for the lignin model compounds degrading enzyme. V.

Seiji Nishikawa<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Eiji Masai<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Takafusa Haraguchi<sup>\*1</sup>, Makari Yamasaki<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Biotechnology Research Laboratory, Kobe Steel Co. Ltd, <sup>\*3</sup>Faculty of Agriculture, the University of Tokyo

Keywords: *Pseudomonas paucimobilis*, *Pseudomonas putida*, gene library,

1987-204

白色腐朽菌による E 段漂白排液の脱色機構

桃原郁夫<sup>\*1</sup>、渋谷往男<sup>\*1</sup>、松本雄二<sup>\*1</sup>、石津 敦<sup>\*1</sup>、H.-m Chang<sup>\*2</sup>

<sup>\*1</sup>東京大学農学部、<sup>\*2</sup>ノースカロライナ州立大学

Decoloration mechanism of E stage bleach effluent by white rot fungi.

Ikuo Momohara<sup>\*1</sup>, Sumio Shibuya<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>, Atsushi Ishizu<sup>\*1</sup>, H.-m Chang<sup>\*2</sup>

\*<sup>1</sup>Faculty of Agriculture, the University of Tokyo, \*<sup>2</sup>North Carolina State University

Keywords: *Phanerochaete chrysosporium*, loblolly pine, *Pinus taeda*, quinone structure

1987-205

白色腐朽菌によるパルプ漂白排水の突然変異原性の変化

渋谷往男、桃原郁夫、松本雄二、石津 敦

東京大学農学部

Changes of mutagenicity of pulp bleach effluent by treatment with white rot fungi.

Sumio Shibuya, Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Phanerochaete chrysosporium*, Ames test, softwood KP

1987-206

トリメチルヨードシランによるリグニン中のエーテル結合の選択的開裂

牧野重人、飯塚堯介、石津 敦

東京大学農学部

Selective cleavage of ether linkage in lignin by trimethylsilyl iodide.

Shigeto Makino, Gyosuke Meshitsuka, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Betula maximowicziana*, *Larix Kaempferi*, *Picea jezoensis*, MWL, molecular weight distribution,

1987-207

リグニンモデル 2 量体の水素化分解

小山 実、金沢健治、杉本義一、山田谷正子

化学技術研究所

Hydrogenolysis of dimeric model compounds of lignin.

Makoto Koyama, Kenji Kanazawa, Gi-ichi Sugimoto, Masako Yamadaya

National Chemical Laboratory for Industry

Keywords: diphenyl ether, diphenyl methane, dibenzyl, metal catalyst

1987-208

ソルボリシスによる針葉樹材の脱リグニン

佐野嘉柘、笹谷宜志

北海道大学農学部

Delignification of softwood by solvolysis.

Yoshihiro Sano, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Keywords: *Abies Mayriana*, cresol water, delignification mechanism, guaiacylglycerol- $\beta$ -guaiacyl ether, veratrylglycerol- $\beta$ -guaiacyl ether, <sup>1</sup>H-NMR

1987-209

有機酸蒸解におけるリグニンの挙動 -フェニルクマランおよびジアリールプロパン構造の反応性

安田征市

名古屋大学農学部

Behavior of lignin during cooking in organic acids. -Reactivity of phenylcoumaran and diarylpropane structures.

Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Keywords: acetic acid cooking, phenylcoumaran, diarylpropane

1987-210

蒸煮・爆砕前処理によるアカシア類の利用

勝部和則<sup>\*1</sup>、嘉手苺幸男<sup>\*2</sup>、志水一允<sup>\*3</sup>、藤井智之<sup>\*3</sup>、須藤賢一<sup>\*3</sup>、長沢定男<sup>\*3</sup>

<sup>\*1</sup>岩手バイオマス研究センター、<sup>\*2</sup>沖縄県林業試験所、<sup>\*3</sup>林業試験場

Utilization of *Acacia* by steam explosion pretreatment.

Kazunori Katsube<sup>\*1</sup>, Yukio Kategaru<sup>\*2</sup>, Kazumasa Shimizu<sup>\*3</sup>, Tomoyuki Fujii<sup>\*3</sup>, Kenichi Sudo<sup>\*3</sup>, Sadao Nagasawa<sup>\*3</sup>

<sup>\*1</sup>Iwate Biomass Research Center, <sup>\*2</sup>Okinawa Prefectural Forest Experiment Station, <sup>\*3</sup>Forestry and Forest Products Research Institute

Keywords: enzymatic hydrolysis, sugar composition, lignin structure

1987-211

爆砕処理によるリグニンの分解機構の解明(II)

Myrtha Karina、棚橋光彦、樋口隆昌

京都大学木材研究所

Degradation mechanism of lignin during steam explosion treatment.

Myrtha Karina, Mitsuhiko Tanahashi, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: guaiacylglycerol- $\beta$ -guaiacyl ether, veratrylglycerol- $\beta$ -guaiacyl ether, <sup>1</sup>H-NMR, GC-MS

1987-212

未利用林産資源の酵素、微生物による変換利用(1)-前処理としてのアスプルンドパルプの製造と解析-

鮫島一彦<sup>\*1</sup>、藤原新二<sup>\*1</sup>、高村憲男<sup>\*1</sup>、黒田健一<sup>\*2</sup>

高知大学農学部、筑波大学農林工学系

Utilization of unused forest resources by conversion with enzyme and microorganism. I. -Preparation and analysis of Asplund pulp as a pretreatment.

Kazuhiko Sameshima<sup>\*1</sup>, Shinji Fujiwara<sup>\*1</sup>, Norio Takamura<sup>\*1</sup>, Ken-ichi Kuroda<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kochi University, <sup>\*2</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba

Keywords: *Betula platyphylla*, *Fagus crenata*, *Zelkova serrata*, *Cryptomeria japonica*, *Chamaecyparis obtuse*, *Pinus densiflora*, enzymatic susceptibility

1987-213

アルカリ性サルファイト・キノン蒸解におけるリグニンの挙動

大井 洋<sup>\*1</sup>、石津 敦<sup>\*1</sup>、中野準三<sup>\*2</sup>

<sup>\*1</sup>東京大学農学部、<sup>\*2</sup>福井工業大学工学部

Behavior of lignin during alkaline sulfite-quinone pulping.

Hiroshi Ohi<sup>\*1</sup>, Atsushi Ishizu<sup>\*1</sup>, Junzo Nakano<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>Faculty of Engineering, Fukui University of Technology

Keywords: *Picea jezoensis*, *Fagus crenata*, *Abies sachalinensis*, gel filtration chromatography

1987-214

N 材クラフト蒸解において最終脱リグニンを阻害する多糖について

松本雄二<sup>\*1</sup>、石津 敦<sup>\*1</sup>、H.-m. Chang<sup>\*2</sup>

<sup>\*1</sup> 東京大学農学部, <sup>\*2</sup> ノースカロライナ州立大学

Studies on the polysaccharides preventing final delignification in kraft pulping of softwood.

Yuji Matsumoto<sup>\*1</sup>, Atsushi Ishizu<sup>\*1</sup>, H.-m. Chang<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup> North Carolina State University

Keywords: *Pinus taeda*, LCC, hemicellulose-consisting sugars

1987-215

A preliminary study on paper aging caused by light.

Jian Li, Gwei Sheng Luo, Wenda Lu, Yu Koh Ming

Northeast Forestry University, China

Keywords: ESCA, FTIR, SEM

1987-216

リグノスルホン酸塩-水系のメゾフェーズ

畠山兵衛<sup>\*1</sup>、広瀬重雄<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup> 製品科学研究所、<sup>\*2</sup> 繊維高分子研究所

Meso phase of lignosulfonate-water system.

Hyo Hatakeyama<sup>\*1</sup>, Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup> Industrial Products Research Institute, <sup>\*2</sup> Institute for Textiles and Polymers

Keywords: DSC, <sup>1</sup>H-NMR, polarization microscope

1987-217

リグニンから誘導される含リン型ポリウレタン

広瀬重雄<sup>\*1</sup>、矢野彰一郎<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup> 製品科学研究所、<sup>\*2</sup> 繊維高分子材料研究所

Polyurethane including phosphor derived from lignin.

Shigeo Hirose<sup>\*1</sup>, Shoichiro Yano<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup> Industrial Products Research Institute, <sup>\*2</sup> Institute for Textiles and Polymers

Keywords: *Fagus crenata*, solvolysis lignin, TG, heat resistance

1987-218

フェノール化リグニンの木材接着剤への応用

小野拓邦<sup>\*1</sup>、須藤賢一<sup>\*1</sup>、唐沢仁志<sup>\*1</sup>、姚 忻<sup>\*2</sup>

<sup>\*1</sup> 林業試験場、<sup>\*2</sup> 黒竜江省林産工業研究所

Utilization of phenolated lignin to wood adhesives.

Hirokuni Ono<sup>\*1</sup>, Kenichi Sudo<sup>\*1</sup>, Hitoshi Karasawa<sup>\*1</sup>, Yao Xin<sup>\*2</sup>

<sup>\*1</sup> Forestry and Forest Products Research Institute, <sup>\*2</sup> Forest Products Research Institute of Heilongjiang Province

Keywords: *Betula platyphylla*, GPC, IR spectroscopy,

1987-219

特別講演、酸素及び過酸化漂白におけるリグニンの挙動

石川久碓

愛媛大学農学部

Invited lecture ; Reactions of lignin during oxygen and peroxide bleaching.

Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords: active oxygen species

### 第 33 回 (1988.11.8-9) ホテルサンルート筑波

1988-101

ポプラの分子育種に関する研究(1) リグニン形成能に関与するアイソペルオキシターゼの性質  
諸星紀幸、西田謙吾、山田恵子、三国順子、片山義博、原口隆英

東京農工大学農学部

Molecular breeding of poplar. I. Characterization of isoperoxidase involved to lignification.

Noriyuki Morohoshi, Kengo Nishida, Keiko Yamada, Junko Mikuni, Yoshihiro Katayama, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Populus euroamericana*, isoelectric focusing, gel filtration chromatography

1988-102

ポプラの分子育種に関する研究(2) ポプラカルの分化誘導と Ti プラスミド導入系の確立  
片山義博、柳田恒一郎、諸星紀幸、原口隆英

Molecular breeding of poplar. II. Induction of poplar callus differentiation and establishment of Ti plasmid introduction system.

Yoshihiro Katayama, Koichiro Yanagida, Noriyuki Morohoshi, Takafusa Haraguchi

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: *Agrobacterium tumefaciens*

1988-103

イネにおけるリグニンの形成と構造

何 蘭芳、寺島典二

名古屋大学農学部

Formation and structure of lignin in rice plants.

Lanfang He, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: *Oryza sativa*, microautoradiography, *p*-hydroxyphenyl lignin, guaiacyl lignin, syringyl lignin, AQ-soda pulping

1988-104

*p*-ヒドロキシフェニルリグニンの性質について

福島和彦、寺島典二

名古屋大学農学部

Properties of *p*-hydroxyphenyl lignin.

Kazuhiko Fukushima, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: *Pinus Thunbergii*, microautoradiography, compression wood, HPLC

1988-105

LCC 生合成時における糖加水分解酵素の関与について

迫 孝、飯森武志、近藤隆一郎、今村博之

九州大学農学部

Participation of carbohydrate hydrolyzing enzyme during biosynthesis of LCC.

Takashi Sako, Takeshi Iimori, Ryuichiro Kondo, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: cellobiose,  $\beta$ -glucosidase, transglycosylation, coniferyl alcohol, isoconiferin

1988-106

過ヨウ素酸リグニンの調製と性状

種田英孝、石津 敦

東京大学農学部

Preparation and characterization of periodate lignin.

Hidetaka Taneda, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, Smith degradation, sugar contents,

1988-107

凍結粉碎を利用した木材酵素糖化とリグニンの抽出について

渡辺隆司、吉村直子、越島哲夫

京都大学木材研究所

Enzymatic saccharification of wood and extraction of lignin using cryomilling.

Takashi Watanabe, Naoko Yoshimura, Tetsuo Koshijima

Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, *Fagus crenata*, ball milling, SEM,

1988-108

オゾン分解によるリグニン化学構造の研究 -ピノレジノール型構造の存在の検討-

松本雄二、南 一守、石津 敦

東京大学農学部

Structural study on lignin by ozonolysis. -Investigation of the presence of pinoresinol structures.

Yuji Matsumoto, Kazumori Minami, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Fagus crenata*, *Picea jezoensis*, *Eucalyptus*, MWL,  $^{13}\text{C}$ -NMR

1988-109

トリメチルヨードシランによるリグニン中のエーテル結合の選択的開裂

牧野重人、飯塚堯介、石津 敦

東京大学農学部

Selective cleavage of ether linkages in lignin by trimethylsilyl iodide.

Shigeto Makino, Gyosuke Meshitsuka, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, MWL, molecular weight distribution

1988-110

Acetylbromide へのリグノセルロースの溶解 -反応機構とリグニンの UV スペクトル

飯山賢治<sup>\*1</sup>、Adrian F. A. Wallis<sup>\*2</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*2</sup>CSIRO, Australia

Dissolution of lignocellulose in acetylbromide. –Reaction mechanism and UV spectra of lignin.

Kenji Iiyama<sup>\*1</sup>, Adrian F.A. Wallis<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>CSIRO, Australia

Keywords: *Pinus radiata*, UV spectroscopy, lignin model compound, GPC

1988-111

酸および加熱処理過程におけるリグニンの縮合について

船岡正光、柴田真美、加古辰成、阿部 勲

三重大学生物資源学部

Condensation of lignin during acid and heat treatment.

Masamitsu Funaoka, Mami Shibata, Tatsunari Kako, Isao Abe

Faculty of Bioresources, Mie University

Keywords: *Picea jezoensis*, *Pseudotsuga taxifolia*, nucleus exchange reaction, nitrobenzene oxidation

1988-112

クラフト蒸解過程における複合中間層および二次壁領域でのリグニンのフラグメンテーションと縮合

船岡正光<sup>\*1</sup>、Vincent L. Chiang<sup>\*2</sup>

<sup>\*1</sup> 三重大学生物資源学部、<sup>\*2</sup>Michigan Technological University

Fragmentation and condensation of lignin in middle lamella and secondary wall during kraft cooking

Masamitsu Funaoka<sup>\*1</sup>, Vincent L. Chiang<sup>\*2</sup>

<sup>\*1</sup>Faculty of Bioresources, Mie University, <sup>\*2</sup>Michigan Technological University

Keywords: *Pseudotsuga taxifolia*, nuclear exchange reaction, nitrobenzene oxidation, middle lamella, secondary wall

1988-113

爆砕処理によるリグニンの分解機構解明(IV)–シナピルアルコール DHP の合成と高圧水蒸気処理

棚橋光彦、Myrtha Karina、樋口隆昌

京都大学木材研究所

Degradation mechanism of lignin during steam explosion. IV. –Synthesis of sinapyl alcohol DHP and its treatment with high pressure steam.

Mitsuhiko Tanahashi, Myrtha Karina, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, GC-MS, acidolysis, syringaresinol, radical reaction

1988-114

リグニンのメカノケミストリー(IV) –フェニルクマランモデル化合物のメカノケミカル反応と其の生成物の過酸化水素反応–

李典 艶、住本昌之

九州大学農学部

Mechanochemistry of lignin. IV. –Mechanochemical reaction of phenylcoumaran type model compounds, and reaction of the products with hydrogen peroxide.

Dian Yan Lee, Masashi Sumimoto

Faculty of Agriculture, Kyushu University

Keywords: stilbene, <sup>1</sup>H-NMR, UV spectroscopy, IR spectroscopy, mass spectrometry

1988-115

酸糖化リグニンのラジカルスルホン化

渡辺正介、飯塚堯介、石津 敦

東京大学農学部

Radical sulphonation of acid hydrolysis lignin.

Masasuke Watanabe, Gyosuke Meshitsuka, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Betula maximowicziana*, sodium sulphite, UV spectroscopy, GPC

1988-116

分別クラフトリグニンのガラス転移

吉田博久<sup>\*1</sup>、R. Mörck、K. Kringstad<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup> 東京都立大学工学部、<sup>\*2</sup>STFI、<sup>\*3</sup> 製品科学研究所

Glass transition of fractionated kraft lignin.

Hirohisa Yoshida<sup>\*1</sup>, R. Mörck<sup>\*2</sup>, K. Kringstad<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Faculty of Engineering, Tokyo Metropolitan University, <sup>\*2</sup>STFI, Sweden, <sup>\*3</sup>Industrial Products Research Institute

Keywords: solubility parameter, polydispersity, molecular weight distribution

1988-117

ソルボリシスリグニンを原料とするポリウレタンの力学特性

中村邦雄<sup>\*1</sup>、R. Mörck<sup>\*2</sup>、A. Reimann<sup>\*2</sup>、K. Kringstad<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup> 大妻女子大学、<sup>\*2</sup>STFI、<sup>\*3</sup> 製品科学研究所

Mechanical properties of polyurethane prepared from solvolysis lignin.

Kunio Nakamura<sup>\*1</sup>, R. Mörck<sup>\*2</sup>, A. Reimann<sup>\*2</sup>, K. Kringstad<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Otsuma Women's University, <sup>\*2</sup>STFI, Sweden, <sup>\*3</sup>Industrial Products Research Institute

Keywords: *Fagus crenata*, PEG

1988-118

特別講演、糖質の生産とその高度利用について

小林昭一

農林水産省食品総合研究所

Invited lecture ; Production of carbohydrates and their advanced utilization.

Shoichi Kobayashi

National Food Research Institute, Ministry of Agriculture, Fishery and Forestry

Keywords: sucrose, chitin, fructan, starch, isomerase, maltoligosaccharide, cyclodextrin

1988-201

カルボニル化合物を助剤とする亜硫酸ソーダ・キノン蒸解

中野準三、宮崎重和、隈原文康

福井工業大学工学部

Sodium sulfite-quinone cooking with carbonyl compounds as additives.

Junzo Nakano, Shigekazu Miyazaki, Fumiyasu Kumahara

Fukui University of Technology

Keywords: *Pinus densiflora*, *Betula maximowicziana*, 1,4-dihydro-9,10-dihydroxyanthracene, formaldehyde

1988-202

アルカリ性サルファイト・キノン蒸解の脱リグニン機構

大井 洋、石津 敦

東京大学農学部

Delignification mechanism of alkaline sulfite-quinone cooking.

Hiroshi Ohi, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, *Abies sachalinensis*, *Fagus crenata*, MWL, DDA, 1,4-dihydro-9,10-dihydroxyanthracene, cellulose,  $\beta$ -ether cleavage,

1988-203

ソルボリシスパルプ化に関する研究(第4報) 蒸解溶媒と蒸解反応

岩田ひろ、可知省吾、荒木 廣、青柳哲夫

日本紙パルプ研究所

Studies on solvolysis pulping. IV. Composition of cooking solvent and cooking reaction.

Hiro Iwata, Shogo Kachi, Hiroshi Araki, Tetsuo Aoyagi

Japan Pulp & Paper Research Institute, Inc.

Keywords: *Fagus crenata*, *Pinus Thunbergii*, cresol, bound solvent

1988-204

硫酸触媒による広葉樹材の常圧パルプ化(第2報)

島本 周、中村雅幸、佐野嘉柘

北海道大学農学部

Pulping of hardwood at atmospheric pressure with sulfuric acid as catalyst. II.

Shu Shimamoto, Masayuki Nakamura, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Keywords: *Betula maximowicziana*, acetic acid, phenol, <sup>1</sup>H-NMR, GPC

1988-205

未利用植物資源のPA法(過酸化水素-アルカリ法)によるパルプ化 -パルプ工業におけるショートサーキットはどこまで可能か-

御田昭雄

化学技術研究所

Pulping of unutilized plant resources by PA method (hydrogen peroxide-alkali). -How far the short circuit of pulp industry could be achieved.

Akio Mita

National Chemical Laboratory for Industry

Keywords: used paper, recycling, non-wood pulp

1988-206

伝統的和紙製造法の化学的研究(2)-木灰の分析と木灰蒸煮処理-

鮫島一彦、藤原新二、堀江大介、高村憲男

高知大学農学部

Chemical characterization of traditional process of Japanese paper production. II. -Analysis of ash and pulping with ash.

Kazuhiko Sameshima, Shinji Fujiwara, Daisuke Horie, Norio Takamura

Faculty of Agriculture, Kochi University

Keywords: *Edgeworthia chrysantha*, *Broussonetia kazinoki* × *B. papyrifera*, Washi paper, ash

1988-特別講演  
森林経営の展望  
熊崎 実

森林総合研究所

Invited lecture ; A perspective on forest management.

Minoru Kumazaki

Forestry and Forest Products Research Institute

1988-207

アラゲカワラタケの1核菌糸体の生理特性とリグニンの分解

吉原一年、上嶋 洋、西山昌史、赤松 勲

四国工業技術試験所

Physiological characteristics of monokariotic mycelia of *Coriolus hirsutus* IFO4917 and the degradation of lignin.

Kazutoshi Yoshihara, Hiroshi Kamishima, Masashi Nishiyama, Isao Akamatsu

Government Industrial Research Institute ,Sikoku

Keywords: *Populus* sp., liquid culture,  $\beta$ -glucosidase, CMCcase, xylanase, laccase

1988-208

白色腐朽菌 *Phanerochaete chrysosporium* のリグニンパーオキシダーゼ生産能についての遺伝的改良

桑原正章、麻田恭彦、打越正延、凌 楓、木村義雄、山本澄人

香川大学農学部

Genetic improvement of lignin peroxidase productivity of white rot fungus *Phanerochaete chrysosporium*.

Masaaki Kuwahara, Yasuhiko Asada, Masanobu Uchikoshi, Ling Feng, Yoshio Kimura, Sumito Yamamoto

Faculty of Agriculture, Kagawa University

Keywords: DNA, mutant, DEAE-Sepharose chromatography,

1988-209

好アルカリ性コリネバクテリウム。ジリグノール分解株のプロトプラスト化及び再生

川上日出国、葛原憲康

名古屋大学農学部

Alkalophilic *Corynebacterium*. Protoplast formation and regeneration of the dilignol degrading strain.

Hidekuni Kawakami, Noriyasu Kuzuhara

Faculty of Agriculture, Nagoya University

Keywords: lignin degradation, lignin model compound, vanillin, protoplast,

1988-210

リグニンモデル化合物分解酵素遺伝子のクローニング(VIII) - *Pseudomonas paucimobilis* SYK-6 の  $\beta$ -エーテル結合開裂酵素-

政井英司\*<sup>1</sup>, 片山義博\*<sup>1\*2</sup>, 西川誠司\*<sup>1</sup>, 山崎真狩\*<sup>3</sup>, 諸星紀幸\*<sup>1</sup>, 原口隆英\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学農学部、\*<sup>2</sup> 神戸製鋼生物学研究所、\*<sup>3</sup> 東京大学農学部

Cloning of the genes for the lignin model compounds degrading enzyme. VIII. - $\beta$ -Ether cleaving enzyme of *Pseudomonas paucimobilis* SYK-6.

Eiji Masai\*<sup>1</sup>, Yoshihiro Katayama\*<sup>2</sup>, Seiji Nishikawa\*<sup>1</sup>, Makari Yamasaki\*<sup>3</sup>, Noriyuki Morohoshi\*<sup>1</sup>, Takafusa Haraguchi\*<sup>1</sup>

\*<sup>1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Biotechnology Research Laboratory, Kobe Steel, Ltd, \*<sup>3</sup>Faculty of Agriculture, the University of Tokyo

Keywords: umbelliferone ether, vanillin ether,

1988-211

電気パルスによるシュードモナス属細菌への遺伝子の導入

鮫島正浩、鴨田重裕、善本知孝

東京大学農学部

Introduction of the genes to *Pseudomonas* by electric pulse.

Masahiro Samejima, Shigehiro Kamota, Tomotaka Yoshimoto

Faculty of Agriculture, the University of Tokyo

Keywords: *Pseudomonas putida*, genetic transformation, plasmid

1988-212

シュードモナス属細菌 TMY1009 株による  $\beta$ -1 型モデル化合物の分解

羽生直人、小松徹史、鴨田重裕、鮫島正浩、善本知孝

東京大学農学部

Degradation of  $\beta$ -1 type lignin model compounds by *Pseudomonas* TMY1009.

Naoto Habu, Tetsushi Komatsu, Shigehiro Kamota, Masahiro Samejima, Tomotaka Yoshimoto

Faculty of Agriculture, the University of Tokyo

Keywords: *erythro*-1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol, HPLC

1988-213

*Fusarium solani* M-13-1 による  $\beta$ -アリアルエーテル結合の開裂と  $\alpha$ -ケトンの還元生成物の絶対配置

片山健至、大浦健二、筒井丈二、十河村男

香川大学農学部

Cleavage of a  $\beta$ -aryl ether linkage by *Fusarium solani* M-13-1 and the absolute configuration of  $\alpha$ -ketonic reduction products.

Takeshi Katayama, Kenji Ohura, Jyoji Tsutsui, Murao Sogo

Faculty of Agriculture, Kagawa University

Keywords: glycerol-2-aryl ether, guaiacylglycerol- $\beta$ -(vanillic acid) ether, UV spectroscopy, HPLC, <sup>1</sup>H-NMR

1988-214

カワラタケ菌体外酵素によるリグニン生分解機構の解析

飯村洋介\*<sup>1</sup>、片山義博\*<sup>1</sup>\*<sup>2</sup>、田村利香\*<sup>1</sup>、諸星紀幸\*<sup>1</sup>、原口隆英\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学農学部、\*<sup>2</sup> 神戸製鋼生物学研究所

Analysis of the biodegradation mechanism of lignin by extracellular enzyme of *Coriolus versicolor*.

Yosuke Iimura\*<sup>1</sup>, Yoshihiro Katayama\*<sup>1</sup>\*<sup>2</sup>, Rika Tamura\*<sup>1</sup>, Noriyuki Morohoshi, \*<sup>1</sup> Takafusa Haraguchi\*<sup>1</sup>

\*<sup>1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Biotechnology Research

Laboratory Kobe Steel, Ltd.

Keywords: laccase III, <sup>13</sup>C-DHP, <sup>14</sup>C-DHP, HPLC, <sup>13</sup>C-NMR

1988-215

木材腐朽菌によるリグニンモデル配糖体の生成について(V)

近藤隆一郎、今村博之

九州大学農学部

Formation of lignin model glycosides by wood-rotting fungi. V.

Ryuichiro Kondo, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: *Betula platyphylla*, *Tyromyces palustris*, *Coriolus versicolor*, *Phanerochaete chrysosporium*, veratryl alcohol, veratraldehyde

1988-216

DHP 及びその配糖体の酵素分解

飯森武志<sup>\*1</sup>、迫 孝<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>、今村博之<sup>\*1</sup>、西田友昭<sup>\*2</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>神戸製鋼生物学研究所

Enzymatic degradation of DHP and its glycoside

Takeshi Iimori<sup>\*1</sup>, Takashi Sako<sup>\*1</sup>, Ryuichiro Kondo<sup>\*1</sup>, Hiroyuki Imamura<sup>\*1</sup>, Tomoaki Nishida<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>Biotechnology Research Laboratory, Kobe Steel, Ltd.

Keywords: *Phanerochaete chrysosporium*, lignin peroxidase, laccase, horse radish peroxidase

1988-217

遊離のフェノール性水酸基を持つ DHP のリグニンペルオキシダーゼによる分解

梅澤俊明、樋口隆昌

京都大学木材研究所

Degradation of DHP with free phenolic hydroxyl group by lignin peroxidase.

Toshiaki Umezawa, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phanerochaete chrysosporium*, phenolic OH, GC-MS,  $\beta$ -O-4 bond cleavage

1988-218

微生物によるリグニン分解(第4報)-高活性、高選択性リグニン分解菌 IZU-154 株を前処理に用いた木材糖化プロセス-

西田友昭、中山雄之、三村精男、高原義昌

神戸製鋼所生物学研究所

Lignin biodegradation by wood rot fungi, IV. -Wood hydrolysis process using highly active and highly selective lignin degrading fungus IZU-154.

Tomoaki Nishida, Tsuyoshi Nakayama, Akio Mimura, Yoshimasa Takahara

Biotechnology Research Laboratory, Kobe Steel Ltd.

Keywords: *Fagus crenata*, *Coriolus versicolor*, wood saccharification, enzymatic hydrolysis, Klason lignin

1988-219

機械パルプの菌体外酵素による漂白

山下民治<sup>\*1</sup>、橘 燦郎<sup>\*2</sup>、大島喜八郎<sup>3</sup>、住本昌之<sup>\*2</sup>

<sup>\*1</sup>中越パルプ工業株式会社、<sup>\*2</sup>九州大学農学部、<sup>\*3</sup>十條製紙株式会社

Bleaching of mechanical pulp by extracellular enzyme.

Tamiharu Yamashita<sup>\*1</sup>, Sanro Tachibana<sup>\*2</sup>, Kihachiro Ohshima<sup>\*3</sup>, Masashi Sumimoto<sup>\*2</sup>

<sup>\*1</sup>Chuetsu Pulp & Paper Co. Ltd, <sup>\*2</sup>Faculty of Agriculture, Kyushu University, <sup>\*3</sup>Jujo Paper Co. Ltd.

Keywords: *Phanerochaete chrysosporium*, *Coriolus versicolor*, brightness, post color number

## 第 34 回 (1989.10.16-17)名古屋大学農学部

1989-101

圧縮試料の X 線回折法などによるマイクロフィブリル配向分布の計測とリグニンの堆積

畑 茂樹、藤田 稔、佐伯 浩

京都大学農学部

Measurement of distribution of microfibril orientation and lignin deposition in the compressed sample by X ray diffraction.

Shigeki Hata, Minoru Fujita, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Keywords: *Cryptomeria japonica*, *Chamaecyparis obtusa*, UV microspectroscopy

1989-102

液体窒素下で破碎された細胞壁断片におけるリグニン分布と多様性の検討

吉永 新、藤田 稔、佐伯 浩

京都大学農学部

Distribution and diversity of lignin in cell wall pieces obtained by cryomilling in liquid nitrogen.

Arata Yoshinaga, Minoru Fujita, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Keywords: *Chamaecyparis obtusa*, *Betula maximowicziana*, *Quercus crispula*, secondary wall, middle lamella, UV microspectroscopy, Mäule color reaction,

1989-103

イチョウにおけるリグニンの形成と構造

福島和彦、寺島典二

名古屋大学農学部

Formation and structure of lignin in ginkgo.

Kazuhiko Fukushima, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: microautoradiography, radio tracer, nitrobenzene oxidation, xylem differentiation

1989-104

草本植物リグニン中の *p*-hydroxyphenyl 核

飯山賢治<sup>\*1</sup>、Thi Bach Tuyet Lam<sup>\*2</sup>, Bruce A. Stone<sup>\*2</sup>

<sup>\*1</sup>東京大学農学部、<sup>\*2</sup>La Trobe 大学生化学科

*p*-Hydroxyphenyl nucleus in herbaceous plant lignin.

Kenji Iiyama<sup>\*1</sup>, Thi Bach Tuyet Lam<sup>\*2</sup>, Bruce A. Stone<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>Department of Biochemistry, La Trobe University, Australia

Keywords: wheat, *Triticum aestivum*, nitrobenzene oxidation, cinnamic acid

1989-105

イネ科植物細胞壁中の LCC 結合 -Ferulic acid bridge-

飯山賢治<sup>\*1</sup>、Thi Bach Tuyet Lam<sup>\*2</sup>、Bruce A. Stone<sup>\*2</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*2</sup> La Trobe 大学生化学科

LCC bonds in cell wall of Gramineous plant. -Ferulic acid bridge.

Kenji Iiyama<sup>\*1</sup>、Thi Bach Tuyet Lam<sup>\*2</sup>、Bruce A. Stone<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup> Department of Biochemistry, La Trobe University, Australia

Keywords: *Triticum aestivum*, wheat internode, ferulic acid, cinnamic acid, diferulic acid

1989-106

E1 リグニンの起源と性状

松本雄二、桃原郁夫、石津 敦

東京大学農学部

Origin and character of E1 lignin.

Yuji Matsumoto, Ikuo Momohara, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: chlorine bleaching, E1 effluent, chlorinated lignin, alkaline treatment, GPC

1989-107

Cloning of bi-functional O-methyltransferase from aspen (*Populus tremuloides*).

Robert C. Bugos, Vincent L. Chiang, Wilbur H. Campbell

Michigan Technological University

Keywords: ion exchange chromatography, affinity chromatography,

1989-108

リグニン生合成制御に関する研究 アンチセンス法を用いたペルオキシダーゼの発現制御

刑部敬史<sup>\*1</sup>、西田謙吾<sup>\*1</sup>、山門幹子<sup>\*1</sup>、片山義博<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター

Studies on the control of lignin biosynthesis. -Regulation of peroxidase expression by antisense RNA technology.-

Keishi Osakabe<sup>\*1</sup>、Kengo Nishida<sup>\*1</sup>、Mikiko Yamakado<sup>\*1</sup>、Yoshihiro Katayama<sup>\*2</sup>、Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Cooperative Research Center, Tokyo University of Agriculture and Technology

Keywords: *Nicotiana tabacum*, antisense RNA, Ti plasmid

1989-109

リグニンモデル化合物分解酵素遺伝子のクローニング(XI)  $\beta$ -アリルエーテル結合開裂酵素遺伝子の解析

政井英司<sup>\*1</sup>、片山義博<sup>\*2</sup>、西川誠司<sup>\*1</sup>、山崎真狩<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 東京大学農学部

Cloning of the gene for lignin model compounds degrading enzyme. XI. -Analysis of the gene encoding the enzyme of  $\beta$ -aryl ether cleavage.

Eiji Masai<sup>\*1</sup>、Yoshihiro Katayama<sup>\*2</sup>、Seiji Nishikawa<sup>\*1</sup>、Makari Yamazaki<sup>\*3</sup>、Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture, <sup>\*2</sup> Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup> Faculty of Agriculture, the University of Tokyo

Keywords: *Pseudomonas paucimobilis*, *Escherichia coli*, umbelliferone ether

1989-110

ビフェニル型リグニンモデル化合物芳香族炭素の化学シフトに及ぼす置換基の影響

青山政和<sup>\*1</sup>, M. Drumond<sup>\*2</sup>, C. L. Chen<sup>\*2</sup>, D. Robert<sup>\*3</sup>

<sup>\*1</sup>北海道立林産試験場、<sup>\*2</sup>ノースカロライナ州立大学、<sup>\*3</sup>C. E. N. G.

Effect of substituent groups on the chemical shift of aromatic carbons of biphenyl type lignin model compounds.

Masakazu Aoyama<sup>\*1</sup>, M. Drumond<sup>\*2</sup>, \* C.L. Chen<sup>\*2</sup>, D. Robert<sup>\*3</sup>

<sup>\*1</sup>Hokkaido Forest Products Research Institute, <sup>\*2</sup>North Carolina State University, <sup>\*3</sup>Centre d' Etudes Nucléaires de Grenoble

Keywords: <sup>13</sup>C NMR, *Picea glauca*, MWL,

1989-111

アルカリ性蒸解における針葉樹リグニンと広葉樹リグニンの反応性の差異(4)ーイオン化示差スペクトルを用いたシリングルリグニンの分布ー

堤 祐司、近藤隆一郎、坂井克己、今村博之

九州大学農学部

Differences in the reactivity between lignins from softwood and hardwood during alkaline cooking. IV. —Distribution of syringyl lignin by ionization difference spectroscopy.

Yuji Tsutsumi, Ryuichiro Kondo, Kokki Sakai, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: *Pinus densiflora*, *Betula platyphylla*, dioxane lignin, syringyl lignin, guaiacyl lignin, GPC

1989-112

核交換法を用いたプロトリグニンの構造解析へのアプローチ

光永 徹、船岡正光、阿部 勲

三重大学生物資源学部

Approach to the structural analysis of proto lignin by the use of nuclear exchange method.

Toru Mitsunaga, Masamitsu Funaoka, Isao Abe

Faculty of Bioresources, Mie University

Keywords: *Picea jezoensis*, *Betula maximowicziana*, *Phyllostachys* sp., *Triticum* sp., nitrobenzene oxidation

1989-113

ESR による粉碎した含水リグノセルロース中のラジカル定量と粉碎挙動の解明

壁谷 洋

四国工業技術試験所

Quantitative determination of radicals in wet milled lignocellulose by ESR and investigation of behavior during milling.

Hiroshi Kabeya

Government Industrial Research Institute, Shikoku

Keywords: TMP, cellulose powder, free radical, enzymatic hydrolysis,

1989-114

リグニンのメカノケミストリー(第7報)  $\beta$ -1 型リグニンモデル化合物のメカノケミカル反応

呉 宗華、松岡昌伸、李 典艶、住本昌之

九州大学農学部

Mechanochemistry of lignin. VII. –Mechanochemical reaction of  $\beta$ -1 type lignin model compounds.

Zong-Hua Wu, Masanobu Matsuoka, Dian-Yan Lee, Masashi Sumimoto

Faculty of Agriculture, Kyushu University

Keywords: ceramic ball mill, vibratory ball mill, KRK type refiner, stilbene

1989-115

リグニンのラジカルスルホン化

渡辺正介、飯塚堯介、石津 敦

東京大学農学部

Radical-sulfonation of lignin.

Shosuke Watanabe, Gyosuke Meshitsuka, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: sodium sulfite, oxygen, ethylguaiacol, GC-MS

1989-116

広葉樹硫酸リグニンの理化学的性質

安田征市、平野淳一

名古屋大学農学部

Physical and chemical properties of sulfuric acid lignins from hardwoods.

Seiichi Yasuda, Junichi Hirano

Faculty of Agriculture, Nagoya University

Keywords: beech, *Fagus crenata*, MWL, Klason lignin, acid-soluble lignin, syringyl lignin, nitrobenzene oxidation, gel filtration,  $^1\text{H-NMR}$

1989-117

硫酸触媒による常圧酢酸パルプ化 –脱リグニン機構とリグニンの性質–

島本 周、佐野嘉拓

北海道大学農学部

Acetic acid pulping at atmospheric pressure with sulfuric acid as a catalyst. –Delignification mechanism and properties of lignin.

Shu Shimamoto, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Keywords: *Betula maximowicziana*, hydrogenolysis, GPC,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$

1989-118

アルコール・バイサルファイト処理による  $\beta$ -O-4 結合の開裂反応について

高木孝夫、坂井克己、宮脇正一、今村博之

九州大学農学部

$\beta$ -O-4 cleavage reactions during alcohol-bisulfite treatment.

Takao Takagi, Kokki Sakai, Shoichi Miyawaki, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: lignin model compounds, 2-propanol, isoeugenol, eugenol

1989-特別講演

葉肉単細胞培養系における木部細胞分化機構

福田裕穂

東北大学理学部

Invited lecture ; Differentiation mechanism of xylem cells in single mesophyll cells culture.

Hiroo Fukuda

Faculty of Science, Tohoku University

Keywords: *Zinnia elegans*, tracheary element, secondary cell wall, lignin deposition, peroxidase

1989-201

リグニンの熱分解ガスクロマトグラフィー(第一報)分解生成物組成に及ぼす無機化合物の影響  
黒田健一<sup>\*1</sup>、井上嘉幸<sup>\*1</sup>、坂井克己<sup>\*2</sup>

<sup>\*1</sup> 筑波大学農林工学系、<sup>\*2</sup> 九州大学農学部

Pyrolysis gas chromatography of lignin. I. Effects of inorganic compounds on the composition of degradation products.

Ken-ichi Kuroda<sup>\*1</sup>, Yoshiyuki Inoue<sup>\*1</sup>, Kokki Sakai<sup>\*2</sup>

<sup>\*1</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba, <sup>\*2</sup>Faculty of Agriculture, Kyushu University

Keywords: *Pinus densiflora*, *Chamaecyparis obtuse*, *Cryptomeria japonica*,

1989-202

膨潤-溶媒和のコンビネーションによる木材成分の迅速分離 -理論および分離挙動-

船岡正光、阿部 勲

三重大学生物資源学部

Rapid separation of wood constituents by the combination of swelling and solvation. -Theory and separation behavior.

Masamitsu Funaoka, Isao Abe

Faculty of Bioresources, Mie University

Keywords: cresol, sulphuric acid, temperature, wood refining

1989-203

膨潤-溶媒和法による木材成分の分離 -分離におよぼす酸およびフェノール誘導体の効果-

船岡正光、深津俊輔、阿部 勲

三重大学生物資源学部

Separation of wood constituents by swelling -solvation method. -Effects of acid and phenol derivatives on separation.

Masamitsu Funaoka, Shunsuke Fukatsu, Isao Abe

Faculty of Bioresources, Mie University

Keywords: cresol, ethylphenol, propylphenol, guaiacol, chlorophenol, GPC

1989-204

リグニンにおけるジフェニルメタン型縮合構造の生成とその解裂

船岡正光、久保村実、阿部 勲

三重大学生物資源学部

Formation and cleavage of diphenylmethane type condensed structure in lignin.

Masamitsu Funaoka, Minoru Kubomura, Isao Abe

Faculty of Bioresources, Mie University

Keywords: *Picea jezoensis*, *Betula maximowicziana*, nuclear exchange, nitrobenzene oxidation

1989-205

$\alpha$ -ケト  $\beta$ -アリアルエーテル構造を有するモデル化合物の光分解

深川伸隆、石津 敦

東京大学農学部

Photolysis of  $\alpha$ -keto,  $\beta$ -aryl ether type lignin model compounds.

Nobutaka Fukagawa, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords:  $\beta$ -aryl ether cleavage, coloration, high pressure mercury lamp,

1989-206

リグニンの水素化分解 -HRI の報告についての検討-

小山 実、金沢健治、小川博嗣

化学技術研究所

Hydrocracking of lignin. -Investigation of the report by HRI.

Makoto Koyama, Kenji Kanazawa, Hirotsugu Ogawa

National Chemical Laboratory for Industry

Keywords: HRI (Hydrocarbon Research Inc.) process, improved Noguchi process,

1989-207

シュードモナス属細菌 TMY1009 株のジアリールプロパン型モデル化合物の C<sub>g</sub> 脱離酵素について

岸 克行<sup>\*1</sup>、羽生直人<sup>\*1\*2</sup>、鮫島正浩<sup>\*1</sup>、善本知孝<sup>\*1</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*2</sup> ダイセル化学株式会社

Studies on the C<sub>g</sub> eliminating enzyme from the diarylpropane type lignin model compounds produced by *Pseudomonas* sp. TMY1009.

Katsuyuki Kishi<sup>\*1</sup>, Naoto Habu<sup>\*1\*2</sup>, Masahiro Samejima<sup>\*1</sup>, Tomotaka Yoshimoto<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>Daicel Chemical Industries Ltd.

Keywords: gel electrophoresis, mass spectrometry

1989-208

リグノスチルベン- $\alpha$ 、 $\beta$ -ジオキシゲナーゼ I に含有される鉄と酵素活性との関連性について

鴨田重裕<sup>\*1</sup>、羽生直人<sup>\*1\*2</sup>、鮫島正浩<sup>\*1</sup>、善本知孝<sup>\*1</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*2</sup> ダイセル化学株式会社

Relationship between iron and enzyme activities in lignostylbene- $\alpha$ ,  $\beta$ -dioxigenase I.

Shigehiro Kamoda<sup>\*1</sup>, Naoto Habu<sup>\*1\*2</sup>, Masahiro Samejima<sup>\*1</sup>, Tomotaka Yoshimoto<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>Daicel Chemical Industries Ltd.

Keywords: gel electrophoresis, Fe-chelater,

1989-209

バイオミメティック Mn/Co 触媒とリグニナーゼによる  $\beta$ -O-4 二量体の酸化分解反応

中川麻理子、島田幹夫、樋口隆昌

京都大学木材研究所

Oxidative degradation of  $\beta$ -O-4 type dimer by biomimetic Mn/Co catalyst and ligninase.

Mariko Nakagawa, Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phanerochaete chrysosporium*, lignin peroxidase, total ion chromatography

1989-210

白色腐朽菌による漂白排液の脱色:モデル化合物の分解・代謝機構の検討

桃原郁夫、松本雄二、石津 敦  
東京大学農学部

Decoloration of bleach effluent by white rot fungi: Degradation of model compounds and investigation of metabolic mechanism.

Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu  
Faculty of Agriculture, the University of Tokyo

Keywords: naphthoquinone, anthraquinone, lignin peroxidase

1989-211

白色腐朽菌による漂白排水の突然変異原性の除去  
渋谷征男、松本雄二、石津 敦  
東京大学農学部

Removal of mutagenicity from bleach effluent by white rot fungi.

Masao Shibuya, Yuji Matsumoto, Atsushi Ishizu  
Faculty of Agriculture, the University of Tokyo

Keywords: *Phanerochaete chrysosporium*, 1,3-dichloroacetone, Ames test

1989-212

シリングル及びビフェニール型リグニンモデル化合物芳香環のリグニンペルオキシダーゼによる開裂

服部武文、島田幹夫、樋口隆昌  
京都大学木材研究所

Aromatic ring cleavage of syringyl and biphenyl type lignin model compounds by lignin peroxidase.  
Takefumi, Hattori, Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Keywords: *Phanerochaete chrysosporium*, non-phenolic syringyl type compounds, <sup>1</sup>H-NMR, GC-MS,

1989-213

カワラタケによるリグニン生分解機構の解析  
飯村洋介、片山義博、田村利香、中村雅哉、諸星紀幸  
東京農工大学農学部

Investigation of lignin biodegradation mechanism by *Coriolus versicolor*.

Yosuke Iimura, Yoshihiro Katayama, Rika Tamura, Masaya Nakamura, Noriyuki Morohoshi  
Faculty of Agriculture, Tokyo University of Agriculture and Technology

Keywords: <sup>14</sup>C tracer, <sup>13</sup>C tracer, <sup>14</sup>C -DHP, <sup>13</sup>C-DHP, GPC

1989-214

木材腐朽菌によるリグニンモデル配糖体の生成について(VII) カワラタケによるキシロース配糖体の生成機構

迫 孝、近藤隆一郎、今村博之  
九州大学農学部

Formation of lignin model glycoside by wood rotting fungi. VII. Formation mechanism of xyloside by *Coriolus versicolor*.

Takashi Sako, Ryuichiro Kondo, Hiroyuki Imamura  
Faculty of Agriculture, Kyushu University

Keywords: <sup>14</sup>C tracer, <sup>14</sup>C-glucose, <sup>13</sup>C tracer, <sup>13</sup>C-glucose, <sup>13</sup>C-NMR

1989-215

木材腐朽菌によるリグニンモデル配糖体の生成について(VIII) カワラタケによるリグニン生分解おけるキシロース配糖体生成の役割

追 孝、山上 陽、近藤隆一郎、今村博之

九州大学農学部

Formation of lignin model glycoside by wood rotting fungi. VIII. The role of the formation of xyloside in biodegradation of lignin by *Coriolus versicolor*.

Takashi Sako, Hikari Yamagami, Ryuichiro Kondo, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University

Keywords: *Fagus crenata*,  $^{14}\text{C}$  tracer,  $^{14}\text{C}$ -glucose, veratryl- $\beta$ -D-xyloside, GPC

1989-216

リグニン・多糖複合体のモデル高分子 —細胞特異性の生医学材料としての応用—

小林一清<sup>\*1</sup>、赤池敏宏<sup>\*2</sup>

<sup>\*1</sup>名古屋大学農学部、<sup>\*2</sup>東京農工大学工学部

Macromolecular models of lignin-polysaccharide complex. —Application to cell-specific biomedical material.

Kazukiyo Kobayashi<sup>\*1</sup>, Toshihiro Akaike<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>Faculty of Engineering, Tokyo University of Agriculture and Technology

Keywords: LCC, oligosaccharide-carrying polystyrene, oligosaccharide, hepatocytes

1989-217

水溶性リグニンの免疫活性及び抗ウイルス活性

鈴木春巳<sup>\*1</sup>、飯山賢治<sup>\*1</sup>、柄倉匡文<sup>\*2</sup>、山崎素直<sup>\*1</sup>、山本直樹<sup>\*2</sup>、戸田昭三<sup>\*1</sup>

<sup>\*1</sup>東京大学農学部、<sup>\*2</sup>山口大学医学部

Immunological and antiviral activities of water soluble lignin.

Harumi Suzuki<sup>\*1</sup>, Kenji Iiyama<sup>\*1</sup>, Tadafumi Tochikura<sup>\*2</sup>, Sunao Yamazaki<sup>\*1</sup>, Naoki Yamamoto<sup>\*2</sup>, Shozo Toda<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>School of Medicine, Yamaguchi University

Keywords: *Lentinus edodes*, bagasse, lignosulfonate, polyanion

1989-218

リグニン樹脂接着剤の製造

佐野嘉拓、遠藤 稔、遠藤健一

北海道大学農学部

Production of lignin based adhesives.

Yoshihiro Sano, Minoru Endo, Kenichi Endo

Faculty of Agriculture, Hokkaido University

Keywords: *Abies sachalinensis*, cresol lignin, kraft lignin, lignin-phenol resin

1989-219

光学活性基を有するリグニン関連型液晶の合成とその物性(1)

春日和行<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup>製品科学研究所、<sup>\*2</sup>繊維高分子材料研究所

Synthesis and properties of lignin-related liquid crystal with optically active groups. I.

Kazuyuki Kasuga\*<sup>1</sup>, Hyoe Hatakeyama\*<sup>1</sup> Tatsuko Hatakeyama\*<sup>2</sup>

\*<sup>1</sup>Industrial Products Research Institute, \*<sup>2</sup>Institute for Textiles and Polymers

Keywords: DSC, X-ray diffraction, vanillic acid methyl ester

1989-特別講演

リグニンはどのように糖と結合するか

越島哲夫

京都大学木材研究所

Invited lecture ; How lignin is bonded to carbohydrate

Tetsuo Koshijima,

Wood Research Institute, Kyoto University

Keywords: *Pinus densiflora*, Björkman LCC, GPC, DDQ,

2,3-dichloro-5,6-dicyano-*p*-benzoquinone,

## 第 35 回 (1990.10.15-16) 東京大学 山上会館

1990-101

水溶性リグニンの溶液中の挙動

渡辺正介、飯塚堯介、石津 敦

東京大学農学部

Behavior of water soluble lignin in aqueous solution.

Masasuke Watanabet, Gyosuke Meshitstlka, Atsushi Ishizu

Faculty of Agriculture. the University of Tokyo.

Abstract: Behavior of water soluble lignin in ion-exchanged water in the presence of surface-active agents, such as sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate(SDB), was investigated with gel filtration chromatography using Sepharose CL-2B. With a surface-active agent, a remarkable change in gel filtration curves of sodium lignosulfonate (LSA). that is, shift to at low molecular weight region was observed. These results seem to indicate the aggregation of LSA molecules which carry both of hydrophilic and hydrophobic domains, and the molecular association of LSA was thought to be attributed to the hydrophobic inter molecular interaction.

1990-102

ポリフェノール類のタンパク質吸着能について

河本晴雄、中坪文明、村上浩二

京都大学農学部

Protein-adsorption capacity of polyphenols.

Haruo Kawamoto, Fumiali Nakatsubo, Kouji Murakami

Protein-adsorption capacity of polyphenols

Abstract: Several kinds of condensed tannins were successfully synthesized and the relationships between the structure and the protein precipitating capacity were examined. This examination revealed that the distribution pattern of the phenolic hydroxyl groups in tannin molecule, not the existence of *o*-dihydroxyl-phenyl groups, is important for higher protein-precipitating capacity. Thus, these results suggest that lignin should also have the protein-adsorption capacity, if the phenolic hydroxyl groups are located in the appropriate positions of lignin molecule. Then, the protein-adsorption capacity of several kinds of lignins was tested. Consequently, thiolignin and steam explosion lignin were found to have the higher capacity than commercial

available immobilized tannin.

1990-103

放射線照射によるリグニンの特性変化について

古屋信子、菱山正二郎、須藤賢一

森林総合研究所

Characterization of lignin from  $\gamma$ -ray irradiated wood

Nobuko Furuya, Shojiro Hishiyama, Ken-ichi Sudo

Forestry and Forest Products Research Institute

Abstract: The chemical feature of lignin from wood irradiated by 25-100 Mrad of  $\gamma$ -ray irradiated was investigated. The dioxane lignin (DL) was isolated from untreated and irradiated woods according to Pepper's method. The yield of DL was higher compared with that of untreated wood, though it depends on the radiation dose. The yield of DL from the wood treated by 50 Mrad of irradiation dose was about 40%, whereas that from the untreated wood was 27%. The average molecular weight of DL from the irradiated wood increased with increasing the irradiation dose. The amounts of phenolic-OH and methoxyl groups in DL decreased with increasing the irradiation dose. The relative amounts of C and H in DL from  $\gamma$ -irradiated wood had a tendency to decrease, whereas that of oxygen increased. The yield of nitrobenzene oxidation products ranged from 11.9 to 18.2% depending to the irradiation dose. This shows that lignin in wood changes both decomposition and condensation by  $\gamma$ -irradiation. From these results, it is indicated that lignin in wood changes in the chemical structure to some extent in molecular weight, functional groups and so on.

1990-104

リグニンの水素化分解 -数種の触媒の検討-

小山 実

化学技術研究所

Hydrocracking of lignin.-Montmorillonite catalysts.

Makoto Koyama

National Chemical Laboratory for Industry

Abstract: A kraft lignin (KL) and lignin model dimers were hydrocracked with Fe-, Ni-, Co-, and Mo-montmorillonite-S (Mo-Mtm-S) as catalysts. Yields of monophenols and benzenes from hydrocracking of 2-hydroxybiphenyl by 450 °C, 50 minutes with Fe-Mtm-S were about 10 and 25 %, respectively. About hydrocracking of KL with Fe-Mtm-S, yields of monophenols were similar to, but depolymerization of KL was more promoted than it with Fe/Alumina-S catalyst.

1990-105

リグノセルロース熱分解物を原料とするポリウレタンの熱的性質

広瀬重雄、畠山兵衛

製品科学研究所

Thermal properties of polyurethanes derived from thermal degradation products of lignocellulose.

Shigeo Hirose, Hyoe Hatakeyama

Industrial Products Research Institute, Tokyo

Abstract: A liquid and charcoal were obtained by the thermal degradation of Eucalyptus. The liquid was distilled at 230 °C and the solid residue was obtained. The residue was found to contain 5.8 mmol/g of the hydroxyl group. Polyurethanes (PU's) were prepared from the residue, polyethylene glycol (PEG) 400 and diphenylmethane diisocyanate (MDI). Thermal degradation of PU's was studied by thermogravimetry (TG). The effect of the addition of residue to PU's is considered in this paper.

1990-106

ユーカリリグニンからのポリウレタンフォームの力学的性質

中村邦雄<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>、J. Meadows<sup>\*3</sup>、P.A. Williams<sup>\*3</sup>、G.O. Phillips<sup>\*3</sup>

<sup>\*1</sup>大妻女子大学、製品科学研究所、<sup>\*3</sup>Northeast Wales Institute

Mechanical properties of polyurethane foam derived from Eucalyptus lignin

Kunio Nakamura<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>, J. Meadows<sup>\*3</sup>, P.A. Williams<sup>\*3</sup>, G.O. Phillips<sup>\*3</sup>

<sup>\*1</sup>Otsuma Women's University, <sup>\*2</sup>Industrial Products Research Institute, <sup>\*3</sup>Northeast Wales Institute

Abstract: Polyurethane (PU) from Eucalyptus lignin (EL) and polyol were prepared as follows: EL was dissolved in polyethylene glycol (PEG) having a molecular weight of 400 at 50 °C for 1 hour. PU foam was obtained by the reaction between the polyol and diphenylmethane diisocyanate (MDI). The EL content in PU foam and MDI/polyol ratio were varied in order to obtain different kinds of PU foam. The density of PU foam, compression strength and elasticity were measured using the weight method and a Lloyd INSTRUMENT T30K Mode1. Thermal properties of the PU foam prepared were measured by differential scanning calorimetry (DSC).

1990-107

リグニン系炭素繊維の基礎物性とその応用

中嶋信之<sup>\*1</sup>、横山 昭<sup>\*1</sup>、須藤賢一<sup>\*2</sup>、志水一允<sup>\*2</sup>

<sup>\*1</sup>日本カーボン株式会社、<sup>\*2</sup>森林総合研究所

Properties and applications of lignin based carbon fiber

Nobuyuki Nakajima<sup>\*1</sup>, Akira Yokoyama<sup>\*1</sup>, Kenichi Sudo<sup>\*2</sup>, Kazumasa Shimizu<sup>\*2</sup>

<sup>\*1</sup>Nippon Carbon Co., Ltd., <sup>\*2</sup>Forestry and Forest Products Research Institute,

Abstract: Preparation methods for lignin based carbon fiber (LCF) were investigated. Raw lignin was extracted from steam-exploded white birch. After mild hydrocracking followed by heat treatment under reduced pressure, the lignin showed excellent spinnability in melt-state. Crystallinity of LCF is somewhat lower than that of another kind of carbon fiber. As to mechanical properties, LCF is classified into general purpose carbon fiber. Tensile strength of LCF is 40-60kg/mm<sup>2</sup>. After steam activation, the specific surface area increased to 2000m<sup>2</sup>/g. The bending strength of LCF/cement composite was about 100kg/cm<sup>2</sup> at 7vol.% fiber content. LCF/Epoxy-resin composite showed the bending strength of 25-30kg/mm<sup>2</sup> and about 3kg/mm<sup>2</sup> of inter laminar strength.

1990-108

*Albizia falcata* 材のリグニン・多糖結合体について

渡辺隆司<sup>\*1</sup>、今村剛士<sup>\*1</sup>、越島哲夫<sup>\*2</sup>、Myrtha Karina<sup>\*3</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>近畿大学農学部、<sup>\*3</sup>LIPI,P3FT

Lignin-carbohydrate complexes from *Albizia falcata* wood.

Takashi Watanabe<sup>\*1</sup>, Takeshi Imamura<sup>\*1</sup>, Tetsuo Koshijima<sup>\*2</sup>, Myrtha Karina<sup>\*3</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Faculty of Agriculture Kinki University, <sup>\*3</sup>Research and Development Centre for Applied Physics. Indonesian Institute of Sciences

Abstract: Lignin-carbohydrate complexes (LCCs) were isolated from tropical hard wood of *Albizia falcata* Backer by a modified Björkman method. After extraction of milled wood lignin from the hard wood, LCCs were isolated by successive extraction of the wood residue with water and 4% aqueous NaOH. NMR and methylation analysis indicated that the alkali-soluble fraction was composed of glucuronoxylan-lignin complex and that a neutral xylan chain existed in the water-soluble LCC fraction.

1990-109

*Forsythia intermedia* のリグナン生合成酵素について

梅澤俊明 (Toshiaki Umezawa)<sup>\*1</sup>、Laurence B. Davin<sup>\*2</sup>、Norman G. Lewis<sup>\*2</sup>

<sup>\*1</sup>Commonwealth Center for Wood Science and Technology/ <sup>\*2</sup>Department of Biochemistry,  
Virginia Polytec Institute and State University

Formation of optically pure lignans by cell free extracts of *Forsythia Intermedia*.

Toshiaki Umezawa, <sup>\*1</sup>, Laurence B. Davin<sup>\*2</sup>, Norman G. Lewis<sup>\*2</sup>

<sup>\*1</sup>Commonwealth Center for Wood Science and Technology/ <sup>\*2</sup>Department of Biochemistry,  
Virginia Polytec Institute and State University

Abstract: A crude cell-free extract from *Forsythia Intermedia* catalyzes the formation of (-)-secoisolariciresinol, and not its (+)-enantiomer, when incubated with coniferyl alcohol in the presence of NAD(P)H and H<sub>2</sub>O<sub>2</sub>. This extract also catalyses the oxidation of (-)-secoisolariciresinol, but not its (+)-enantiomer, to (-)-matairesinol. This is the first report of an enzyme reaction specifically involved in the coupling between two phenyl-propanoid monomers to afford an optically pure lignan.

1990-110

リグノール類の脱水素重合

内田洋介、寺島典二

名古屋大学農学部

Dehydrogenative polymerization of lignols

Yousuke Uchida, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Abstract: In order to examine the factors affecting formation of condensed structures in protolignin macromolecule, coniferyl alcohol, *p*-coumaryl alcohol and sinapyl alcohol were polymerized dehydrogenatively under different pHs and in the presence of different kinds of polysaccharides. The proportion of three main dilignols,  $\beta$ -0-4,  $\beta$ -5, and  $\beta$ - $\beta$  types, formed in the earliest stage of polymerization was affected greatly by the pH. Under low pH and in the presence of an acidic polysaccharide, pectin, the proportion of condensed type  $\beta$ -5 dimer, dehydrodiconiferyl alcohol, was higher than that found under high pH and in the absence of pectin or in the presence of less acidic hemicelluloses.

1990-111

広葉樹培養細胞のリグニン生成とペルオキシターゼアイソザイムの基質特異性について

堤 裕司、坂井克己

九州大学農学部

Lignin biosynthesis and substrate specificities of peroxidase isoenzymes with respect to syringyl and guaiacyl structures in angiosperm tree callus cultures.

Yuji Tsutsumi, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We investigated the possibility that substrate specificities of peroxidase isoenzymes can

control syringyl lignin contents in xylem tissues. Peroxidase isoenzymes from *Populus* callus cultures were fractionated to three isoenzyme groups, soluble peroxidase (SPO), ionically bound peroxidase (IPO) and wall bound peroxidase (WPO). The substrate specificities of these isoenzyme groups with respect to syringyl and guaiacyl substrates were investigated. The specificity of IPO to

syringyl substrate was the highest, among three peroxidase isoenzyme groups. Though the severe water stress applied to the calluses elevated both their lignin content and peroxidase levels, the specificity to syringyl substrate and syringyl lignin content determined by nitrobenzene oxidation were decreased. The peroxidase isoenzyme groups from *Cryptomeria* calluses exhibited the lower specificity to a syringyl substrate. These results suggest that the syringyl lignin biosynthesis is controlled not only by the lignin monomer supply but also by the substrate specificity of peroxidase in the last step of lignin formation, that is dehydrogenative polymerization catalyzed by peroxidase in angiosperm xylem tissues.

1990-112

食用担子菌の生産するフェノール酸化酵素

小藤田久義、太田朋子、松下敦史、麻田恭彦、桑原正章

香川大学農学部

Phenol oxidase and peroxidase produced by edible mushrooms.

Hisayoshi Kofujita, Tomoko Ohta, Atsushi Matsushita, Yasuhiko Asada,

Masaaki Kuwahara

Faculty of Agriculture, Kagawa University,

Abstract: Phenol oxidase and peroxidases were produced by *Lentinus edodes* and *Pleurotus ostreatus* in liquid and solid state cultures containing low or high nitrogen source. Lignin peroxidase activity was negligible in these culture conditions. Laccase produced in the wheat bran medium by *L. edodes* and Mn(II)-peroxidase produced in the glucose-peptone medium by *P. ostreatus* were purified to homogeneity by various chromatography. In most properties of each enzyme, laccase of *L. edodes* and Mn(II)-peroxidase of *P. ostreatus* were similar to that of *Coriolus versicolor* or *Phanerochaete chrysosporium*. Both of these enzymes degraded the phenolic  $\beta$ -O-4 lignin substructure model compound, syringylglycerol- $\beta$ -guaiacyl ether (I). The structure of degradation products indicated that these two enzymes catalyze alkyl-aryl cleavage of substrate I.

1990-113

木材腐朽菌による木材の水溶性化挙動について

迫 孝、近藤隆一郎、坂井克己

九州大学農学部

Water solubilization of wood by white-rot fungi during wood decaying process.

Takashi Sako, Ryuichiro Kondo and Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: In previous papers, we reported that *Coriolus versicolor* transformed lignin model compounds into their xylosides in various sugar media. We tried to clarify the possibility of the formation of lignin-glycosides during the biodegradation of lignin by *C. versicolor* in  $^{14}\text{C}$ -glucose and  $^{13}\text{C}$ -glucose media. On the basis of the results of the incorporation of radioactivities into fungus treated lignin and the  $^{13}\text{C}$ -NMR spectrum of the treated lignin, it was suggested that lignin was possibly transformed into its xylosides by *C. versicolor*. To get a better understanding of biodegradation of wood by wood-rot fungi, we attempted to decay beech wood meal with by white-rot fungi, *C. versicolor* and *Phanerochaete chrysosporium* for various period, and investigated the water soluble fraction of decayed wood meals. In *C. versicolor* cultivation, the lignin components in the water soluble fraction were seemed to be degraded severely. On the other hand, the dissolved lignin components from wood meals decayed by *P. chrysosporium* were seemed to be relatively stable in the culture medium. Therefore, it was suggested that these fungi might have different catabolic system to degrade lignin.

1990-114

ベラトリル  $\beta$ -D-キシロシド共存下におけるリグニンペルオキシターゼによるリグニンモデル化合物の分解

服部武文、島田幹夫、樋口隆昌

京都大学木材研究所

Degradation of a lignin model compound by lignin peroxidase in the presence of veratryl  $\beta$ -D-xyloside

Takefumi Hattori, Mikio Shimada, Takayoshi Higuchi

Wood Research Institute, Kyoto University

Abstract: Addition of veratryl alcohol and/or veratryl  $\beta$ -D-xyloside enhanced C $\alpha$ -C $\beta$  cleavage reaction of 1,2-bis(4-methoxyphenyl)propane-1,3-diol (I) which was a poorer substrate for lignin peroxidase than veratryl alcohol. The rate of degradation (I) was greater with veratryl alcohol than with veratryl  $\beta$ -D-xyloside, however veratryl  $\beta$ -D-xyloside was more stable than veratryl alcohol during reaction. Mixed type of competitive and noncompetitive inhibition pattern of Lineweaver-Burk plots obtained suggests that veratryl alcohol not only prevent lignin peroxidase from inactivation but also acts as a radical mediator.

1990-115

キノン型化合物のリグニンペルオキシターゼによる分解

桃原郁夫、松本雄二、石津 敦

東京大学農学部

Degradation of a quinone model compound by lignin peroxidase.

Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Keywords: *Phanerochaete chrysosporium*, lignin peroxidase, superoxide anion, quinone, decolorization, veratryl alcohol

Abstract: A quinone model compound, 2-hydroxy-1,4-naphthoquinone (HNQ), is degraded by lignin peroxidase when veratryl alcohol is present. Spectral study of this reaction system indicated that the presence of HNQ inhibits the oxidation of veratryl alcohol by lignin peroxidase and, thus, the formation of veratraldehyde starts only after the degradation of HNQ. Degradation rate was remarkably increased by the increase in veratryl alcohol concentration. Degradation was partly and completely prevented by adding a OH $\cdot$  scavenger (mannitol) and a O $_2$ -scavenger (Mn $^{2+}$ ), respectively. These results suggest that active oxygen species formed in lignin peroxidase - H $_2$ O $_2$  - veratryl alcohol system play an important role in HNQ degradation.

1990-116

フェノール性  $\beta$ -O-4 型リグニンモデル二量体のリグニンペルオキシターゼによる分解

横田信三<sup>\*1</sup>、(京大木研)梅澤俊明<sup>\*2</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup>宇都宮大学農学部、<sup>\*2</sup>京都大学木材研究所

Degradation of phenolic  $\beta$ -O-4 lignin model dimers by lignin peroxidase.

Shinsou Yokota<sup>\*1</sup>, Toshiaki Umezawa<sup>\*2</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Utsunomiya University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Abstract: Degradation of three kinds of phenolic  $\beta$ -O-4 lignin model dimers, 1-(4-hydroxy-3-methoxy-phenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (I), 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol (II) and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxy-phenoxy)-1,3-propanediol (III), by lignin peroxidase was investigated. Of these three

substrates, substrate III was degraded to the following six compounds: guaiacol (IV), syringaldehyde (V), syringic acid (VI), 2,6-dimethoxy-*p*-hydroquinone (VII), 2-(2-methoxy-phenoxy)-2-propenal (IX), and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propene-1-one (X). The results showed that substrate III was degraded via alkyl-aryl cleavage, Ca-Cb cleavage, and Ca oxidation by lignin peroxidase.

1990-117

リグニンペルオキシダーゼ (LiP) 系による新しいシュウ酸分解反応とその生理的意義

島田幹夫<sup>\*1</sup>、馬 登波<sup>\*1</sup>、樋口隆昌<sup>\*1</sup>、赤松やすみ<sup>\*2</sup>

<sup>\*1</sup>京都大学木材研究所、<sup>\*2</sup>福井グリーンセンター

A new enzymatic decarboxylation of oxalic acid by lignin peroxidase (Lip) system and its physiological role.

Mikio Shimada<sup>\*1</sup>, Denbo Ma<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>, Yasumi Akamatsu<sup>\*2</sup>,

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>General Green Center, Fukui Prefecture.

Abstract: A new enzymatic decarboxylation of oxalic acid by lignin peroxidase (LiP) system) was discovered. Oxidation of veratryl alcohol by LiP was potently inhibited by oxalic acid. The inhibition analysis clearly showed that the type of inhibition is noncompetitive. The apparent noncompetitive inhibition of LiP is explained as such that the veratryl alcohol cation radical intermediate formed by LiP is reduced back to veratryl alcohol by oxalic acid and consequently formation of veratraldehyde is blocked. The addition of oxalic acid into the ligninolytic culture of *Phanerochaete chrysosporium* also inhibited decomposition of synthetic lignin to CO<sub>2</sub>. The results indicate that oxalic acid as a secondary metabolite of white-rot fungi controls lignin decomposition on one side and veratryl alcohol acts as a mediator for decomposition of oxalic acid on the other.

1990-118

特別講演: リグニンの生化学: 生合成と生分解

樋口隆昌

京都大学木材研究所

Special lecture: Lignin Biochemistry: Biosynthesis and Biodegradation.

Takayoshi Higuchi

Wood Research Institute, Kyoto University

Abstract: Lignin biosynthesis via shikimate-cinnamate pathways in plants, and the biosynthetic differences of guaiacyl- and syringyl lignins between gymnosperms and angiosperms have been elucidated by tracer experiments using <sup>14</sup>C labeled precursors and the following enzyme reactions. The main cleavage mechanisms of propyl side chain and aromatic ring opening of lignin model compounds and synthetic lignin (DHP) by white-rot fungi and their enzymes, lignin peroxidase and laccase have been elucidated using <sup>2</sup>H, <sup>13</sup>C and <sup>18</sup>O-labeled lignin substructure dimmers with <sup>18</sup>O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O. Side chains and aromatic rings of these substrates were cleaved via aryl cation radical and phenoxy radical intermediates, in reaction mediated only by lignin peroxidase and laccase.

1990-201

リグニンのメカノケミストリー(第7報)ベラトリルグリセロール-β-シリンガアルデヒドエーテルのメカノケミカル反応

呉 宗華、住本昌之

九州大学農学部

Mechanochemistry of lignin. VII. Mechanochemical reaction of veratryl-β-syringaldehyde ether.

Zonghua Wu, Masashi Sumimoto

Faculty of Agriculture, Kyushu University

Abstract: Veratrylglycerol- $\beta$ -syringaldehyde ether (M) was treated with CBM, VBM and KRK-refiner to find out the mechanochemical conversion products. Under the conditions treated, about 20% of the starting materials (M) were converted to give veratryl propan-1-on-3-ol 1, syringaldehyde 2, 2,6-dimethoxy-*p*-hydroquinone 3, 2,6-dimethoxy-*p*-benzoquinone 4, vanillin 5, veratrylalcohol 6, syringaldehydeglycol ether 7 and a condensation product 8. Formation of a chromophore 2,6-dimethoxy-*p*-benzoquinone 4, a leucochromophore 2,6-dimethoxy-*p*-hydroquinone 3, and para-carbonylphenols 2 and 5 should be deeply related to the color of unbleached pulp and color reversion of bleached mechanical pulp.

1990-202

高収率パルプ製造時のリグニンの挙動 (III) *p*-カルボニルフエノールを有する  $\beta$ -O-4 型モデル化合物の合成とそのメカノケミストリー

伊藤和貴<sup>\*1</sup>、橘 燦郎<sup>\*2</sup>、住本昌之<sup>\*1</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>愛媛大学農学部

Behaviours of lignin during production of high-yield pulp. III. - Synthesis and mechanochemical conversions of  $\beta$ -O-4 lignin model compound having a para-carbonyl phenol.-

Kazutaka Ito<sup>\*1</sup>, Sanro Tachibana<sup>\*2</sup>, Masashi Sunimoto<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>Faculty of Agriculture, Ehime University

Abstract: Trials for the improved method of synthesis of  $\beta$ -O-4 lignin model compounds (I) [3-methoxy-4-hydroxy- $\alpha$ -(2-methoxyphenoxy)- $\beta$ -hydroxypropiophenone] were made first. The second one (II) [3,5-dimethoxy-4-hydroxy- $\alpha$ -(2-methoxyphenoxy)- $\beta$ -hydroxypropiophenone], however, had to be synthesized by the relatively different method. By the Mechanical treatments of the latter model compound (II) as a representative of a biphenyl model (III) and a biphenyl ether model (IV) with VBM and CBM, 2,6-dimethoxy-*p*-benzoquinone and others were obtained in reasonable yields.

1990-203

クラフト蒸解中難分解性リグニンの漂白過程における反応

細谷修二、島田謹爾、富村洋一

森林総合研究所

Reactions of pulping-resistant structure in lignin during bleaching.

Shuji Hosoya, Kinji Shimada, Yoichi Tomimura

Forestry and Forest Products Research Institute

Abstract: Reactions of veratrylglycerol- $\alpha$ -ethyl- $\beta$ -guaiacyl ether (VEG) during bleaching were investigated. This lignin model compound represents the kraft pulping-resistant and oxygen bleaching-resistant structures in lignin. By chlorine treatment, about 3 moles of chlorine per mole of VEG were very quickly taken up for the unfavorable chlorination reaction. Only after this chlorination reaction was observed the extensive demethylation reaction which leads to favorable delignification reaction.  $\alpha$ -Ethyl ether was never cleaved by chlorine treatment. Nitrogen dioxide and chlorine dioxide were not reactive to VEG. Acetic acid containing small amount of HCl (0.1% w/v) effectively cleaved the  $\alpha$ -ether bond giving almost theoretical yield of ethyl acetate. Acetic acid treatment of KP and oxygen bleached KP (KOP) resulted in large drop in kappa number (Fig. 2). As a conclusion, we propose new non-chlorine bleaching sequence: either Oxygen-Acid Treatment-Chlorine Dioxide or Acid Treatment-Oxygen-Chlorine Dioxide.

1990-204

さらしパルプ中に検出されるダイオキシンの前駆体に関する一考察 塩素経換反応におよぼすリグニンの影響

阿部善作<sup>\*1</sup>、P. Ljungquist<sup>\*2</sup>、F. de Sousa<sup>\*2</sup>、K. P. Kringstad<sup>\*3</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>STFI、<sup>\*3</sup>Norske Skogindustrier AS

An investigation on precursors of dioxins detected in bleached kraft pulp (Influence of lignin on chlorine substitution reaction in chlorine water)

Zensaku Abe<sup>\*1</sup>、Pirre Ljungquist<sup>\*2</sup>、Filipe de Sousa<sup>\*2</sup>、Knut P. Kringstad<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>STFI, Stockholm, Sweden, <sup>\*3</sup>Norske Skogindustrier AS, Honefoss, Norway

Abstract: The investigation was done to obtain a better understanding of the reason why the ratio of 2,3,7,8-tetrachlorodibenzofuran (TCDF) to 1,2,7,8-TCDF detected in bleached kraft pulp is almost two and of the precursors of PCDFs. The ratios of 2,3,7,8-TCDF to 1,2,7,8-TCDF formed during the chlorination of unchlorinated dibenzofuran without pulp in chlorine water at different reaction conditions are about one, respectively. And also the ratio with bleached pulp is one. But 2,3,7,8-TCDF was formed more than three times of 1,2,7,8-TCDF during the chlorination of dibenzofuran with unbleached pulp using chlorine water. These results show that lignin of unbleached pulp oriented chlorine substitution in the chlorination using chlorine water and that unchlorinated dibenzofuran may be a precursor of PCDFs.

1990-205

NO<sub>2</sub>前処理酸素漂白法の機構について

大井 洋、Thomas. J. McDonough

Institute of Paper Science and Technology

Mechanism of nitrogen dioxide pretreatment for oxygen bleaching.

Hiroshi Ooi, Thomas. J. McDonough

Institute of Paper Science and Technology

Abstract: Pretreatment of kraft pulp with nitrogen dioxide has been shown to be an effective method for both improvement of delignification and protection of carbohydrate degradation in oxygen bleaching. However, the mechanism of its action is not clear. The objective of this research is to learn more about the mechanism.

1990-206

硫酸触媒による広葉樹材の常圧酢酸パルプ化 -パルプ化条件の検討

佐野嘉拓、島本 周

北海道大学農学部

Abstract: Aqueous acetic acid pulping of hardwoods at atmospheric pressure with a sulfuric acid catalyst pulping conditions.

Yoshihiro Sano and Shu Shimamoto

Faculty of Agriculture, Hokkaido University

Abstract: Pulping of hardwoods at atmospheric pressure with 90% AcOH containing a small amount of sulfuric acid was investigated. The hardwoods were boiled for 0.5 hours in 90% AcOH for pretreatment, and then for 2-3 hours in 90% AcOH with 1.6-2.0% H<sub>2</sub>SO<sub>4</sub> of wood for pulping. The hardwoods used were classified roughly into three groups on basis of the results of pulping. The 1st class (birch) is pulped with ease by these procedure, the 2nd class (alder, beech, eucalyptus and poplar) with less difficulty and the 3rd class (acacia) with difficulties. Also lignin model compounds with β-ether were degraded under similar conditions to the pulping of hardwoods in order to clarify the reaction mechanism of lignin. The β-ether compounds were found to be reacted by the same

mechanism as acetic acid pulping without H<sub>2</sub>SO<sub>4</sub> at elevated temperatures.

1990-207

硫酸触媒による広葉樹材の常圧パルプ化 –酢酸リグニンの樹脂接着剤への応用

中村雅幸、佐野嘉拓

北海道大学農学部

Pulping of hardwood at atmospheric pressure with sulfuric acid catalyst. –Preparation of lignin based resin adhesives.

Masayuki Nakamura, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Utilization of lignin in the substrate of phenol resins was investigated. Commercial kraft lignin and acetic acid lignin (AWL) prepared by acetic acid pulping of birch at atmospheric pressure were used as lignin. A mixture of lignin and phenol was condensed with HCHO in aqueous methanol under alkaline conditions in order to produce phenol-type resins. When 80% of phenol was replaced by each lignin, the resulting resins met JIS for phenol-type resins. When 20% resorcinol added to the resins, the press temperature was depressed to 100°C. AWL and lignin model compounds were reacted with HCHO under acidic conditions in order to yield more activated hydroxymethylated lignin. Lignin reacted under acidic conditions were found to contain twice amounts of hydroxymethyl groups than that under alkali conditions.

1990-208

オイルパーム副産物のケミサーモメカニカルパルプ化

赤松 勲<sup>\*1</sup>、上嶋 洋<sup>\*1</sup>、細川 純<sup>\*1</sup>、D.H.A.H. Hassan<sup>\*2</sup>

<sup>\*1</sup> 四国工業試験所, <sup>\*2</sup> Palm Oil Research Institute of Malaysia

Chemi-thermomechanical pulp of oil palm by-products.

Isao Akamatsu, Hiroshi Kamishima, Jun Hosokawa, Datuk Haji Abdul Halim Hassan

Government Industrial Research Institute of Shikoku

Abstract: With increasing demand of pulp and paper production, the new raw materials for pulp have been investigated with the purpose of higher utilizing of ligno-cellulosic oil palm by-products. Empty fruit bunch frond and trunk were pulped by anthraquinone-KP and TMP process. From the yield and sheet properties, frond was selected as the optimum raw material and CTMP process the appropriate one. The fungus attack to frond was prevented by pretreatment with some chemicals, including alkalis, bunch ash. Plant scale CTM-pulping showed almost the same results as the laboratory studies using the alkali pretreated fronds. The rolled paper produced corrugating medium and corrugated boards with the satisfied strengths. The characteristics of CTMP waste water were also studied and the biological treatability was tested.

1990-209

未利用林産資源の酵素、微生物による変換利用(2)高知県産広華樹 35 種の水蒸煮処理パルプの酵素糖化率

鮫島一彦<sup>\*1</sup>、藤原新二<sup>\*1</sup>、黒田健一<sup>\*2</sup>、高村意男<sup>\*1</sup>

高知大学農学部、筑波大学農林工学系

Enzymatic and microbial conversion of unused forest product resources for further utilization. II. The susceptibility to the enzymatic saccharification of steam-cooked pulps made from thirty-five hardwoods of Kochi growth.

Kazuhiko Sameshima<sup>\*1</sup>, Shinji Fujiwara<sup>\*1</sup>, Kenichi Kuroda<sup>\*2</sup>, Norio Takamura<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agr., Kochi University, <sup>\*2</sup>Institute of Agricultural and Forestry Engineering, Tsukuba

University

Abstract: The Asplund pulps made from thirty-five Japanese hardwoods of Kochi growth were tested for their susceptibilities to the enzymatic saccharification with *Trichoderma viride* cellulase, "Meicelase P-1". After the chemical analyses of both wood meals of the sample woods and the pulps were made, the morphological features such as the fiber cell wall area and the fiber cell wall thickness of each wood samples were measured using art image analysis system. The overall correlations between the susceptibilities and the chemical and the morphological features showed that only the lignin contents of both wood meals and pulps have the strongest correlations. Detailed analyses are now being undertaken.

1990-210

微生物 (IZU-154 株) によるクラフトパルプの漂白 (第 2 報)

藤田弘毅<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>、坂井克己<sup>\*1</sup>、樫野由憲<sup>\*2</sup>、西田友昭<sup>\*2</sup>、高原義昌<sup>\*2</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>神戸製鋼所

Bibleaching of kraft pulp by the fungus, IZU-154

Koki Fujita<sup>\*1</sup>, Ryuichiro Kondo<sup>\*1</sup>, Kokki Sakai<sup>\*1</sup>, Yoshinori Kashino<sup>\*2</sup>, Tomoaki Nishida<sup>\*2</sup>, Yoshimasa Takahara<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>Biotechnology Research Lab., Kobe Steel, Ltd.,

Abstract: The fungus, IZU-154 exhibited the high activity of brightening the beech kraft pulp. The pulp brightness increased by 21 points to 49% by a five-day treatment associated with a corresponding decrease in Kappa number from 20.9 to 9.3. Combined fungal (F) and chemical (CED) bleaching gave a pulp with the almost same brightness (88%) and bleaching yield (94%) as a conventionally CEDED bleached pulp. The FCED bleaching process could significantly reduce the use of chlorine-based chemicals and the pollution load of waste liquors, compared to the conventional CEDED process. This is also the first report that softwood kraft pulp was brightened by the fungal treatment; i.e. IZU-154 treatment increased the brightness of Japanese red pine (*Pinus densiflora*) kraft pulp by 31 point to 55.9% and decreased kappa number from 35.4 to 5.3.

1990-211

ジリグノール分解性好アルカリ性細菌のプロトプラスト融合及び融合株の性質

葛原憲康、川上日出国

名古屋大学農学部

Protoplast fusion of dilignol degradable alkalophilic bacteria and properties of the fusants.

Noriyasu Kuzuhara, Hidekuni Kawakami

Faculty of Agriculture, Nagoya University

Abstract: In order to improve lignin degrading ability of alkalophilic bacteria, intergeneric protoplast fusion was carried out. The procedure for protoplast fusion from two strains, *Corynebacterium* CM-432 and *Acinetobacter lwoffii* CM-401 has been established. As the selective pressure of the fusants, antibiotics, kanamycin and penicillin were used. Some promising fusants were isolated. The lignin model compounds degrading ability and APPL generating ability of the fusants were superior to those of the parental strains. However, the fusants have grown only on the medium of pH 8.5 and have been devoid of the adaptability for wide pH range such as parental strains.

1990-212

担子菌 *Phanerochaete chrysosporium* 及び *Bjerkandera adusta* の生産するリグニンパーオキシダーゼとその遺伝子

桑原正章、木村義雄、岡 豊則、麻田恭彦  
香川大学農学部

Characterization of lignin peroxidases and its genes from basidiomycetes *Phanerochaete chrysosporium* and *Bjerkandera adusta*.

Masaaki Kuwahara, Yoshio Kimura, Toyonori Oka, Yasuhiko Asada  
Faculty of Agriculture, Kagawa University

Abstract: The basidiomycetes *Phanerochaete chrysosporium* and *Bjerkandera adusta* produce multiple extracellular glycosylated heme peroxidases called ligninases or lignin peroxidases. We have purified and characterized major lignin peroxidases of their enzymes. The lignin peroxidase of *B. adusta* exhibited close similarity to lignin peroxidase of *P. chrysosporium* with respect to their basic properties. Also, lignin peroxidase genes have been cloned from a *P. chrysosporium* DNA library and a *B. adusta* DNA library. Nucleotide sequencing of the gene of *B. adusta* has revealed that the lignin peroxidase structural gene contains 1,116 bp of protein-encoding sequence of which 69 bp encode the signal peptide. Amino acid sequence homology between the coding gene of *B. adusta* and the lignin peroxidase gene of *P. chrysosporium* is 61%.

1990-213

合成 DNA プローブを用いたハイブリダイゼーションによるリグノスチルベン- $\alpha$ ,  $\beta$ -ジオキシケナーゼ産生遺伝子の検出

鮫島正浩、鴨田重裕  
東京大学農学部

Detection of the gene encoding lignostilbene  $\alpha$ ,  $\beta$  dioxygenases by hybridization with synthetic oligonucleotide probes.

Masahiro Samejima, Shigehiro Kamoda  
Faculty of Agriculture, University of Tokyo

Abstract: Lignostilbene a, b dioxygenases (LSDs) are the key enzyme responsible for the cleavage of the C  $\alpha$ -C  $\beta$  double bonds in the metabolism of lignin related compounds by *Pseudomonas* sp. TMY1009 (Fig.1). To elucidate the catalytic mechanism of LSD, detailed knowledge of the enzyme structure is required. The analysis of the gene is enable to determine the primary structure of the enzyme. In this study, to clone the gene encoding LSDs, genomic library of *Pseudomonas* sp. TMY1009 was constructed with a cosmid vector and two oligonucleotides corresponding to the partial amino acid sequences of LSD-I were synthesized. Hybridization between the library and two probes was conducted and several positive colonies were detected (Table 1). The recombinant cosmid (pMSH25) from one of the positive colonies were digested with several appropriate restriction enzymes and the physical map of this cosmid was determined. Furthermore, the location of LSD gene was analyzed by Southern hybridization (Fig.2 and 3).

1990-214

リグニンモデル化合物分解酵素遺伝子のクローニング(XV)10.5 kbp EcoRI 断片の構造および機能の解析

西川誠司<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、山崎真狩<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部, <sup>\*2</sup> 東京農工大学共同研究開発センター, <sup>\*3</sup> 東京大学農学部

Cloning of the genes involved in degradation of lignin model compounds (X V )

Seiji Nishikawa<sup>\*1</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Makarl Yamasaki<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup> Faculty of Agriculture, University of Tokyo

Abstract: We already reported the isolation of the 10.5 kbp *EcoRI* DNA restriction fragment

from *P. paucimobilis* SYE-6 chromosomal DNA. When this DNA fragment was inserted in the *EcoRI* site of vector plasmid pKT 230, this recombinant plasmid (pVAO1) could transform the vanillic acid-negative strain *P. putida* PpY1100 to vanillic acid-positive phenotype. One of the genes carried on this fragment was protococatechuate 4,5-dioxygenase gene and recently complete nucleotide sequence of this was determined [1]. In this study, we showed that the location of protococatechuate 4,5-dioxygenase, 4-carboxy-2-hydroxymuconate-6-semialdehyde dehydrogenase and 2-pyrone-4,6-dicarboxylic acid hydrolase genes on the 10.5 kbp *EcoRI* fragment isolated from *Pseudomonas paucimobilis* SYK-6 chromosomal DNA.

[1] Noda, Y. and Nishikawa, S. et al. *J. Bacteriol.*, 1990, Vol. 172, No. 5, 2704-2709.

1990-215

リグニンモデル化合物分解酵素遺伝子のクローニング(XVI)  $\beta$ -エーテラーゼ( $\beta$ -アリールエーテル開裂酵素)遺伝子の解析

政井英司<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、山崎真狩<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup>東京農工大学農学部, <sup>\*2</sup>東京農工大学共同研究開発センター, <sup>\*3</sup>東京大学農学部

Molecular cloning and analysis of  $\beta$ -etherase gene of *Pseudomonas paucimobilis* SYK-6

Eiji Masai<sup>\*1</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Makari Yamasaki<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Faculty of Agriculture, the University of Tokyo

Abstract:  $\beta$ -Aryl ether cleavage is essential to the biological degradation of lignin. In this study, we succeeded in the first isolation of  $\beta$ -etherase gene from cosmid genomic library of *Pseudomonas paucimobilis* SYK-6. 1.9 kbp *Sal* I fragment encoding  $\beta$ -etherase was subcloned into pUC19 and pTTQ19. This gene was expressed in *E. coli* and expressed products were analyzed. Analysis of nucleotide sequence of this gene is carrying out.

1990-216

フェニルアラニンアンモニアリアーゼとその遺伝子

黒田宏之

京都大学木材研究所

Phenylalanine ammonia-lyases and their genes.

Hiroki Kuroda

Wood Research Institute, Kyoto University

Abstract: PAL and the genes were preliminary examined before studying PAL genes from woody plants. First, GenBank and EMBL databases were surveyed by using IDKAS for the primer design in relation to PCR amplification of the genes. Some of the primers were successfully applied to the *Hind*III digested DNA fragment from IPBPAL (sweet potato). The PCR products cover ca. 200 bp fragments localized on the high homologous region. Further studies are now on progress. Secondary, visualizing PAL activities, especially on the PAGE gel, was intended by using fluorescent TLC plate. The product was not visualized on the gel, to which crude enzyme extract was charged, but the method worked before the PAGE. The threshold concentration for the detection was less than 0.2 mM, which is equivalent to <0.2 nmole/ml. Detecting the product on the gel may need more sensitive another method.

1990-217

PCRを用いたフェニルアラニンアンモニアリアーゼ遺伝子の解析

山門幹子<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>

\*1 東京農工大学農学部、\*2 東京農工大学共同研究開発センター

Phenylalanine ammonia-lyase genes isolated by PCR method.

Mikjko Yamakado\*1, Shinya Kawai\*1, Yoshihiro Katayama\*2, Noriyuki Morohoshi\*1

\*1 Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*2 Cooperative Research Center, Tokyo University of Agriculture and Technology

Abstract: Polymerase chain reaction (PCR) is an *in vitro* method for the primer-directed enzymatic amplification of specific DNA sequences. We have used this technique to isolate phenylalanine ammonia-lyase (PAL) genes. The primers corresponding to highly conserved regions of the PAL genes were used and amplified partial genomic clones from poplar and tobacco plants. The nucleotide sequences of PCR products showing ~78.9% similarity with those of PAL genes for bean and parsley, and 89% similarity at the deduced amino acid level.

1990-218

アンチセンス RNA 法によるペルオキシダーゼの発現抑制

刑部敬史\*1、川合伸也\*1、片山義博\*2、諸星紀幸\*1

\*1 東京農工大学農学部、\*2 東京農工大学共同研究開発センター

Antisense RNA inhibition of peroxidase gene expression in transgenic tobacco.

Keishi Osakahe, Shinya Kawai, Yoshihiro Katayama, Noriyuki Morohoshi.

\*1 Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*2 Cooperative Research Center, Tokyo University of Agriculture and Technology

Abstract: In order to inhibit of lignin forming peroxidase activities, we have attempted to introduce of antisense peroxidase gene into *N. tabacum*. Peroxidase isoenzymes were extracted from transformants and separated by isoelectric focusing. From the results of isoelectric focusing, dramatic changes were not observed between isoenzyme patterns of wild type and those of transformants. And we obtained 9 clones containing parts of tobacco peroxidase genes (TPOX genes) by polymerase chain reaction method. Parts of TPOX genes were determined.

1990-219

*Agrobacterium tumefaciens* による樹木形質転換系の確立

梶田真也\*1、川合伸也\*1、片山義博\*2、諸星紀幸\*1、我彦広悦\*3、佐野 浩\*3、秦 邦男\*4

\*1 東京農工大学農学部、\*2 東京農工大学共同研究開発センター、\*3 秋田県立農業短期大学、\*4 十条製紙株式会社

Construction of transformation system of woody plant using *Agrobacterium tumefaciens*.

Shinya Kajita\*1, Shinya Kawai\*1, Yoshihiro Katayama\*2, Noriyuki Morohoshi\*1, Hiroetu Wabiko\*3, Hiroshi Sano\*3, Kunio Hata\*4

\*1 Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*2 Cooperative Research Center, Tokyo University of Agriculture and Technology, \*3 Akita Prefectural College of Agriculture, \*4 Jujo Paper Co., LTD

Abstract: Poplar leaf disks were inoculated with *Agrobacterium tumefaciens* LBA 4404 carrying a disarmed Ti plasmid vector pB1121. T-DNA of this plasmid encodes two genes, one is neomycin phosphotransferase II gene and the other is  $\beta$ -glucuronidase gene. The leaf disks were then transferred to selective medium containing kanamycin. Transformed callus were obtained within 10 days, and maintained by fortnightly subculture. These transformants stained with X-Gluc., while untransformed callus contrastively didn't. This transformation system will contribute to the genetic engineering of woody plants.

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1991-101

急速凍結置換固定法による細胞壁木化過程の観察

猪股書恵、高部圭司、佐伯 浩

京都大学農学部

Observations on lignification process of cell wall by rapid-freeze and substitution method.

Fumie Inomata, Keiji Takabe, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Abstract: Lignification process of cell wall in conifer tracheid was observed by rapid-freeze and substitution method. The ultrastructural images indicate that the wall materials of newly deposition form an amorphous thin layer lining the cell wall. This layer consists of polysaccharides and much water. Subsequently cellulose microfibrils and hemicelluloses may be assembled to form hydrophilic ordered structure. Lignified region of the wall hardly suffers the ice crystal damage, showing that lignification cause the removal of water from unligified cell wall. In the later stage of secondary wall lignification, egg-shaped rough- and/or smooth endoplasmic reticula appear in cytosol. They may participate in biosynthesis and/or transport of lignin precursor.

1991-102

広葉樹の生育地・管孔配列・細胞壁厚とリグニン成分

呉 晋、深沢和三、大谷 諒

北海道大学農学部

Lignin composition in hardwoods in relation to habitat, porosity and cell wall thickness in wood.

Jing Wu, Kazumi Fukazawa, Jun Ohtani

Faculty of Agriculture, Hokkaido University

Abstract: Guaiacyl (G) and syringyl (S) lignins were detected by VIS microspectrophotometry using Mäule color reaction test. 110 hardwood species in 94 genera and 51 families from 3 habitats of Yunnan, China, have been investigated. The monomer composition of lignin in a particular area of wood tissue was influenced by the kind of cell elements, vessel arrangement of woods, tree habitat and cell wall thickness. GS ratio among certain cells or tree could not be fixed by this method, but a rough estimation of it was made by the analysis from the spectrum. The variations may suggest the evolutionary stages of tree phylogeny.

1991-103

カエデ属におけるリグニン分布の多様性

平井陽子、深沢和三、呉 晋

北海道大学農学部

Distribution of lignins on the genus *Acer*.

Yoko Hirai, Kazumi Fukazawa, Jing Wu

Faculty of Agriculture, Hokkaido University

Abstract: Distribution of lignins on the genus *Acer* was investigated by Mäule reaction, Klason method and nitrobenzene oxidation. The Klason lignin content ranges from 20 to 25%, but some species have very high lignin contents (28-30%). The syringaldehyde-vanillin ratio (S/V) ranges from 0.3 to 3.0. The species which has higher lignin content has lower S/V values. All species were classified into 7 types by these results and absorption spectra of Mäule reaction.

1991-104

タケ、ササ細胞壁中のいくつかの成分について

橘 燦郎<sup>\*1</sup>、大久保克美<sup>\*1</sup>、G.H.N. Towers<sup>\*2</sup>

<sup>\*1</sup> 愛媛大学農学部、<sup>\*2</sup> ブリティッシュコロンビア大学

Some phenolic components of the cell walls of bamboos (*Phyllostachys edulis* and *Phyllostachys bambusoides* Sieb. et Zucc.) and bamboo grass (*Sasa kurilensis* Makino et Shibata).

Sanro Tachibana<sup>\*1</sup>, Katsumi Ohkubo<sup>\*1</sup>, G.H.N. Towers<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Ehime University, <sup>\*2</sup> Department of Botany, The University of British Columbia, Canada

Abstract: 4,4'-Dihydroxytruxillic acid (DTA), a photodimer of *p*-coumaric acid, and 4,4'-dihydroxy-3,3'-dimethoxytruxillic acid (FAD), a photodimer of ferulic acid, were identified as components of the cell walls of stems and leaves of the bamboo (*Phyllostachys edulis*) and the bamboo grass (*Sasa kurilensis* Makino et Shibata). Caffeic acid, sinapic acid, 5-hydroxyferulic acid as well as *p*-coumaric acid and ferulic acid were also identified. The amounts were determined by peak areas using GC/MS with stearyl alcohol as an internal standard. Existence of the two feruloyl esters, O-(5-feruloyl- $\alpha$ -L-arabinofuranosyl)-(1 $\rightarrow$ 3)-O- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 4)-D-xylopyranose and 5-O-feruloyl- $\alpha$ -L-arabino-furanose, in the hydrolysis products of the bamboo (*Phyllostachys bambusoides* Sieb. et Zucc.) cell walls was confirmed on TLC plate through comparison of the R<sub>f</sub> values with that of authentic samples.

1991-105

ヘミセルロース中におけるシナピルアルコールの脱水素重合

吉田晋一、棚橋光彦、篠田善彦

岐阜大学農学部

Dehydrogenative polymerization of sinapyl alcohol in hemicelluloses solutions.

Shinichi Yoshida, Mitsuhiko Tanahashi, Yoshihiko Shinoda

Faculty of Agriculture, Gifu University

Abstract: In a plant cell wall, lignin was deposited in the matrix of polysaccharides through the lignification process. To demonstrate the effect of hemicelluloses on dehydrogenative polymerization, sinapyl alcohol was dehydrogenated with horseradish peroxidase/H<sub>2</sub>O<sub>2</sub> in the presence of pectin by Zulaufverfahren. Main reaction products, which were syringylglycerol- $\beta$ -sinapyl alcohol ether, syringaresinol and unknown compound, were isolated after the acetylation by PTLC and analyzed by NMR and MS spectrometry. As a results, unknown compound identified 1,5-di(3,5-dimethoxy-4-hydroxyphenyl)-4-hydroxymethyl-5-hydroxy-1-pentene ( $\beta$ - $\gamma$  type). This substructure would be presented in native lignin, and generated by ionic reaction through the extended quinone-methide-intermediate.

1991-106

リグニン-グルクロン酸間エステル結合の酸化的開裂とその定量分析への応用

今村剛士<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>、桑原正章<sup>\*1</sup>、越島哲夫<sup>\*2</sup>

<sup>\*1</sup> 京都大学木質科学研究所、<sup>\*2</sup> 近畿大学農学部

Oxidative cleavage of ester linkages between lignin and glucuronic acid and its application to their quantitative analysis.

Takeshi Imamura<sup>\*1</sup>, Takashi Watanabe<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>, Tetuo Koshijima<sup>\*2</sup>

<sup>\*1</sup> Wood Research Institute, Kyoto University, <sup>\*2</sup> Faculty of Agriculture, Kinki University

Abstract: Conjugated acid between 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and protonic acid, which is more electrophilic than DDQ, was subjected to the oxidative cleavage of ester bonds between alkylaromatic compounds and glucuronic acid. When DDQ-TFA conjugate was

allowed to react with benzylglucuronate, the ester bonds were quantitatively cleaved, while ethyl glucuronate was inert to the reaction due to its high oxidation potential. Application of the selective oxidation to the determination of lignin-glucuronic acid bonds in lignin-carbohydrate complexes (LCCs) is reported.

1991-107

イネのリグニンの  $^{13}\text{C}$  による選択的標識

謝 益民、寺島典二

名古屋大学農学部

Selective  $^{13}\text{C}$  enrichment of rice stalk lignin

Yimin Xie, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Abstract: Carbon-13 enrichment of a specific carbon of rice stalk lignin was carried out by administration of coniferin- $[\alpha-^{13}\text{C}]$  and 4-O- $\beta$ -D-glucoferulic acid- $[\alpha-^{13}\text{C}]$  to a growing rice plant. The  $^{13}\text{C}$  content of a side chain  $\alpha$ -carbon of rice stalk lignin reached about 10 times of the natural abundance. In the  $^{13}\text{C}$ -NMR spectra of cellulolytic enzyme lignin and acetal lignin showed intense signals corresponding to  $\alpha$ -carbons. The enhanced signals provide useful information about structure of lignin and the linkages between lignin and carbohydrates in rice plant.

1991-108

ラジオトレーサー法によるリグニン試料中の残留炭水化物量の測定

今井貴規、寺島典二

名古屋大学農学部

Quantitative determination of the residual carbohydrate in lignin-preparations by radiotracer technique.

Takanori Imai, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Abstract: When myo-inositol- $[2-^3\text{H}]$  was administered to a magnolia shoot, radioactivity was mainly incorporated into xylose obtained by sulfuric acid hydrolysis of newly formed xylem, whereas, no radioactivity was incorporated into vanillin and syringaldehyde obtained by nitrobenzene oxidation. This result indicates that xylan was labeled selectively in the tissue. To estimate the amount of residual carbohydrate remaining in Klason lignin, the xylan-labeled wood tissue was treated with sulfuric acid, and the radioactivity of the insoluble solid lignin was determined. The amount of residual carbohydrate originating from xylan in Klason lignin was estimated to be about 8 %.

1991-109

マイクロオートラジオグラフ法による樹幹先端部の木部分化とリグニン不均一形成に関する研究

福島和彦<sup>\*1</sup>、寺島典二<sup>\*1</sup>、高部圭司<sup>\*2</sup>

<sup>\*1</sup>名古屋大学農学部, <sup>\*1</sup>京都大学農学部

Heterogeneous lignification during the apical growth of magnolia shoot studied by microautoradiography

Kazuhiko Fukushima<sup>\*1</sup>, Noritsugu Terashima<sup>\*1</sup>, Keiji Takabe<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>Faculty of Agriculture, Kyoto University

Abstract: Heterogeneous formation of lignin in the primary xylem of magnolia was visualized by microautoradiography and UV microscopy. Protoxylem in the vascular bundle consists of some vessels with lignified spiral secondary wall and undifferentiated parenchyma whose lignification is much delayed than other kind of cells. The cells around the primary xylem were differentiated to be

thick wall cells and lignified after the formation of secondary xylem. UV spectra showed that the vessel wall lignin of primary xylem was similar to that of secondary xylem and that pith lignin was similar to fiber secondary wall lignin which is syringyl-rich. It is proposed that lignification in the elongating shoot would proceed in accordance with cell differentiation under definite controlled manner.

1991-110

リグニン化学構造の不均一性

深川伸隆、飯塚堯介、西山正樹、石津 敦

東京大学農学部

Structural inhomogeneity of lignin

Nobutaka Fukagawa, Gyosuke Meshitsuka, Masaki Nishiyama, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Abstract: Structural inhomogeneity of lignin was clearly demonstrated by the isolation of two distinctive lignin fractions from birchwood periodate lignin. The first one is a predominately syringyl-rich, mostly  $\beta$ -O-4 linked lignin fraction, which has a molecular weight of not lower than a milled wood lignin. The second one is a low molecular weight fraction of guaiacyl-rich and highly condensed structure.

1991-111

核交換および過ヨウ素酸酸化の併用によるリグニン芳香核構造の解析

船岡正光<sup>\*1</sup>、Y.-Z. Lai<sup>\*2</sup>

<sup>\*1</sup> 三重大学生物資源学部、<sup>\*2</sup>NewYork 州立大、ESPRI

Structural analysis of lignin by a combined nucleus exchange - periodate oxidation method.

Masamitsu Funaoka<sup>\*1</sup>, Y.-Z. Lai<sup>\*2</sup>

<sup>\*1</sup>Faculty of Bioresources, Mie University, <sup>\*2</sup>Empire State Paper Research Institute, State University of New York

Abstract: The phenolic hydroxyl group is one of the most important functionalities significantly affecting the reactivity of lignin during various modification processes. The free phenolic hydroxyl content of lignin has been estimated by several methods such as UV and NMR spectroscopies, potentiometric titration or periodate oxidation. However, these conventional processes give only the data on its total amount. The combined nucleus exchange-periodate oxidation method provides the quantitative information on the distribution of phenolic hydroxyl group in guaiacyl and syringyl, condensed and non-condensed, and diphenylmethane type units which are important as secondarily formed condensed structures. In the present paper, the theory, the procedure, and its application to softwood and hardwood protolignins, isolated lignins and pulp residual lignins are discussed.

1991-112

TMSiI 処理によるリグニン中めエーテル結合の選択的開裂 -低分子生成物の性状

藤野謙一、飯塚堯介、石津 敦

東京大学農学部

Selective cleavage of ether bonds in lignin by trimethylsilyl iodide. - The character of the low molecular weight products -

Kenichi Fujino, Gyosuke Meshitsuka, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Abstract: Trimethylsilyl iodide cleaves ether bonds in lignin selectively under very mild reaction conditions. Applying this agent to guaiacylglycerol- $\beta$ -guaiacyl ether as a model compound, it has been

proposed that the cleavage reaction results from the iodination of the benzyl carbon followed by the formation of a  $\alpha$ - $\beta$  double bond and the cleavage of the  $\beta$ -aryl ether bond. In this paper we applied this agent to a periodate lignin. Some acetate derivatives of the degradation products were separated by TLC and analyzed by means of GC-MS.

1991-113

1,2-ジアリール-1,3-プロパンジオールの塩酸中の挙動

岩瀬幸彦、安田征市

名古屋大学農学部

Behavior of 1, 2-diaryl-1, 3-propanediol in hydrochloric acid.

Yukihiko Iwase, Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: 1,2-Diguaiacyl-1,3-propanediol [ $\alpha$ - $^{13}\text{C}$ ], one of lignin structural models, was synthesized and then treated in refluxing 0.2N hydrochloric acid. The  $^{13}\text{C}$  NMR analysis of the products strongly supported the already proposed reaction mechanism of so-called "acidolysis" and, at the same time, confirmed no rearrangement of a methyl group in contrast with easy rearrangement of a hydrogen atom and a phenyl nucleus. Treatment of models in refluxing 5% hydrochloric acid afforded less low-molecular-weight compounds and more condensation products in comparison with acidolysis. Treatment of the models in concentrated hydrochloric acid recovered the starting compounds together with condensation products and tentative chlorides. These results accord the fact that hydrochloric acid lignin contains less condensed structural unit than sulfuric acid lignin.

1991-114

ウド (*Alaria cordata*) シンナミルアルコールデヒドロゲナーゼの精製

日尾野隆<sup>\*1</sup>、柴田大輔<sup>\*1</sup>、梅沢俊明<sup>\*2</sup>、樋口隆昌<sup>\*3</sup>

<sup>\*1</sup> 三井植物バイオ研究所、<sup>\*2</sup> 京都大学木質科学研究所、<sup>\*3</sup> 日本大学農獣医学部

Isolation and characterization of cinnamyl alcohol dehydrogenase from *Alaria cordata*.

Takashi Hibino<sup>\*1</sup>, Daisuke Shibata<sup>\*1</sup>, Toshiaki Umezawa<sup>\*2</sup>, Takayoshi Higuchi<sup>\*3</sup>

<sup>\*1</sup>Mitsui Plant Biotechnology Research Institute, <sup>\*2</sup>Wood Research Institute, Kyoto University,

<sup>\*3</sup>College of Agriculture and Veterinary Medicine, Nihon University

Abstract: A cinnamyl alcohol dehydrogenase (CAD) from *Alaria cordata* was purified about 2100 fold to homogeneity. The molecular weight of the enzyme was estimated by Superose 12 column to be 72,000. The enzyme preferred cinnamaldehydes and cinnamyl alcohol as substrates. The purified protein was subjected to BrCN cleavage and the resulting peptides were separated using reverse-phase HPLC for amino acid sequencing.

1991-115

エレクトロポレーション法によるアンチセンス PAL 遺伝子のタバコへの導入

日尾野隆<sup>\*1</sup>、伊藤恵美子<sup>\*1</sup>、柴田大輔<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>、永井伸夫<sup>\*3</sup>、下坂 誠<sup>\*3</sup>、岡崎光雄<sup>\*3</sup>

<sup>\*1</sup> 三井植物バイオ研究所、<sup>\*2</sup> 日本大学農獣医学部、<sup>\*3</sup> 信州大学応用生物科学科

Phenylalanine ammonia-lyase antisense gene transfer into tobacco by electroporation.

Takashi Hibino<sup>\*1</sup>, Emiko Itoh<sup>\*1</sup>, Daisuke Shibata<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>, Nobuo Nagai<sup>\*3</sup>,

Makoto Shimosaka<sup>\*3</sup>, Mitsuo Okazaki<sup>\*3</sup>

<sup>\*1</sup>Mitsui Plant Biotechnology Research Institute, <sup>\*2</sup>Wood Research Institute, Kyoto University,

<sup>\*3</sup>Faculty of Textile Science and Technology, Shinshu University

Abstract: Phenylalanine ammonia-lyase (PAL) is the key enzyme in the formation of secondary metabolites including lignin precursors. To control the production of lignin in plant cells, we

constructed antisense genes using a PAL cDNA isolated from tobacco suspension cells. They were introduced into tobacco protoplasts by electroporation.

1991-116

ユーカリゲノムライブラリーの作成

日尾野隆, 伊藤恵美子, 柴田大輔

三井植物バイオ研究所

Construction of a genomic library from Eucalyptus (*E. saligna*)

Takashi Hibino, Emiko Itoh, Daisuke Shibata

Mitsui Plant Biotechnology Research Institute

Abstract: We isolated genomic DNA from callus of Eucalyptus using CTAB (cetyltrimethylammonium bromide). DNA fragments which was partially digested with Sau3AI were ligated with EMBL3. The DNAs were packaged into phage particles to obtain a genomic library, resulting one million recombinants.

1991-117

交雑ヤマナラシの宿主・ベクター系の構築及びアンチセンス RNA 法によるリグニン生合成の解析  
梶田真也<sup>\*1</sup>、三浦 進<sup>\*1</sup>、山門幹子<sup>\*1</sup>、山田恵子<sup>\*2</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、秦 邦男<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 十条製紙株式会社

Agrobacterium-mediated transformation of poplar and using antisense or sense gene fragment to study gene function of lignin biosynthesis.

Shinya Kajita<sup>\*1</sup>, Susumu Miura<sup>\*1</sup>, Mikiko Yamakado<sup>\*1</sup>, Keiko Yamada<sup>\*2</sup>, Shinya Kawai<sup>\*1</sup>

Yoshihiro Kataywa<sup>\*2</sup>, Kunio Hata<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup> Jujo Paper Co. Ltd.

Abstract: The long generation time of the tree means that genetic improvement by classical breeding is a slow process. Genetic engineering should be helpful in solving this problem. We have established a transformation system mediated binary vector of non-oncogenic *Agrobacterium tumefaciens* LBA4404 and applied this system to a analysis of the functional relationships of genes encoding enzymes of lignin biosynthesis pathway. So we introduced antisense and sense gene fragment into poplar hybrid clone and tobacco.

1991-118

リグニンモデル化合物分解酵素遺伝子のクローニング. XVIII.  $\beta$ -エーテラーゼ遺伝子の塩基配列と C $\alpha$ -デヒドロゲナーゼ遺伝子のクローニング

政井英司<sup>\*1</sup>、窪田祥子<sup>\*1</sup>、片山義博<sup>\*2</sup>、川合伸也<sup>\*1</sup>、山崎真狩<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 東京大学農学部

Cloning of the genes involved in degradation of lignin model compounds (XVII). Sequencing of the  $\beta$ -etherase gene and cloning of the C $\alpha$ -dehydrogenase gene from *Pseudomonas paucimobilis* SYK-6.

Eiji Masai<sup>\*1</sup>, Sachiko Kubota<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Shinya Kawai<sup>\*1</sup>, Makari Yamasaki<sup>\*3</sup>,

Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup> Faculty of Agriculture, the University of Tokyo

Abstract: We have isolated *Pseudomonas paucimobilis* SYK-6 which could grow on various lignin dimeric compounds as a sole carbon source. Cleavage of  $\beta$ -aryl ether is the most important

process in the lignin degradation because this linkage is the most abundant. We have already reported the detection of the activity of  $\beta$ -etherase in a cellular membrane fraction of *P. paucimobilis* SYK-6. This enzyme catalyzed the unique and reductive cleavage of arylglycerol- $\beta$ -aryl ether (C $\alpha$  carbonyl type). Here, we report the sequencing of the  $\beta$ -etherase gene. This gene contains an open reading frame of 843bp and the molecular weight of deduced protein is 32,070. We named this gene ligE. The polypeptide expressed in *Escherichia coli* transformant was identified. In addition, we also found the C $\alpha$ -dehydrogenase gene (ligD) for which the enzyme catalyzes the C $\alpha$ -dehydrogenation of arylglycerol- $\beta$ -aryl ether (C $\alpha$  alcohol type) in the 24kb Sal I fragment containing ligE.

1991-119

リグニンモデル化合物分解酵素遺伝子のクローニング(XIX) ビフェニル型化合物分解に関する遺伝子の単離と解析

花城 薫<sup>\*1</sup>、政井英司<sup>\*1</sup>、片山義博<sup>\*2</sup>、川合伸也<sup>\*1</sup>、西川誠司<sup>\*1\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup>東京農工大学農学部, <sup>\*2</sup>東京農工大学共同研究開発センター, <sup>\*3</sup>コスモ石油株式会社

Cloning of the genes involved in degradation of lignin model compounds. XIX.

Kaoru Hanashiro<sup>\*1</sup>, Eiji Masai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Shinya Kawai<sup>\*1</sup>, Seiji Nishikawa<sup>\*1\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Kosumo Oil Co.Ltd.

Abstract: *Pseudomonas paucimobilis* could grow on various lignin dimeric compounds as a sole carbon source. In particular, it is characteristic of this strain to degrade biphenyl compounds. We have already reported about the metabolism of biphenyl structure in lignin. Here we tried to isolate the gene involved in degradation of biphenyl compounds. We isolated the several mutants of *P. paucimobilis* SYK-6 deficient in degradation of compound (1) and (3). The gene which restore the wild's phenotype of mutants were isolated from cosmid genomic library of *P. paucimobilis* SYK-6.

1991-120

リグノスチルベン- $\alpha, \beta$ -ジオキシゲナーゼ産生遺伝子のクローニングと発現・同定

鴨田重裕、佐分義正

東京大学農学部

Cloning, expression and identification of a lignostilbene- $\alpha, \beta$ -dioxygenase gene from *Pseudomonas paucimobilis* TMY1009.

Shigehiro Kamoda, Yoshimasa Saburi

Faculty of Agriculture, the University of Tokyo,

Abstract: Lignostilbene- $\alpha, \beta$ -dioxygenases (LSDs) are the key enzyme responsible for the cleavage of the interphenyl C $\alpha$ -C $\beta$  double bonds of stilbene type structure in the metabolism of dimeric lignin-related compounds by *Pseudomonas paucimobilis* TMY1009. Though LSD is similar to meta-cleavage dioxygenase in having nonheme iron, LSD is a new type dioxygenase which excels those in stability. To get the knowledge of the primary structure, it is one aim, cloning the gene encoding LSD has been done. The BamHI-KpnI fragment (8kbp) encoding a LSD gene was ligated in pUC19 at the same restriction enzyme site. *E.coli* JM109 carrying this plasmid produced LSD little. In this study, a SalI fragment (1.9kbp) was subcloned, the LSD gene on this fragment was expressed, and the products was identified.

1991-特別講演

リグニン化学における標識実験法

寺島典二

名古屋大学農学部

Invited lecture: Tracer method in lignin chemistry.

Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Abstract: Every wood chemist encounter serious difficulties in investigating the structure and reaction of lignin in the cell wall, because lignin is a structurally inhomogeneous macromolecule and it is impossible to isolate lignin in its unaltered state, or to depolymerize lignin into monomeric or oligomeric building units quantitatively. The nondestructive analysis of lignin labeled selectively with radioisotope or stable isotope at specific hydrogen and/or carbon gives useful information that is not obtained by any other methods. An outline and discussion are given of the recent advances in application of this technique to the studies on formation, structure and reaction of lignin in the cell wall.

1991-201

カワラタケが分泌するリグニン分解酵素とタンパク分解酵素の関係について -リグニン分解性ラッカーゼ (III) の糖鎖の役割

中村雅哉<sup>\*1</sup>、西田篤実<sup>\*1</sup>、吉武彰文<sup>\*2</sup>、片山義博<sup>\*3</sup>、飯村洋介<sup>\*3</sup>、諸星紀幸<sup>\*3</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> ヘキストジャパン、<sup>\*3</sup> 東京農工大学農学部

Production of ligninolytic laccase and proteolytic enzymes in *Coriolus versicolor*.

Masaya Nakamura<sup>\*1</sup>, Atsumi Nishida<sup>\*1</sup>, Akifumi Yoshitake<sup>\*2</sup>, Yoshihiro KaLayama<sup>\*3</sup>,

Yousuke limura<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*3</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Haechst Japan Ltd., <sup>\*3</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: Ligninolytic laccase ( laccase III ) from *Coriolus versicolor* was known to be anionic glycoprotein. Structural analysis of this enzyme showed that laccase III contained at least four N-linked carbohydrate chains. Judging from the time course changes of laccase and protease activities in the culture fluids containing tunicamycin, these four carbohydrate chains had a protective function to maintain enzymatic activity under proteolytic condition. In particular, high proteolytic activity was identified in nitrogen starved culture filtrates. Partial characterization of proteases induced by nitrogen starvation stress is carrying out.

1991-202

リグニンパーオキシターゼの触媒サイクル

桃原郁夫、松本雄二、石津 敦

東京大学農学部

Catalytic cycle of lignin peroxidase.

Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Abstract: The formation of super oxide during the lignin peroxidase (Li-P) reaction was confirmed by the reaction of super oxide with tetranitromethane (TNM). In the presence of H<sub>2</sub>O<sub>2</sub>, veratryl alcohol, Mn<sup>2+</sup>, and TNM, trinitromethane anion was perhaps only one product by the Li-P reaction and veratraldehyde formation is not found. The same result was obtained when the above reaction was carried out under a nitrogen atmosphere. On the other hands, veratraldehyde was formed under the same condition as the above when *m*-chloroperbenzoic acid (CPBA) was used as an oxygen donor. Oxygen consumption which was observed during the Li-P reaction with veratryl alcohol, Mn<sup>2+</sup>, and H<sub>2</sub>O<sub>2</sub> was not observed in the presence of CPBA instead of H<sub>2</sub>O<sub>2</sub>. These results

strongly suggest that super oxide formation and oxygen uptake are independent of the substrate radicals.

1991-203

広葉樹培養細胞のリグニン生成とペルオキシターゼアイソザイムの基質特異性について(その3)

堤 祐司、坂井克己

九州大学農学部

Lignin biosynthesis and substrate specificity of peroxidase isoenzymes with respect to syringyl and guaiacyl structure in angiosperm tree callus cultures. III.

Yuji Tsutsumi, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We have been investigating the possibility that substrate specificities of peroxidases can control syringyl/guaiacyl ratio of lignin in xylem tissues. It was found that the syringyl specific peroxidase (SyPO) was present in the ionically bound peroxidase (IPO) group extracted from callus culture of *Populus alba*. This SyPO isoenzyme specifically catalyzed the hydrogen peroxide-oxidation of syringyl substrates such as syringaldazine and 2,6-dimethoxyphenol but not the dehydrogenative polymerization of coniferyl alcohol. The IPO group from a *Populus alba* tree also exhibited the highest specificity for syringyl substrate among three peroxidase groups in both spring and summer. Whole peroxidase activities, especially syringyl oxidizing activity of IPO were decreased in summer.

1991-204

カワラタケによるリグニンモデル化合物のフェノール性水酸基のキシロース配糖化

山上 陽、近藤隆一郎、坂井克己

九州大学農学部

Xylosidation of phenolic hydroxyl group of lignin model compounds by *Coriolus versicolor*.

Hikari Yamagami, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: In previous reports we showed that primary alcoholic hydroxyl groups of lignin model compounds were bioconverted into their xylosides, in glucose media that were inoculated with *Coriolus versicolor*. In the present work, the xylosidation of phenolic hydroxyl group of lignin model compounds was investigated. When added to a culture of *C. versicolor*, methyl-guaiacol (MeG), a phenolic lignin model compounds, was bioconverted into 2-methoxy-4-methylphenyl- $\beta$ -D-xyloside (MeG-Xyl). The formation of HG-Xyl was also observed in holocellulose media. When the cultivation was performed under nitrogen atmosphere to avoid the rapid consumption of MeG by laccase in the medium 28% of MeG was bioconverted into MeG-Xyl for 24 hours. Therefore, it can be concluded that not only alcoholic but phenolic hydroxyl group of lignin model compounds were transformed into their xylosides by *C. versicolor*. Furthermore, it was observed that the xyloside formation activity of *C. versicolor* was activated by the exogenous addition of phenolic compounds into the medium.

1991-205

バイオミメティックフタロシアニン鉄錯体による $\beta$ -O-4型リグニンモデル化合物の酸化分解  
谷原佳文<sup>\*1</sup>、服部武文<sup>\*1</sup>、(信大織)白井江芳<sup>\*2</sup>、島田幹夫<sup>\*2</sup>

<sup>\*1</sup> 京都大学木質科学研究所, <sup>\*2</sup> 信州大学繊維学部、

The biomimetic degradation of  $\beta$ -O-4 lignin model dimers by t-BuOH in the presence of octacarboxyphthalocyaninato-iron (III) catalyst.

Yoshifurmi Tanihara<sup>\*1</sup>, Takefumi Hattori<sup>\*1</sup>, Hirofusa Shirai<sup>\*2</sup>, Mikio Shimada<sup>\*1</sup>

\*<sup>1</sup>Wood Research Institute, Kyoto University, \*<sup>2</sup>Faculty of Textile Science and Technology, Shinshu University

Abstract: The biomimetic degradation of a  $\beta$ -O-4 lignin substructure model dimer, 4-ethoxy-3-methoxy-aryl-glycero- $\beta$ -vanillyl alcohol ether (I), by *tert*-butylhydroperoxide in the presence of octacarboxyphthalocyaninato-iron (III) (Fe(III)Pc) was investigated. The substrate (I) was oxidatively degraded by catalysis of Fe(III)Pc in aqueous solution at pH 3 at room temperature. This catalyst was found to mimic a lignin peroxidase (LiP) activity, yielding both C-C bond cleavage and aromatic ring opening products derived from  $\beta$ -O-4 substrate (I). The  $\beta$ -O-4 dimer (II) formed from substrate (I) was also degraded to give C-C bond cleavage products, vanillin and 4-O-ethylvanillic acid, in alkaline solution at room temperature.

1991-206

硫酸触媒を用いた広葉樹材の常圧酢酸パルプ化 -高分子リグニンの利用研究のための多量リグニン簡易分離法としての評価

堀崎敬史、島谷啓二、佐野嘉拓、笹谷宜志

北海道大学農学部

Pulping of hardwoods at atmospheric pressure with aqueous acetic acid containing a small amount of sulfuric acid -Characterization of resulting acetic acid lignins as raw materials for utilization studies of polymeric lignins.

Yoshifumi Horisaki, Keiji Shimatani, Yoshihiro Sano, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Abstract: Acetic acid lignins (AWL) can be produced without tedious operation and in quantity from the reaction solution obtained by atmospheric pulping with aqueous acetic acid containing a small amount of sulfuric acid. Therefore, the lignins may be used in the utilization studies of lignins with large quantities, if they are modified less greatly during the pulping. To determine the possibility, the chemical structure of AWLs was characterized by the elemental analysis, analysis of functional groups by <sup>1</sup>H-NMR and other methods, several degradation procedures average molecular weights and so forth.

1991-207

広葉樹クラフトパルプ中のキシランとリグニンの関係

種田英孝、松倉紀男、秦邦男

十條製紙

Characterization of xylan and lignin in hardwood kraft pulp

Hidetaka Taneda, Motoo Matsukura, Kunio Hata

Jujo Paper Co., Ltd.

Keywords: 広葉樹クラフトパルプ・ヘミセルロース・キシラン・リグニン・カッパー価・未晒パルプ  
hardwood kraft pulp, hemicellulose, xylan, lignin, kappa number, unbleached pulp

Abstract: Relation between lignin and xylan in hardwood kraft pulp was investigated. From the unbleached pulp and oxygen delignified pulp, xylan was isolated, and then lignin contents in these fractions, xylylans, extracted pulps and extraction liquors were measured by the use of Kappa number method. In the case of chlorine and alkali treated pulp and bleached pulp, chlorine contents of the fractions were measured instead of the lignin contents. These results show that about half of the residual lignin in kraft pulp exists in xylan fraction. It may suggest that the lignin should be linked with xylan chemically.

1991-208

酸素・アルカリ脱リグニン過程における炭水化物の崩壊機構(1)糖の分解に及ぼすリグニンの影響  
についてのモデル実験

安本光夫、松本雄二、石津 敦  
東京大学農学部

Effects of lignin structure on carbohydrate degradation during oxygen bleaching.

Mitsuo Yasumoto, Yuji Matsunoto, Atsushi Ishizu

Faculty of Agriculture, The University of Tokyo

Abstract: Methyl  $\beta$ -D-glucopyranoside (Me $\beta$ G) was treated with oxygen under an oxygen bleaching condition in the presence or absence of various types of lignin model compounds as well as waste liquor lignin obtained by oxygen bleaching of pine kraft pulp. When lignin model compounds were absent, Me $\beta$ G wasn't degraded at all. In the presence of phenolic lignin compounds without  $\alpha$ -carbonyl group, Me $\beta$ G was degraded to a significant extent, which was proportional to the amount of added model compounds. Whereas the whole waste liquor lignin didn't show any degradation effect, its high molecular weight fraction showed strong effect on the Me $\beta$ G degradation.

1991-209

酸素酸化パルプ化による稲わらリグニンの変化(1)

陳 克利、伊藤博徳、林 治助  
北海道大学工学部

Variation of rice straw lignin with NaOH-O<sub>2</sub> pulping.

Ke-Li Chen, Hironori Itoh, Jisuke Hayashi

Faculty of Engineering, Hokkaido University

Abstract: Rice straw is readily pulped by oxygen oxidation after alkali soaking. To investigate changes of lignin and polysaccharides during the pulping, waste liquors of soaking and pulping were subjected to a series of extraction of acid-precipitated solid (AP), acid-soluble lignin (ASL) and polysaccharides, and then were analyzed. Because of the existence of nitrogen in the straw, all the products contained nitrogen. Purified AP from soaking waste liquor did not contain nitrogen, but pulped lignin still retained high content of nitrogen, nearly equal to 5 times that of the straw. It also showed that the lignin subject to oxidation was degraded to a great extent.

1991-210

アルカリ・アルコール・アントラキノン蒸解について

阿部善作  
九州大学農学部

Alkali-alcohol-anthraquinone pulping.

Zensaku Abe

Faculty of Agriculture, Kyushu University

Abstract: This investigation was carried out to obtain better understandings of alkali-alcohol-anthraquinone pulping. It was compared with other pulpings; alkali-alcohol pulping, alkali-anthraquinone pulping, and kraft pulping. As the results were shown in Fig.1, alkali-alcohol-anthraquinone pulping can produce unbleached pulp of the lowest lignin content at high pulp yield.

1991-211

アルコール・バイサルファイト処理によるリグニンモデル化合物の $\beta$ -O-4結合開裂反応の特徴(その2)

宮脇正一、坂井克己

九州大学農学部

Characteristics of the  $\beta$ -O-4 bond cleavage reaction during an alcohol-bisulfite treatment of lignin model compounds (II)

Shoichi Miyawak, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: Lignin model compounds shown in Fig.1 were synthesized and subjected to alcohol-bisulfite (AB) treatment and alcohol-phosphate buffer (AP) treatment at 160°C for 30 and 60 min. Substituents at the position para to the  $\beta$ -O-4 bond in the ring A provided no large influence on yields of isoeugenol and phenols derived from the ring B that were produced by the  $\beta$ -O-4 bond cleavage in the AB treatment. Recovery of starting materials after the AB treatment was about the same as those after the AP treatment of the same compounds. We now presume that the  $\beta$ -O-4 bonds in phenolic lignin units are cleaved homolytically during the AB treatment. Radical intermediates formed by the homolysis may be stabilized by a rapid electron transfer from bisulfite anions and/or bisulfite radicals.

1991-212

リグニンのメカノケミストリー (XII) (5,5')-( $\beta$ -O-4)型三量体リグニンモデル化合物の合成とそのメカノケミストリー

伊藤和貴、住本昌之

九州大学農学部

Mechanochemistry of lignin. XII. -Synthesis and mechanochemical conversions of (5-5')-( $\beta$ -O-4) type of trimer lignin model compound.

Kazutaka Itoh, Masashi Sumimoto

Faculty of Agriculture, Kyushu University

Abstract: Trials for the improved method of synthesis of (5-5')-( $\beta$ -O-4) type of trimeric lignin model compounds (I) and (II) were made by application of benzyltri-n-butylammonium bromide as a phase-transfer catalyst. Mechanochemical treatments of the model compound (I) with VBM and CBM furnished a (5-5')-( $\beta$ -O-4) type of trimer having a para-carbonyl phenol (III), and a pair of oxidation products of 3-methoxy-5-substituted para-benzoquinone (IV), and 2-(2-methoxy-phenoxy)-3-hydroxypropionic acid (V), and the other product (VI).

1991-213

リグニンのメカノケミストリー (XIII) Veratrylglycerol- $\beta$ -syringaldehyde ether の反応とその機構について

呉 宗華、住本昌之

九州大学農学部

Mechanochemistry of lignin. XIII. Mechanochemical reductions and mechanisms of veratrylglycerol- $\beta$ -syringaldehyde ether.

Wu Zonghua, Masashi Sumimoto

Faculty of Agriculture, Kyushu University

Abstract: To clarify the mechanochemical reaction mechanisms of veratrylglycerol- $\beta$ -syringaldehyde ether (M), comparative treatments of the compound (M) were made with VBM under nitrogen or air. Treatments under nitrogen resulted in the significant decrease in the yields of 3,5-dimethoxy-*p*-hydroquinone and 3,5-dimethoxy-*p*-benzoquinone but a little increase in the yields of syringaldehyde compared to those under air. This strongly suggested that  $\cdot\text{O}_2\text{H}$  radical is formed in the aqueous media to react with syringaldehyde moiety. Addition of normal paraffin alcohols served as  $\cdot\text{OH}$  radical scavengers showed that the mechanochemical reactions were heavily retarded. The

formation of adduct of phthalic hydrazide with  $\cdot\text{OH}$  radical fully confirmed the presence of  $\cdot\text{OH}$  radical in the aqueous media of VBM during the treatments. Likely to those in the media of super sound, the aqueous media of mechanical pulping produces  $\cdot\text{O}_2\text{H}$ ,  $\cdot\text{H}$ , and  $\cdot\text{OH}$  radicals to convert mainly lignin.

1991-214

*Phanerochaete chrysosporium*による塩素化フェノール類の代謝 (2) 塩素置換位置とフェノール性水酸基のメチル化の影響

小野克正、桃原郁夫、松本雄二、石津 敦

東京大学農学部

Metabolism of chlorinated phenols by *Phanerochaete chrysosporium*.

Katsumasa Ono, Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Abstract: When chloroguaiacols were treated with lignin peroxidase (Li-P) in the presence of veratryl alcohol (VA), they were oxidized easily and oxidation of VA does not proceed until the reaction of chloroguaiacol was completed, indicating that VA oxidation is strongly inhibited by chloroguaiacols. On the other hand, chloroveratrol did not show any inhibiting effect on VA oxidation and, even under a very low  $\text{H}_2\text{O}_2$  concentration, spectral change was not observed in the absence of VA. These results coincide with the observation that metabolism of chlorophenols by *P. chrysosporium* are prohibited by methylation reaction which is apparently active throughout the life time of this fungus.

1991-215

リグニン分解菌 (IZU-154 株) によるクラフトパルプ漂白廃液の処理

李 宣鎬<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>、坂井克己<sup>\*1</sup>、西田友昭<sup>\*2</sup>、高原義昌<sup>\*2</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>神戸製鋼株式会社生物研究所

Decolorization of kraft bleaching effluent by the lignin-degrading fungus IZU-154

Seen-Ho Lee<sup>\*1</sup>, Ryuichiro Rondo<sup>\*1</sup>, Kokki Sakai<sup>\*1</sup>, Tomoaki Nishida<sup>\*2</sup>, Yoshimasa Takahara<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, <sup>\*2</sup>Biotechnology Research Laboratory, Kobe Steel, Co. Ltd.

Abstract: In the previous reports, we showed that biomechanical pulping and biobleaching were successfully performed by the treatment with a hyperligninolytic fungus IZU-154. In the present work, we tried to decolorize the bleaching effluent from an alkaline-extraction stage (E1) by the fungus IZU-154. To establish an effective color removal process, various cultivation parameters of IZU-154 and treatment conditions of E1 effluent with the fungus were investigated. Under the best conditions employed here, a treatment with IZU-154 for 24 hours in the presence of a small amount of glucose resulted in 95% reduction of color of an undiluted E1 effluent containing 7,500 color unit. On the other hand, when the effluent was treated with *Phanerochaete chrysosporium* and *Coriolus versicolor* under the same conditions, only 58% and 19% of the color were removed after a 48-hour incubation. The elucidation of the mechanism of color reduction by the fungus IZU-154 is now in progress.

1991-216

機械パルプの微生物処理に関する研究 (VIII) 光退色におよぼすカルボニル基の影響

橘 燦郎<sup>\*1</sup>、神谷英伸<sup>\*1</sup>、足立幸男<sup>\*1</sup>、大久保克美<sup>\*1</sup>、住本昌之<sup>\*2</sup>

愛媛大学農学部、九州大学農学部

Studies on biological treatment of mechanical pulps (VIII)

Effect of carbonyl groups on light-induced color reversion of mechanical pulps

Sanro Tachibana<sup>\*1</sup>, Hidenobu Kamitani<sup>\*1</sup>, Yukio Adachi<sup>\*1</sup>, Katsuni Ohkubo<sup>\*1</sup>, Masashi Sumimoto<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Ehime University, <sup>\*2</sup>Faculty of Agriculture, Kyushu University

Abstract: The effect of carbonyl groups on light-induced color reversion of mechanical pulps was examined. For the first time, reduction of seven model compounds containing  $\alpha$ -carbonyl group with KBH<sub>4</sub> accompanied with or without phase transfer catalyst (PTC) was conducted to find out an effective reduction method for the groups. The model compounds could not be reduced with KBH<sub>4</sub> only, however, the reduction of the model compounds with KBH<sub>4</sub> proceeded significantly by addition of small amount of PTC. Based on the results obtained from the model experiments, mechanical pulps were treated with KBH<sub>4</sub> accompanied with PTC before and after bleaching. Light-induced color reversion of bleached groundwood pulp (GP) was suppressed 33 to 44% by pretreatment of GP with KBH<sub>4</sub> accompanied with PTC. However, in the case of thermomechanical pulp (TMP) and pressurized groundwood pulp (PGW), the depression of the color reversion was 11 to 19% and 11 to 23%, respectively, to that of the untreated pulp. It is suggested that the effect of carbonyl groups on the color reversion of mechanical pulps is not so high.

1991-217

リグノセルロースのリン酸エステル化によるヒドロゲル化(第3報)吸水性に及ぼすリグニンの影響

齊藤直人、関 一人、吉田兼之、青山政和

北海道林産試験場

Hydrogelation of lignocellulosic materials by phosphorylation. III. Effect of lignin content on the water absorbency.

Naoto Saito, Kazuto Seki, Kaneyuki Yoshida, Hasakazu Aoyama

Hokkaido Forest Products Research Institute

Abstract: To investigate the effect of pretreatment with acidic sodium chlorite on swelling behavior of phosphorylated lignocellulosic materials, chlorite treated wood meals containing various amounts of lignin were prepared. In the early stage of delignification, the procedure was quite selective in removing lignin, and no significant change in carbohydrate content was observed. Water absorbency of chlorite treated wood meals followed by phosphorylation with phosphoric acid and urea rapidly increased with increasing degree of delignification during the first 65 %. When wood meals were treated with chlorite three times, maximum water absorbency (141 gH<sub>2</sub>O/g) was obtained. Degree of delignification of the treated wood meals was 65 %, and their carboxyl group content was maximum (0.48 mmol/g). These results indicate that delignification and carboxyl group content of wood meals play an important role in hydrogelation of the phosphorylated products.

1991-218

リグニンのヒドロキシアシル化 (I) リグニンとグリセロールの反応

菱山正二郎<sup>\*1</sup>、大原誠資<sup>\*1</sup>、須藤賢一<sup>\*2</sup>

<sup>\*1</sup>森林総合研究所、<sup>\*2</sup>群馬女子短期大学

Hydroxyalkylation of lignin. I. Reaction of lignin with glycerol.

Shojiro Hishiyama<sup>\*1</sup>, Seiji Ohara<sup>\*1</sup>, Kenichi Sudo<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Gunma Womens Junior College.

Abstract: In the case of the preparation of polyurethane from lignin, it is necessary to modify lignins to the derivatives which possess high reactivity to isocyanates. Then in this study, we tried to introduce alcoholic hydroxyl groups into lignin model compounds. Three kinds of lignin model compounds (phenol, guaiacol, syringol) were treated with glycerol  $\alpha$ -monochlorohydrin. The products having alcoholic hydroxyl groups were identified based on the NMR and MS spectra. The

reaction of these modified model compounds with isocyanates are now carried on.

1991-219

Synthesis and properties of lignin based epoxy resins.

Klaus Hofmann<sup>\*1</sup>, Wolfgang G. Glasser<sup>\*2</sup>

<sup>\*1</sup>Industrial Products Research Institute, Tsukuba, <sup>\*2</sup>Virginia Polytechnic Institute and State University

Abstract: Lignin from steam-exploded yellow poplar wood was chain-extended by hydroxypropylation of the hydroxyl groups. Depending on the amount of propylene oxide used chain-extended hydroxypropyl lignins (CEHPL) with various polyether chain lengths were obtained which had a wide range of viscoelastic properties. Endcapping of the poly(propylene oxide) segments with ethylene oxide and subsequent epoxidation with epichlorohydrin yielded segmented, star-like epoxy resins. Fractionation by precipitation in acetone:hexane solvent systems was carried out to obtain poly(propylene oxide) homopolymer free resins with different molecular weights and narrow molecular weight distributions. Curing of these compounds with m-PDA yielded materials which ranged from elastomers to rigid solids, depending on the molecular weight and the level of chain-extension. Also their mechanical properties showed a wide variation whereby the short chain-extended, high molecular weight materials exhibited strengths and moduli in the same order as those of a commercial DGEBA based resin.

1991-220

リグノセルロース系ポリウレタン分子複合材料の力学的性質

中村邦雄<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>

<sup>\*1</sup>大妻女子大学, <sup>\*2</sup>製品科学研究所

Molecular composites consisting of polyurethanes from lignocellulosics.

Kunio Nakamura<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>

<sup>\*1</sup>Otsuna Women's University, <sup>\*2</sup>Industrial Products Research Institute, Tokyo

Abstract: Solvolysis lignin and wood tar were used in the preparation of molecular composites consisting of paper and polyurethane (PU). The composites of filter paper (FP)-solvolysis lignin (SL)-diphenylmethanediisocyanate (MDI) (FP-SL-MDI), FP-SL-polypropyleneglycol (PPG)-MDI (FP-SL-PPG-MDI), FP-wood tar (WT)-MDI (FP-WT-MDI) and FP-WT-PPG-MDI systems were prepared. Mechanical properties of these composites were investigated by a tensile test machine. The tensile strength of the composites of FP-WT-MDI system increased with increasing the amount of PU/FP (g/g). The maximum stress of the composites was five times higher than that of filter paper. It is found that PPG acts as a soft segment in those systems.

1991-221

リグニン分解物を原料とする液晶性全芳香族ポリエーテルの合成と熱的性質

広瀬重雄<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*1</sup>

<sup>\*1</sup>製品科学研究所、<sup>\*2</sup>織高研

Synthesis and thermal analysis of liquid crystalline aromatic polyethers derived from degradation products of lignin.

Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*1</sup>

<sup>\*1</sup>[Industria] Products Research Institute, <sup>\*2</sup>Research Institute for Polymers and Textiles

Abstract: Aromatic polyethers were synthesized by the condensation of 4,4'-difluoro-3,3'-dinitro-benzophenone with potassium salts of hydroquinone derivatives such as 2,5-dimethoxyhydroquinone, 2,5-dimethylhydroquinone and hydroquinone. Average molecular weights of the

obtained polyethers were in the order of  $10^4$ . Thermal properties of the polyethers were studied by thermogravimetry and differential scanning calorimetry. Polyethers started to decompose at ca. 250 °C and their glass transition temperatures were in the range of 140 °C to 189 °C. The liquid crystalline phase of *p*-chlorophenol solutions of polyethers was observed using a polarizing microscope.

1991-222

バクテリアセルロース製造における炭素源としての低分子酸・アルコール類

鮫島一彦、西村高明、高村憲男

高知大学農学部

Evaluation of low molecular acids and alcohols as the carbon source for the production of bacterial cellulose.

Kazuhiko Sameshina, Takaaki Nishimura, Norio Takamura

Faculty of Agriculture, Kochi University

Abstract: Low molecular nine acids and six alcohols were evaluated as the carbon source for the production of bacterial cellulose. A bacteria, *Acetobacter xylinum* ATCC 10245 under the Hestrin-Schram's medium system was used for the evaluation. Among alcohols, glycerol gave the best cellulose yield (152% ; based on the membrane yield from glucose) and the inositol (89%) followed. Among the acids, lactic acid gave the best yield (71%) and the pH of the culture medium increased from 6.0 to 9.2. Acetic acid gave a little cellulose yield (11.7%) but the pH of the culture medium went up to 7.95 as in the case of lactic acid.

1991-特別講演

リグニンのメカノケミストリーとパルプ漂白

住本昌之

九州大学農学部

Mechanochemistry of lignin in pulping and its relation to pulp bleaching.

Masashi Sumimoto

Department of Forest Products, Kyushu University

Abstract: Mechanochemical treatments of various types of lignin model compounds with CAM, VBM, and laboratory refiner disclosed that O<sub>2</sub>H, OH, and H radicals were produced in the aqueous media of mechanical pulping, similarly to those in the aqueous media of super sound. Effective attack of such radicals to either syringyl glycerol- $\beta$ -guaiacyl ether or (5-5')-biphenyl type of model compound having  $\alpha$ -carbinol furnished the corresponding para-carbonyl phenol, and 3-methoxy-5-substituted *p*-benzoquinone, respectively. Furthermore, mechanical treatment of a 5-substituted-*p*-carbonyl phenol ether produced a pair of chromophore, *p*-benzoquinone and a leucochromophore, *p*-hydroquinone. Alkaline H<sub>2</sub>O<sub>2</sub> bleaching destructs most of the chromophore but the leucochromophores, which are believed to be the major cause of color reversion of bleached mechanical pulp.

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1992-101

担子菌 *Coriolus versicolor* によるリグニン分解機構の解析

飯村洋介、川合伸也、片山義博、諸星紀幸

東京農工大学農学部

Elucidation of lignin biodegradation mechanism by basidiomycete *Coriolus versicolor*.

Yousuke Iimura, Shinya Kawai, Yoshihiro Katayama, Noriyuki Morohoshi

Department of Applied Biological Science, Tokyo University of Agriculture and Technology

Abstract: A white-rot basidiomycete, *Coriolus versicolor* secretes a number of extracellular laccases. In polymeric lignin metabolism by *C. versicolor* laccase activity was closely related to the accumulation of water soluble intermediates. In this fungus, a multitude of laccase gene related DNA sequence was observed. We have cloned and sequenced a gene coding for the ligninolytic Laccase III and homologous laccases of *C. versicolor*.

1992-102

白色腐朽菌のリグニン分解に関与する酵素系に関する研究(I)自然界より分離したリグニン分解菌のリグニン分解特性及び菌体外酵素活性

平井浩文、近藤隆一郎、坂井克己

九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi. I. Lignin-degrading characteristic and extracellular enzyme activities of new isolates of white-rot fungi.

Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyusyu University

Abstract: We previously reported that new isolates of white-rot fungi, YK-472 and YE-624, showed much higher ligninolytic activity and selectivity in beech-wood lignin than typical lignin-degrading fungi, *Phanerochaete chrysosporium* and *Coriolus versicolor*. In the present work, we investigated their lignin-degrading characteristic and extracellular enzyme activity. The fungi YK-472 and YK-624 degraded birch dioxane lignin and residual lignin in unbleached kraft pulp (UKP) much higher than *P. chrysosporium* and *C. versicolor*. During fungal treatment of beech wood meals, the fungus YK-624 which degraded beech-wood lignin, showed much higher activity of extracellular peroxidase in the medium than *P. chrysosporium*.

1992-103

*Phanerochaete chrysosporium* の生産するセロビオース脱水素酵素の性質とリグノセルロース生分解におけるその役割

鮫島正浩<sup>\*1</sup>、カール・エリック L. エリクソン<sup>\*2</sup>

<sup>\*1</sup> 東京大学農学部、<sup>\*1</sup> ジョージア大学生化学科

Cellobiose dehydrogenases from *Phanerochaete chrysosporium*. Enzymatic properties and functions in lignocellulose biodegradation.

Msahiro Samejima<sup>\*1</sup>, Karl Erik L. Eriksson<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, University of Tokyo, <sup>\*2</sup>Department of Biochemistry, Center for Biological Resources a Recovery, University of Georgia

Abstract: In relation to lignocellulose biodegradation by *Phanerochaete chrysosporium*, enzymatic properties of cellobiose oxidase (CBO) and cellobiose : quinone oxidoreductase (CBQ), especially the specificity of electron acceptors for these enzymes, were investigated. CBO can reduce quinones as well as CBQ in the presence of cellobiose. FAD is a common prosthetic group for both enzyme. Therefore, these reductions are conducted by FAD. Atmospheric oxygen is a poor electron acceptor for both CBO and CBQ. In contrast, cytochrome c is utilized as an effective electron acceptor by CBO. The pH dependence experiment and the stopped flow analysis suggest that the reduction of cytochrome c is depending on the function of heme prosthetic group in CBO indicating that cytochrome c is a most possible electron acceptor for CBO in vivo system. The amount of CBO in the cellulolytic culture increases in the course of the fungal growth. Therefore all of these results suggests that CBO participates in cellulose biodegradation rather than lignin

biodegradation. On the other hand, CBQ produces in the later stage of the cellulolytic culture like as a secondary metabolite. Therefore, CBQ has less importance in cellulose biodegradation.

1992-104

*Phanerochaete chrysosporium* の芳香環開裂酵素について

西田篤実、中村雅哉、中川麻里子

森林総合研究所

Aromatic ring cleavage enzyme from *Phanerochaete chrysosporium*.

Atsumi Nishida, Masaya Nakamura, Mariko Nakagawa

Forestry and Forest Products Research Institute

Abstract: In an investigation of vanillic acid metabolism by *Phanerochaete chrysosporium*, aromatic ring cleavage enzyme is very unstable so the purification of the enzyme is very difficult. In this time, we succeeded in the purification of hydroxyquinol 1,2-dioxygenase and clarified the some properties. The native molecular weight of this enzyme is 94,000 Dalton and the subunit molecular weight are 40,000 and 52,000 Dalton (by SDS-Page). The enzyme is inactivated with  $Fe^{2+}$  and -SH chelator. Optimum pH is 6.0-6.5 and pH stability is 6.5-7.5 in phosphate buffer.

1992-105

マツノカタワタケによる  $\beta$ -O-4 型リグニンサブストラクチャーモデル二量体の分解

横田信三<sup>\*1</sup>、海野 清<sup>\*1\*2</sup>、梅澤俊明<sup>\*3</sup>、佐藤素子<sup>\*1</sup>、吉沢伸夫<sup>\*1</sup>

<sup>\*1</sup> 宇都宮大学農学部、<sup>\*1\*2</sup> 巴川製紙株式会社、<sup>\*3</sup> 京都大学木質科学研究所

Degradation of  $\beta$ -O-4 lignin substructure model dimers by *Cryptoderma pini*.

Shiunzou Yokota<sup>\*1</sup>, Kiyoshi Unno<sup>\*1\*2</sup>, Toshiaki Umezawa<sup>\*3</sup>, Motoko Satoh<sup>\*1</sup>, Nobuo Yoshizawa<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Utsunomiya University, <sup>\*2</sup> Tomoegawa Paper Co. Ltd., <sup>\*3</sup> Wood Research Institute, Kyoto University

Abstract: Degradation of a non-phenolic (1-(4-ethoxy-3-methoxyphenyl)-2-(2,6-di-methoxy-phenoxy)-1,3-propanediol (I)) and a phenolic (1-(4-hydroxy-3-methoxy-phenyl)-2-(2,6-dimethoxy-phenoxy)-1,3-propanediol (II))  $\beta$ -O-4 lignin substructure model dimers by the intact cells of *Cryptoderma pini*, and activities of lignin-degrading enzymes in the extracellular culture fluid of the fungus were investigated. In the degradation of substrate (I) by the fungus, degradation products were formed via O-C4 cleavage and  $\beta$ -etherified aromatic ring opening. On the other hand, substrate (II) was degraded via alkyl-aryl cleavage. In addition, activities of laccase and Mn(II)-dependent peroxidase were detected in the extracellular fluid of the fungus culture.

1992-106

有機溶媒中におけるペルオキシダーゼの反応

吉田晋一<sup>\*1</sup>、中尾博一<sup>\*2</sup>、渡辺隆司<sup>\*1</sup>、桑原正章<sup>\*1</sup>、麻田恭彦<sup>\*2</sup>

<sup>\*1</sup> 京都大学木質科学研究所、<sup>\*1</sup> 香川大学農学部

Reaction of peroxidase in organic solvents.

Shinichi Yoshida<sup>\*1</sup>, Hirokazu Nakao<sup>\*2</sup>, Takashi Watanabe<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>, Yasuhiko Asada<sup>\*2</sup>

<sup>\*1</sup> Wood Research Institute, Kyoto University, <sup>\*2</sup> Faculty of Agriculture, Kagawa University

Abstract: Horseradish peroxidase (HRP) was modified with methoxypolyethylene glycol-succinimidyl succinate (MPSS, MW 5000) to dissolve in organic solvent. The modified HRP retained over 85% of the original activity in potassium phosphate buffer, and its  $K_m$  value and  $V_{max}$  were about the same as those of native enzyme. Similarly, lignin peroxidase (LiP) was purified from culture filtrate of *Phanerochaete chrysosporium*, and modified with MPSS under neutral pH condition. The hydrophobically modified HRP and LiP were soluble in benzene. Reaction of both modified

peroxidases in organic solvent is reported\_

1992-107

透析膜法によるシナピルアルコールの酵素的脱水素重合

小川昌士、棚橋光彦、重松幹二、篠田善彦

岐阜大学農学部

Enzymatically dehydrogenative polymerization of sinapyl alcohol by dialysis membrane method.

Masashi Ogawa, Mitsuhiko Tanahashi, Mikiji Shigematsu, Yoshihiko Shinoda

Faculty of Agriculture, Gifu University

Abstract: In a plant cell wall, a lignin was deposited in the matrix of polysaccharides through the lignification process. To prepare the closer model of a native lignin, sinapyl alcohol was polymerized with horseradish peroxidase/H<sub>2</sub>O<sub>2</sub> in the presence of xylan or pectin by dialysis membrane method, and their chemical structures were investigated. As a result, the ratio of acidolysis monomers to syringaresinol was determined about 20 :1 in xylan and about 10 :1 in pectin. Further, there was a little benzyl phenyl ether in dehydrogenation polymer (DHP) fraction of the LCC/xylan. The degree of polymerization of the DHP was decided to be twenty-five by the determination of phenolic hydroxyl group and yield of acidolysis monomers. Dehydrogenative polymerization of monolignols by the dialysis membrane method would sufficiently simulate the lignification process in a plant cell wall.

1992-108

抗ウイルス活性を有する水溶性腐朽バガスリグニンの化学構造

梶原淳一<sup>\*1</sup>、服部武文<sup>\*2</sup>、城野浩之<sup>\*1</sup>、島田幹夫<sup>\*2</sup>

日本ケミカルリサーチ株式会社、京都大学木質科学研究所

Characterization of antiviral water-soluble lignin from bagasse degraded by *Lentinus edodes*.

Junichi Kajihara<sup>\*1</sup>, Takefumi Hattori<sup>\*2</sup>, Hiroyuki Shirono<sup>\*1</sup>, Mikio Shimada<sup>\*2</sup>

<sup>\*1</sup>JCR Pharmaceuticals Co. Ltd., <sup>\*2</sup>Wood Research Institute, Kyoto University

Abstract: We characterized water soluble lignin (WSL) which is responsible for antiviral activity of lignin complex (LC) extracted from bagasse degraded by *Lentinus edodes*. The results of potassium permanganate oxidation show that WSL contains larger amounts of condensed type structures than MWL. However, the methoxyl content of WSL was lower than that of MWL. Thus, the new evidence is that the quantities of benzene rings in WSL were obviously reduced, which suggests that bagasse lignin were modified to those rich in ring opening or quinone moieties during the decay process. The hydrolysis of WSL with aqueous sodium hydroxide yielded oxalic acid and formic acid, which indicates WSL contains oxalate and formate esters possibly derived from the aromatic-ring opening structures.

1992-109

リグニン構造単位の選択的標識に関する研究(I)

福島和彦<sup>\*1</sup>、松井直之<sup>\*1</sup>、鎌田 要<sup>\*1</sup>、安田征市<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup>名古屋大学農学部、<sup>\*2</sup>USDA 林産物研究所

Studies on the selective radio-labeling of lignin structural units in tree xylem (I).

Kazuhiko Fukushima<sup>\*1</sup>, Naoyuki Matsui<sup>\*1</sup>, Kaname Kamada<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>1</sup>Faculty of Agriculture, Nagoya University, <sup>2</sup>United States Dept. of Agriculture, Forest Products Laboratory, U.S.A.

Abstract: For the selective labeling of lignin structural units, monolignol glucosides are considered as suitable precursors. However, during a long term metabolism after the administration of these labeled precursors, a certain proportion of interconversion between each units (*p*-hydroxy-

phenyl, guaiacyl, syringyl) was often observed. To avoid this conversion,  $\gamma$ -hydrogens labeled monolignol glucosides were employed. If the conversions occur, these  $\gamma$ -hydrogens must be released because in lignin biosynthetic pathway, it is considered that OMT functions for *p*-hydroxy cinnamic acids which has no  $\gamma$ -hydrogens. In this study,  $\gamma$ -hydrogens in monolignol glucosides were labeled with deuteriums, and their behavior during the dehydrogenated polymerization was investigated using the preparing DHP. It was found the  $\gamma$ -hydrogens were stable through the reaction.

1992-110

リグニン構造単位の選択的標識に関する研究(II)

松井直之<sup>\*1</sup>、福島和彦<sup>\*1</sup>、安田征市<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup>名古屋大学農学部、<sup>\*2</sup>USDA 林産物研究所

Studies on the selective radio-labeling of lignin structural units in tree xylem (II)

Naoyuki Matsui<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>United States Dept. of Agriculture, Forest Products Laboratory, U.S.A.

Abstract: To achieve the selective labeling of lignin structural units, the  $\gamma$ -position of lignin C6-C3 units was labeled by the administration of  $\gamma$ -<sup>3</sup>H labeled monolignol glucosides to the plants. The newly formed lignin was degraded to C6-C3 units by thioacidolysis, and the radioactivity of degradative products (derived from guaiacyl, syringyl units) were measured. The perfectly selective labeling was expected, however, a considerable proportion of interconversion was observed in the angiospermous trees administered with *p*-glucocoumaryl alcohol and coniferin. When syringin was administered, little conversion was observed. These suggest that new route (or mechanism) of interconversion which does not pass the cinnamic acids exists in the lignin biosynthesis.

1992-111

広葉樹樹幹先端部における木部分化とリグニン不均一形成に関する研究

福島和彦<sup>\*1</sup>、高部圭司<sup>\*2</sup>、寺島典二<sup>\*3</sup>、安田征市<sup>\*1</sup>

<sup>\*1</sup>名古屋大学農学部、<sup>\*2</sup>京都大学農学部、<sup>\*3</sup>USDA 林産物研究所

Studies on the heterogeneous formation of lignin in the elongating shoot of *Magnolia kobus*.

Kazuhiko Fukushima<sup>\*1</sup>, Keiji Takabe<sup>\*2</sup>, Noritsugu Terashima<sup>\*3</sup> and Seiichi Yasuda<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>Faculty of Agriculture, Kyoto University, <sup>\*3</sup>United States Dept. of Agriculture, Forest Products Laboratory, U.S.A.

Abstract: The differences in lignification between the vessel of primary xylem and that of secondary xylem are discussed. The vessels of primary xylem of *Magnolia kobus* have thickened spiral secondary wall. This secondary wall lignifies in the early stage of shoot formation. However, the lignification of the compound middle lamella is fairly delayed. This pattern of lignification is quite different from that of secondary xylem. In addition, surprisingly, it was found that the vessel of primary xylem with lignified secondary wall dramatically elongated (approximately 3.5 fold) like a spring coil during the growth of the shoot.

1992-112

雲南省産カエデ属数種のリグニンの分布

平井陽子、深沢和三

北海道大学農学部

Distribution of lignins on the genus *Acer* in Yunnan.

Yoko Hirai, Kazumi Fukazawa

Faculty of Agriculture, Hokkaido University

Abstract: Distribution of lignins of 5 species on the Genus *Acer* in Yunnan was investigated by Mäule reaction, ultraviolet microscopy and Klason method. Absorption spectra of Mäule reaction show that all 5 species were syringyl lignin rich in all elements.

1992-113

*Forsythia sp.* のリグナン生合成の初発段階を触媒する(+)-ピノレジノールシンターゼ

片山健至<sup>\*1\*2</sup>, L.B. Davin<sup>\*1</sup>, D.L. Bedga<sup>\*1</sup>, N.G. Lewis<sup>\*1</sup>

<sup>\*1</sup>ワシントン州立大学、<sup>\*2</sup>香川大学農学部

(+)-Pinoresinol synthase: The first enzymatic step committed to lignan biosynthesis in the *Forsythia sp.*

Takeshi Katayama<sup>\*1, \*2</sup>, Laurence B. Davin<sup>\*1</sup>, Diana L. Bedgar<sup>\*1</sup>, Norman G. Lewis<sup>\*1</sup>

<sup>\*1</sup>Institute of Biological Chemistry, Washington State University, <sup>\*2</sup>Faculty of Agriculture, Kagawa University

Abstract: Detailed fractionation studies have determined that in the insoluble residue from *Forsythia sp.* (*F. suspensa* and *F. intermedia*) there exists a coniferyl alcohol coupling enzyme which catalyzes preferential formation of (+)-pinoresinol in the absence of cofactors. When NAD and malate were supplied, the stereoselectivity of the coupling reaction was enhanced. Sinapyl alcohol does not serve as a substrate for this enzyme i.e. in this case stereoselective coupling does not occur. Thus, lignan biosynthesis in the *Forsythia sp.* is initiated by the coupling of the two coniferyl alcohol molecules to give (+)-pinoresinol, this being the first isolable product of stereoselective coupling.

1992-114

(+)-ピノレジノールのエナンチオ特異的還元

片山健至<sup>\*1\*2</sup>, L.B. Davin<sup>\*1</sup>, Alex Chu<sup>\*1</sup>, N.G. Lewis<sup>\*1</sup>

<sup>\*1</sup>ワシントン州立大学、<sup>\*2</sup>香川大学農学部、

Enantiospecific reduction of (+)-pinoresinol

Takeshi Katayama<sup>\*1, \*2</sup>, Laurence B. Davin<sup>\*1</sup>, Alex Chu<sup>\*1</sup>, Norman G. Lewis<sup>\*1</sup>

<sup>\*1</sup>Institute of Biological Chemistry, Washington State University, <sup>\*2</sup>Faculty of Agriculture, Kagawa University

Abstract: Time-course experiments using *Forsythia intermedia* cell-free extracts, incubated with coniferyl alcohol in the presence of NADPH and H<sub>2</sub>O<sub>2</sub>, revealed that formation of (-)-secoisolariciresinol was linear over the time period examined. But, these crude cell-free extracts also catalyzed formation of (±)-pinoresinols as the initial coupling products. The (+)-enantiomer was then selectively depleted, as a function of time, from the incubation mixture, with concomitant formation of (-)-secoisolariciresinol. By contrast, the (-)-antipode remained unchanged. Next, the cell-free extracts were incubated with (±) and (+)-pinoresinols. Formation of (-)-secoisolariciresinol from the (+)-antipode was again observed, but only required NADPH as a cofactor.

1992-115

Lignan biogenesis: Towards elucidating regio- and enantiospecific methylation/glucosylation transformations beyond matairesinol.

Shuji Ozawa, Laurence B. Davin, Norman G. Lewis

Institute of Biological Chemistry. Washington State University

Abstract: Since the pathway from (+)-pinoresinol to (-)-matairesinol in *Forsythia intermedia* is characterized by highly enantioselective enzymatic conversions, it was of interest to establish whether comparable enantioselectivity was extended into arctigenin/arctiin formation, and if the

apparent regioselectivity of methylation was controlled at this stage. But, in contrast to previous enantioselective enzymatic steps affording (-)-matairesinol, it was found that both (+)- and (-)-antipodes of matairesinol served as substrates for methylation –with the naturally occurring (-)-enantiomer slightly preferred. Surprisingly, the major enzymatic products were (+)- and (-)-isoarctigenins rather than the naturally occurring regio-isomer, (-)-arctigenin. Thus, *O*-methylation of matairesinol was neither enantioselective or regioselective. Further, only monomethylation was observed, since no evidence for dimethyl matairesinol formation occurred. Taken together, it is proposed that regioselective methylation of matairesinol does not proceed to give arctigenin directly. Instead, regioselective glucosylation is presumed to first occur to afford matairesinoside. Subsequent methylation affords arctiin, which is converted into arctigenin via action of a  $\beta$ -glucosidase.

1992-116

*Forsythia koreana* のリグナン生合成酵素

梅澤俊明、黒田宏之、五十幡俊成、島田幹夫

京都大学木質科学研究所

Enantioselective lignan formation by cell-free extracts of *Forsythia koreana*.

Toshiaki Umezawa, Hiroyuki Kuroda, Toshinari Isohata, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Cell-free extracts from *Forsythia koreana* catalyzed the formation of (-)-secoisolariciresinol, as well as (-)-pinoresinol and (-)-lariciresmol. When incubated with coniferyl alcohol in the presence of NADPH and H<sub>2</sub>O<sub>2</sub>. The extracts also catalyzed the formation of (-)-secoisolariciresinol from (±)-lariciresinol. The mechanisms of the enantioselective (-)-secoisolariciresinol formation are discussed.

1992-117

ウド (*Aralia cordata*) シンナミルアルコールデヒドロゲナーゼ cDNA の単離および解析

日尾野隆<sup>\*1</sup>、柴田大輔<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup> 三井植物バイオ研究所、<sup>\*2</sup> 日本大学農獣医学部

Isolation and characterization of a cDNA encoding cinnamyl alcohol dehydrogenase from *Aralia cordata*.

Takashi Hibino<sup>\*1</sup>, Daisuke Shibata<sup>\*1</sup>, Takayoshi Higuchi<sup>\*1</sup>

<sup>\*1</sup>Mitsui Plant Biotechnology Reserch Institute, <sup>\*2</sup>College of Agriculture and Veterinary Medicine, Nihon University

Abstract: We isolated a full-length cDNA clone encoding cinnamyl alcohol dehydrogenase (CAD; EC1.1.1.195) from *Aralia cordata* by oligonucleotide-screening derived from amino acid sequence of *A. cordata* CAD protein. The cDNA clone comprised a open reading frame of 1080 base pairs. The partial amino acid sequences of peptides isolated from the purified CAD of *A. cordata* were found in that deduced from the cDNA nucleotide sequence. This showed the cDNA clone encodes CAD of *A. cordata*.

1992-118

樹木フェニルプロパノイド系生合成酵素遺伝子群の単離・解析

早川敏雄<sup>\*1</sup>、大坪祐二<sup>\*1</sup>、刑部祐里子<sup>\*1</sup>、川合伸也<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、片山義博<sup>\*2</sup>、秦 邦男<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 十条製紙株式会社

Isolation and analysis of the genes encoding the enzymes for phenylpropanoids biosynthesis in woody plants

Toshio Hayakawa<sup>\*1</sup>, Yuuji Ootsubo<sup>\*1</sup>, Yuriko Osakabe<sup>\*1</sup>, Shinya Kawa<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Kunio Hata<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup>JuJo Paper. Co., LTD.

Abstract: We use *Populus kitakamiensis* as a model for analysis of lignification in woody plants. For the analysis of gene regulation in lignification process and molecular breeding of lignin less tree, it is necessary to isolate the genes encoding enzymes for lignin biosynthesis. We isolated some phenylalanine ammonia-lyase, O-methyltransferase, and peroxidase genes from the poplar genome. And some of them were characterized.

1992-119

アンチセンス RNA 法を用いた樹木の分子育種

川合伸也<sup>\*1</sup>、三浦 進<sup>\*1</sup>、梶田真也<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、片山義博<sup>\*2</sup>、秦 邦男<sup>\*3</sup>

<sup>\*1</sup>東京農工大学農学部、<sup>\*2</sup>東京農工大学共同研究開発センター、<sup>\*3</sup>十条製紙株式会社

Molecular breeding of woody plants by using antisense RNA method,

Shinya Kawai<sup>\*1</sup>, Susumu Miura<sup>\*1</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Kunio Hata<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology <sup>\*3</sup>JuJo Paper. Co., LTD.

Abstract: Cells of the hybrid poplar (*Populus kitakamiensis*) were transformed by *Agrobacterium*-mediated gene transfer and regenerated into plants from the transformed calli. T-DNA of plasmid DNA, pBI121, bearing marker genes encoding beta-glucuronidase (GUS) and neomycin phospho-transferase (NPTII) were introduced by non-oncogenic *Agrobacterium tumefaciens* LBA4404 using leaf disk method. The transformed cells grew into calli on the selective medium containing kanamycin and calli regenerated into plants. The kanamycin resistant plants were analysed by Southern blot hybridization and a fluorometric assay for GUS. All kanamycin resistant plants had two marker genes and were confined as transformants. And sense or antisense genes for phenylalanine ammonia-lyase or peroxidase derived from the poplar genome were introduced into the poplar and the transformants were regenerated into plants.

1992-120

リグニンビフェニル型化合物の分解酵素遺伝子の解析

窪田祥子<sup>\*1</sup>、片山義博<sup>\*2</sup>、花城 薫<sup>\*1</sup>、木村尚代<sup>\*1</sup>、政井英司<sup>\*1</sup>、川合伸也<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup>東京農工大学農学部、<sup>\*2</sup>東京農工大学共同研究開発センター

Cloning of the genes involved in degradation of biphenyl structure of lignin compounds.

Sachiko Kubota<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Kaoru Hanashiro<sup>\*1</sup>, Hisayo Kinura<sup>\*1</sup>, Eiji Masai<sup>\*1</sup>, Shinya Kawai<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology

Abstract: *Pseudomonas paucimobilis* SYK-6 is able to grow on DDVA (biphenyl structure of lignin) as a sole carbon source. We have already reported that the metabolism of DDVA proceeds via intermediates, OH-DDVA, 5-carboxyvanillate. The first step in the catabolism of DDVA by SYK-6 is the demethylation of DDVA to OH-DDVA. In this study we report, using as a host strain for the nitrosoguanidine mutant NT1 which was isolated for loss of the ability to use DDVA as a carbon source, we isolated the genes involved in DDVA catabolism.

1992-121

### $\beta$ -アリアルエーテル開裂酵素遺伝子群の機能と構造

政井英司<sup>\*1</sup>、窪田祥子<sup>\*1</sup>、片山義博<sup>\*2</sup>、川合伸也<sup>\*1</sup>、山崎真狩<sup>\*3</sup>、諸星紀幸<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 東京大学農学部

Structures and functions of the genes involved in the cleavage of  $\beta$ -aryl ether.

Eiji Masai<sup>\*1</sup>, Sachiko Kubota<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Shinya Kawai<sup>\*1</sup>, Makari Yamasaki<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology,<sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology,<sup>\*3</sup>Faculty of Agriculture, the University of Tokyo

Abstract: *Pseudomonas paucimobilis* SYK-6 is able to assimilate various types of dimeric lignin compounds. Cleavage of arylglycerol- $\beta$ -aryl ether is essential in the lignin degradation. We have already characterized the  $\beta$ -etherase gene (*ligE*). Here, we isolated and characterized the C $\alpha$ -dehydrogenase gene (*ligD*). C $\alpha$ -dehydrogenase catalyzes the oxidation of arylglycerol- $\beta$ -aryl ether and this process produces the specific substrate for  $\beta$ -etherase. Homology search showed that *ligD* had a homology with ribitol dehydrogenase family. Mapping and sequencing analysis indicated *ligD* and *ligE* were separated by an open reading frame encoding another  $\beta$ -etherase gene (*ligF*).  $\beta$ -etherase activity of *ligF* expressed in *Escherichia coli* was more than 100 times as high as that of *ligE*. We found that *ligF* was homologous to glutathione S-transferase. Drastic acceleration of  $\beta$ -etherase activity was observed in the reaction mixture including *ligF* by addition of glutathione.

1992-201

### リグニンの熱分解ガスクロマトグラフィー(第4報)単難リグニンの熱分解ガスクロマトグラフィー

黒田健一<sup>\*1</sup>、山口 彰<sup>\*1</sup>、坂井克己<sup>\*2</sup>

<sup>\*1</sup> 筑波大学農林工学系、<sup>\*2</sup> 九州大学農学部

Analysis of lignin by pyrolysis-gas chromatography. IV. Pyrolysis-gas chromatography of sugi wood, its lignin preparations and synthetic lignin.

Kenichi Kuroda<sup>\*1</sup>, Akira Yamaguchi<sup>\*1</sup>, Kokki Sakai<sup>\*2</sup>

<sup>\*1</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba, <sup>\*2</sup>Faculty of Agriculture, Kyushu University

Abstract: Curie-point pyrolysis of wood and several isolated lignins from sugi (*Cryptomeria japonica* D. Don) and synthetic lignin was performed. Pyrolysis products were analyzed by GC and GC/MS. Total yields of selected pyrolysis products were ordered as follows: wood > DHP > MWL > alcohol bisulfite lignin > HC1-lignin > DL >> KL. Py-GC of lignin gave different product distribution profiles from that of wood meal; coniferyl alcohol was the most abundant lignin marker product in the wood pyrolysate, and a minor product in its lignin pyrolysate. These findings showed that analytical pyrolysis data may help in achieving a better understanding of the structural change of lignin.

1992-202

### リグニンのメカノケミストリー(XVI) グアイアシルグリセロール- $\beta$ -グアイアシルエーテルのメカノケミストリー

伊藤和貴、住本昌之、田中浩堆

九州大学農学部

Mechanochemistry of lignin. XVI. Mechanochemical conversions of guaiacylglycerol- $\beta$ -guaiacyl ether.

Kazutaka Itoh, Masashi Sumimoto, Hiroo Tanaka

Faculty of Agriculture, Kyushu University

Mechanochemical conversions of vanillyl alcohol I,  $\alpha$ -methyl vanillyl alcohol II, and

guaiasyglycerol- $\beta$ -guaiacyl ether IV were investigated. Two types of conversions occurred by the treatment of compound IV with VBM. The major reaction furnished firstly the corresponding *p*-carbonyl phenol 4, which afforded six products similarly to the case of syringylglycerol- $\beta$ -guaiacyl ether, but strangely included 2-methoxy-*p*-hydroquinone 5. The minor reaction involved abstraction of phenolic H atom followed by dimerization to give compound 10 which was oxidized further via compound 11 to 12.

1992-203

爆砕処理よりリグニンの分解機構の解明(VI) シリングル型リグニンモデル化合物の水蒸気処理

M. Karina<sup>\*1\*2</sup>、上野直之<sup>\*2</sup>、棚橋光彦<sup>\*2</sup>、桑原正章<sup>\*3</sup>

<sup>\*1</sup>LIPI-PPPFT、<sup>\*2</sup>岐阜大学農学部、<sup>\*3</sup>京都大学木質科学研究所

Degradation mechanism of lignin by steam explosion. VI. - Steam treatment of syringyl type of lignin model compound.

M. Karina<sup>\*1\*2</sup>, Naoyuki Uenot<sup>\*2</sup>, Mitsuhiko Tanahashi<sup>\*2</sup>, Masaaki Kuwahara<sup>\*3</sup>

<sup>\*1</sup>LIPI-PPPFT, <sup>\*2</sup>Faculty of Agriculture, Gifu University, <sup>\*3</sup>Wood Research Institute, Kyoto University

Abstract. In order to explain the degradation mechanism of lignin by steam explosion, syringyl-glycerol- $\beta$ -sinapylalcohol ether (SS) was used in the present study. This model compound was subjected to the steam treatment, 230 °C, 2.9 MPa for 4 min. Steam treatment of S-DHP and S-LCC was also subjected to the steam treatment. The major degradation product obtained from steamed SS was syringaresinol. Other products found were sinapyl alcohol, sinapaldehyde, dehydrosinapyl alcohol and syringaldehyde. On the other hand,  $\beta$ -oxysinapylalcohol as the major degradation product of acidolysis was not detected. This result suggested that the degradation mechanism of lignin by steam explosion is different from acidolysis. By the condition used.  $\beta$ -ether linkage of SS was cleaved homolytically and formed sinapyl alcohol radical. These radicals were homocoupled to give syringaresinol, and reduction of sinapyl alcohol radical formed sinapyl alcohol. The results obtained from steam treated S-DHP and S-LCC were similar with that from SS. However, from steamed S-DHP, sinapaldehyde was obtained much more than that of sinapyl alcohol. The difference in the amounts of the degradation products possibly due to the different oxidation levels of the C6-C3 units of the molecule. In the SS, each phenolic unit was subjected to one-electron oxidation (the oxidation level is similar to the sinapyl alcohol radical). In the S-DHP, to produce a polymer, one-electron oxidation occurred twice (the oxidation level is similar to sinapyl aldehyde radical). On the other hand, from steamed S-LCC, sinapyl alcohol was produced much higher than that of sinapaldehyde. Sinapyl alcohol radical results from the cleavage of  $\beta$ -ether by steam treatment was reduced by the hemicellulose exist in S-LCC.

1992-204

機能性リグノフェノール誘導体の調製およびその特性

松江淳介、船岡正光

三重大学農学部

Preparation of functional lignophenols and their characteristics.

Junsuke Matsue, Masamitsu Funaoka

Faculty of Bioresources, Mie University

Abstract: A new conversion technique (SS Conversion Process) of protolignins and technical lignins into functional lignophenols has been developed. The characteristics of this process are as follows : 1. Rapid conversion at room temperature. 2. No special chemicals and equipment. 3. Selective phenolation at  $\alpha$ -positions of lignin side chains. 4. Disappearance of conjugated systems. The resulting lignophenols have high reactivity and new functions as phenolic polymers. In the

present paper, the characteristics and procedure of SS conversion process are described, compared with conventional phenolation techniques.

1992-205

高度の縮合構造を有する酸リグニンの可溶性リグノスルホン酸への変換

松下泰幸、安田征市

名古屋大学農学部

Conversion of highly condensed acid lignin into water-soluble lignosulfonate.

Yasuyuki Matsushita, Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: Conversion of highly condensed sulfuric acid lignin into water-soluble lignosulfonate was investigated. At first, sulfuric acid lignin was phenolized to enhance its reactivity. Two methods were tried to convert phenolized SAL into water-soluble lignosulfonate. One was hydroxymethylation, followed by neutral sulfite treatment, and the other was sulfomethylation with hydroxymethane sulfonate. Sulfur content introduced by the two-step procedure was higher than that by the one-step method and commercial lignosulfonates. The two-step method gave higher molecular weight products than the one-step procedure, maybe because of polymerization during hydroxymethylation and sulfonation.

1992-206

カルボキシメチル化リグニンの合成とその特性について

木村泰章、熊田直子、滝沢正博、中村昌允

ライオン株式会社、素材開発センター

Synthesis and properties of carboxymethylated lignin.

Yasuaki Kimura, Naoko Kumada, Masahiro Takizawa, Masayoshi Nakamura

Advanced Materials Research Center, Lion Co., Ltd.

Abstract: The purpose of this study is to synthesize a water-soluble dispersing agent from water-insoluble lignin which is obtained from softwood by acetic acid-digestion. The dispersing agent was synthesized by carboxymethylation of the lignin with monochloroacetic acid. This carboxymethylation was successfully performed by heterogeneous reaction of the lignin dipped into 48% NaOH-aq. and monochloroacetic acid in 2-propanol (IPA). We found this carboxymethylated lignin was easily soluble in water and had a calcium sequestering capacity of 130mg-CaCO<sub>3</sub>/g and a dispersing power for Fe<sub>2</sub>O<sub>3</sub> particles.

Keywords: 酢酸蒸解・リグニン・脱アセチル化リグニン・カルボキシメチル化リグニン・Caイオン捕捉能・分散能、dispersing agent, acetic acid cooking, deacetylated lignin, carboxymethylated lignin, calcium ion sequestering capacity, dispersibility

1992-207

リグニンを原料とするポリエステルポリウレタンの調製と熱的性質

広瀬重雄<sup>\*1</sup>、小橋川健<sup>\*2</sup>、畠山兵衛<sup>\*1</sup>

<sup>\*1</sup>製品科学研究所、<sup>\*2</sup>トロピカルテクノセンター

Preparation and thermal properties of polyester-polyurethanes derived from lignin.

Shigeo Hirose<sup>\*1</sup>, Ken Kobashigawa<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*1</sup>

<sup>\*1</sup>Industrial Products Research Institute, <sup>\*2</sup>Tropical Technology Center Ltd..

Abstract: Polyurethane foams (PU) could successfully be prepared by the following procedure. A mixture consisting of a ethylene glycol (EG) solution of kraft lignin and polyester-polyol (PES, diol-type polycaprolactone, molecular weight 550) was reacted with diphenylmethane diisocyanate (MDI)

in the presence of a small amount of water, tin catalyst and silicone surfactant. Thermal properties of PU's were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). Mechanical properties of the obtained foams were also studied by compression test. The effect of the addition of kraft lignin to PU's is considered in this paper.

1992-208

Synthesis and thermal properties of liquid crystalline aromatic copolyesters from phenols related to lignin.

M. Acevedo, Shigeo Hirose, Hyoe Hatakeyama

Industrial Products Research Institute

Abstract: New aromatic copolyterephthalates combining two hydroquinones such as: methoxy-hydroquinone (MHQ), 2,6-dimethoxyhydroquinone (DHQ) and 4,4'-dihydroxy-3,3',5,5'-tetramethoxy-biphenyl (THQ), have been synthesized and characterized starting with lignin-related phenols. These copolymers showed liquid crystalline properties according to the observation by polarizing microscopy and differential scanning calorimetry.

1992-209

中温硬化型リグニン樹脂接着剤の製造

島谷啓二、佐野嘉拓

北海道大学農学部

Preparation of medium-temperature setting lignin-based wood adhesives.

Keiji Shimatani, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: The utilization of kraft lignin in the substrate of medium-temperature setting wood adhesives was investigated. A mixture of the lignin and phenol was hydroxymethylated under alkali conditions with various molar ratios of formaldehyde and methanol at 80 °C for 2 hours. Resorcinol or wattle tannin and paraformaldehyde were added to the hydroxymethylated products in order to prepare the adhesives. The adhesives yielded high bonding strength and water resistance at hot pressing temperature of 100 °C. The hydroxymethylated products were analyzed by GPC, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, HPLC and so forth.

1992-210

酢酸リグニンの繊維化

久保智史<sup>\*1</sup>、浦木康光<sup>\*1</sup>、佐野嘉拓<sup>\*1</sup>、笹谷宜志<sup>\*1</sup>、小川正人<sup>\*2</sup>

<sup>\*1</sup>北海道大学農学部, <sup>\*2</sup>北海道大学理学部

Preparation of lignin fiber from acetic acid lignin.

Satoshi Kubo<sup>\*1</sup>, Yasumitsu Uraki<sup>\*1</sup>, Yoshihiro Sano<sup>\*1</sup>, Takashi Sasaya<sup>\*1</sup>, Masato Ogawa<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Faculty of Science, Hokkaido University

Abstract: Acetic acid lignin (AWL) which was prepared from birch chips by atmospheric acetic acid

pulping containing H<sub>2</sub>SO<sub>4</sub> had a melt spinnability. However the lignin fiber spun out of AWL had a rough surface and had some micropores probably due to the elimination of low molecular weight volatile materials. In this study, we tried heat treatment of AWL as pretreatment to solve these problems. The heat treatment at 160 °C reduced the amount of micropores of the surface. Consequently the treatment gave a easily spinning condition.

1992-211

硫酸触媒による常圧酢酸パルプ化 –単離リグニンの化学構造  
堀崎敬史、島谷啓二、佐野嘉拓、笹谷宜志  
北海道大学農学部

Pulping at atmospheric pressure with aqueous acetic acid containing a small amount of sulfuric Acid. –Chemical structure of isolated lignins.

Yoshifumi Horisaki, Keiji Shimatani, Yoshihiro Sano, Takashi Sasaya  
Faculty of Agriculture, Hokkaido University

Abstract: Cellulose, hemicellulose, and lignin can be recovered quantitatively without tedious operation by atmospheric pulping with aqueous acetic acid containing a small amount of sulfuric acid. We reported that acetic acid lignins (AWL) with large amounts of phenolic hydroxyl groups had high reactivity, which may be useful for the substrate of synthetic phenol polymers. To examine the chemical structure of AWLs in detail, the content of phenolic and aliphatic hydroxyl, carbonyl and carboxyl groups, degree of condensation and so forth in AWLs were determined. And the effects of polysaccharides on delignification during pulping were also examined.

1992-212

The high efficiency of cellulose production by *Acetobacter xylinum* ATCC 10245 in a new culture medium with a sulfite pulping waste fraction.

Siripong Premet、鮫島一彦、高村憲男  
高知大学農学部

The high efficiency of cellulose production by *Acetobacter xylinum* ATCC 10245 in a new culture medium with a sulfite pulping waste fraction.

Siripong Premet, Kazuhiko Sameshima, Noiro Takamura  
Faculty of Agriculture, Kochi University

Abstract: A new culture medium named KC medium (based on KOCHI) is a compound with a fraction of sulfite pulping waste (commercially available), glucose, yeast extract, peptone and buffer compounds. This nutrient culture medium showed high efficiency for cellulose production than the standard culture medium. *Acetobacter xylinum* ATCC 10245 was cultured in KC medium at static condition, and 2% glucose KC medium gave high cellulose membrane yield (about 300%) than 2% glucose standard medium.

1992-213

クラフトパルプ残留リグニンの特性 –S-S プロセスによる評価  
浜口佳織、船岡正光  
三重大学農学部

Characterization of kraft pulp residual lignin by swelling-solvation process.

Kaori Hamaguchi, Masamitsu Funaoka  
Faculty of Bioresources, Mie University

Abstract: Swelling-solvation (SS) technique was applied to separate and characterize kraft pulp residual lignins. The SS process has originally been developed for the quantitative separation of lignin with selective structural modifications from lignocellulosics. The key point of this process is to destroy carbohydrates by concentrated sulfuric acid under the solvation of lignin with cresol. The mass balance of residual lignins in the SS reaction system was determined in detail, and properties of SS separated residual lignins were compared with those of dissolved lignins subjected to the same SS treatment. Through these data, the chemical and polymeric characteristics of pulp residual lignins were discussed.

1992-214

リグニンの酵素分解に関する研究(III)メンブランフィルターを用いた培養系におけるクラフトパルプ  
残留リグニンの挙動

蔵敷賢二、近藤隆一郎、坂井克己

九州大学農学部

Modification of residual lignin in unbleached kraft pulp by extracellular enzymes excreted from white-rot fungi in a cultivation system using a membrane filter.

Kenji Kurashiki, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: In a previous work, we demonstrated the modification of dioxane lignin by extracellular enzymes excreted from white-rot fungi using two membrane filters of different thickness, and suggested that the degradation of the low-molecular-weight dioxane lignin depended on the distance between the hyphae and the lignin sample. In the present experiment, some beech unbleached kraft pulp sheets were treated in this cultivation system. About 10% of residual lignin in kraft pulp was degraded by treatment with *Phanerochaete chrysosporium* or *Coriolus versicolor* if the thin membrane filter was used, although almost 100% of lignin was recovered in the thick-membrane system. The ligninolytic activities of fungus YK-624, and YK-472 which were isolated from decayed wood were superior to those of *P. chrysosporium* and *C. versicolor* in the thin-membrane system. Consequently, it was suggested that the degradation of the residual lignin in kraft pulp also depended on the distance between the hyphae and the surface of kraft pulp sheet.

1992-215

リグニン分解菌によるクラフトパルプ漂白廃液の処理(IV)自然界より分離したリグニン分解菌によるクラフトパルプ漂白廃液の脱色

李 宣鎬、近藤隆一郎、坂井克己

九州大学農学部

Decolorization of kraft bleaching effluent by lignin-degrading fungi. IV. Screening of wood-rotting fungi for efficient decolorization of kraft bleaching effluent.

Seon-Ho Lee, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: To find a more efficient system for the decolorization of kraft pulp bleaching (E1) effluent, we have performed screening for high-decolorization fungi from 152 strains of isolated wood-rotting fungi. We observed that most of the guaiacol-colorization positive fungi showed the efficient decolorization of the E1 effluent. A highly significant correlation between the decolorization of the E1 effluent and the degradation of lignin in wood was not observed for isolated wood-rotting fungi. From decay wood samples we could isolate three fungi (MZ-227, MZ-400 and YK-624) having high decolorization activity of the E1 effluent with additional nutrients. Moreover, the fungus KS-62 showed the excellence in the decolorization and the reduction of the UV absorbance (280 nm) of the E1 effluent without any additional nutrients.

1992-216

酸処理によるクラフトパルプの無塩素漂白

細谷修二、富村洋一、島田謹爾

森林総合研究所

Acid treatment as one stage of non-chlorine bleaching.

Shuji Hosoya, Yoichi Tomimura, Kinji Shimada

Forestry and Forest Products Research Institute

Abstract: Beech kraft pulp of a kappa number 20.5 was successfully delignified by 95 % acetic acid treatment with a small amount of hydrochloric acid at a refluxing temperature. The degree of delignification and the decrease in pulp viscosity highly depended on the amounts of hydrochloric acid added. The delignification was accelerated by the addition of nitrates and the selectivity increased. Finally the kappa number below five was achieved with the viscosity above twenty c.p.. Better result was also obtained in aqueous solution, without using acetic acid, by adjusting the pH with sulfuric acid and applying the alkaline extraction after acid treatment.

1992-217

クラフトパルプの無塩素漂白. オゾン漂白におけるパルプ粘度低下の機構  
岸本崇生、中坪文明、村上浩二  
京都大学農学部

Non-chlorine bleaching of kraft pulps. Mechanism of viscosity drop in ozone bleaching.

Takao Kishimoto, Fumiaki Nakatsubo, Koji Murakami

Faculty of Agriculture, Kyoto University

Abstract: A oxygen-bleached hardwood kraft pulp was treated with ozone at low consistency in acidic aqueous medium with sulfuric or oxalic acid and in methanol. These reaction conditions have been found to inhibit carbohydrate degradation. Here, we considered that the viscosity drop may be caused by two reactions, direct glycosidic bond cleavage during ozone bleaching and indirect reaction caused by carbonyl groups formed by oxidation. As a result of these experiments, it is indicated that methanol inhibits the direct glycosidic bond cleavage, not oxidation, contrary to the expectation reported earlier.

1992-218

漂白過程で生じる有機塩素化合物の性状  
新谷博幸、松本雄二、飯塚堯介、石津 敦  
東京大学農学部

Nature of chlorinated organic compounds.

Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka and Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo,

Abstract: Unbleached hardwood kraft pulp, oxygen semibleached hardwood kraft pulp and unbleached softwood MCC pulp were chlorinated at various levels of chlorine ratio (0.1-0.3). The most significant difference between chlorinated lignin from softwood and that from hardwood is water solubility. Chlorolignin formed from hardwood kraft pulp is highly water soluble and, thus, considerable part of TOC (total organic carbon) and TOCl (total organic chlorine) are found in chlorination liquor, whereas only small part of chlorolignin became water soluble during chlorination of softwood pulp. Chemical structure of chlorolignin in oxygen semibleached pulp was quite different from that in non-semibleached pulp, and the former lignin was dissolved out more easily than the latter.

1992-219

リグニンペルオキシダーゼによるクロロフェノールの分解  
藤井里絵、小野克正、松本雄二、石津 敦、桃原郁夫  
東京大学農学部、森林総合研究所

Inhibition of lignin peroxidase oxidation of veratryl alcohol by chlorophenols.

Rie Fujii, Katsumasa Ono, Ikuo Monohara, Yuji Matsumoto, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Abstract: When veratryl alcohol (VA) is treated with lignin peroxidase (Lip) in the presence of chlorophenols, the VA-oxidation is inhibited in a special manner. The inhibition period, which is defined as the time until VA-oxidation started, was analyzed in terms of concentrations of VA and chlorophenols. In the presence of an enough amount of VA, the inhibition period was proportional to the concentration of chlorophenols. With the increase in the concentration of VA, the inhibition period decreased and reached a minimum value. Kinetic analyses of this reaction indicated the presence of highly reactive species which are capable of degrading chlorophenols.

1992-220

クラフトパルプ前処理酸素漂白法の機構と新しい前処理方法の検索

大井 洋、田尻政直、岩永雄三、青柳哲夫、大内基弘

日本紙パルプ研研究所

Mechanism of pretreatment for oxygen bleaching of kraft pulp and a new pretreatment.

Hiroshi Ohi, Masanao Tajiri, Yuzo Iwanaga, Tetsuo Aoyagi, Motohiro Ohuchi

Japan Pulp a Paper Research Institute

Abstract: A new pretreatment method with nitrite, acid and oxygen for oxygen bleaching was proposed while mechanism of various pretreatments was discussed in this study. Although the pretreatment called Samuelson's S3 process fairly improves oxygen bleaching, it requires the two-stages pretreatment. Furthermore, in its first stage, the reaction is done with gas-phase nitrogen dioxide and a pulp of high consistency. These defects were removed for the new pretreatment method. For the improvement of oxygen bleaching, nitrite has an important role both in the second stage of S3 process and the new method. In the new method, oxygen should have an important effect on the oxidation of lignin and its activation for oxygen bleaching.

1992-特別講演 S-1

森林環境と微生物 -森林ときのこの共生

小川 真

株式会社、関西総合環境センター・生物環境研究所

Forest environment and microorganisms. Symbiosis between forest tree and mushroom.

Makoto Ogawa

The General Environmental Technos Co. Ltd.

Keywords: evolution, wood rotting fungi, mycorrhiza, vesicular-arbuscular mycorrhiza,

1992-特別講演 S-2

セルロース系材料の機能変換

京都大学化学研究所

宮本武明

Functionality conversion of cellulosic materials by chemical modifications and structural controls.

Takeaki Miyamoto

Institute for Chemical Research, Kyoto University

Abstract: Recently cellulose has been reevaluated as a functional material to meet diverse needs of today's society. This is mainly due to the unique reactivities and molecular characteristics of cellulose, which is nontoxic, biodegradable, biocompatible, hydrophilic, chiral, and semi-rigid. Rather simple chemical modifications allow the conversion of cellulose to materials of novel functions for practical use, while conserving the cellulose characteristics mentioned above. Currently in the author's laboratory, by means of chemical modifications and structural controls, naturally occurring polymers like cellulose and chitin are attempted to be converted from mere

structural polymers to new materials with special functions. This presentation intends to illustrate examples of cellulose modifications as broadly as possible. The topics include (i) substituents distribution control of conventional cellulose derivatives, (ii) thermoplasticization of cellulose and its applications, (iii) thermotropic liquid crystals and LB films from cellulose, (iv) highly dielectric cellulose derivatives, and (v) preparation and functionalization of oligosaccharides.

## 第 38 回 (1993.11.15-16) 四国電力株式会社 総合研究所

1993-101

熱分解ガスクロマトグラフィーによる広葉樹型リグニンの分析 (I) アルカリ性ニトロベンゼン酸化との比較

和泉明子、黒田健一、山口 彰

筑波大学農林工学系

Analysis of hardwood lignin by pyrolysis-gas chromatography. I. Comparison of pyrolysis with alkaline nitrobenzene oxidation using synthetic lignin.

Akiko Izumi, Kenichi Kuroda, Akira Yamaguchi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Several synthetic lignins (DHPs) with various syringyl/guaiacyl ratios were prepared by the dialysis method, and Curie-point pyrolyzed at 500°C for 4 s. The products were identified by GC/MS and estimated by GC with FID. The observed pyrolysis products were same as those from tochinoki (*Aesculus turbinata*). Yields of degradation products and their S/V ratios were compared with those by alkaline nitrobenzene oxidation.

1993-102

熱分解ガスクロマトグラフィーによる日本産針葉樹の分析

黒田健一、山口 彰

筑波大学農林工学系

Analysis of some Japanese softwoods by pyrolysis-gas chromatography.

Kenichi Kuroda, Akira Yamaguchi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: To find out any difference in lignins between softwood species, an analytical pyrolysis technique, pyrolysis combined with gas chromatography (Py-GC), was applied to 16 Japanese softwoods. Twenty-five peaks of lignin-derived monomer pyrolysis products, 21 guaiacyl and 4 p-hydroxyphenyl type products, were displayed on all Py-GC traces of the softwoods pyrolyzed at 500 °C for 4 s: no remarkable qualitative differences, hence, were observed. However, the Py-GC traces differed quantitatively. Distribution of *trans*-coniferyl alcohol in the lignin-derived products indicated that the pyrograms of Japanese softwoods examined are grouped into three types: the alcohol distribution in the selected lignin-derived products is (a) more than 20%, (b) around 15% and (c) less than 10%.

1993-103

ユーカリ属の組織化学的方法によるリグニンの分析 (I)

渡辺陽子<sup>\*1</sup>、深沢和三<sup>\*1</sup>、船田 良<sup>\*1</sup>、浅田隆之<sup>\*2</sup>、小名俊博<sup>\*2</sup>

<sup>\*1</sup> 北海道大学農学部、<sup>\*2</sup> 王子製紙株式会社林木育種研究所

Lignin analysis of Eucalyptus by histochemical methods (I)

Yoko Watanabe<sup>\*1</sup>, Kazumi Fukazawa<sup>\*1</sup>, Ryo Funada<sup>\*1</sup>, Takayuki Asada<sup>\*2</sup>, Toshihiro Ona<sup>\*2</sup>

\*<sup>1</sup>Faculty of Agriculture, Uokkaido University, \*<sup>2</sup>Oji Institute for Forest Tree Improvement

Abstract: Lignin heterogeneity of Eucalyptus was investigated by using histochemical methods (Mäule reaction and ultraviolet microscopy). Absorption spectra of Mäule reaction showed that all samples were syringyl lignin rich type in all elements.

1993-104

樹木クラウンゴール細胞壁の化学構造と組織構造に関する研究

枝重有祐、富村洋一、藤井智之、石井 忠

森林総合研究所

Structural analysis of crown gall cell wall of *Populus kitakamiensis*.

Yusuke Edashige, Yoichi Tomimura, Tomoyuki Fujii, Tadashi Ishii

Forestry and Forest Products Research Institute

Abstract: Cell wall material was isolated from crown gall tumor and sound part of *Populus kitakamiensis*. Crown gall cell wall contained larger amount of lignin than the sound part and the lignin was rich in condensed type. There was little difference in cell wall polysaccharides between them. The main hemicellulosic polysaccharide was 4-*O*-methylglucuronoxylan, which is a typical hemicellulose of hardwood. Callose, which is induced in infected cells, was not detected in the crown gall cell wall. Microscopic observation indicated that crown gall was consisted of normal cells, but that rapid cell division induced by *Agrobacterium tumefaciens* made cambium abnormal form.

1993-105

リグニン化学構造の不均一性に関する研究 - $\beta$ -*O*-4 構造の *erythro*, *threo* 比のリグニン存在部位による相違

松本雄二、南 一守、飯塚堯介、石津 敦

東京大学農学部

Structural heterogeneity of lignin. The ratio of *erythro* and *threo* type of arylglycerol- $\beta$ -aryl ether structure in different part of cell wall.

Yuji Matsunoto, Kazumori Minami, Gyosuke Meshitsuka, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Abstract: Ozonation method was applied to investigate how *erythro* and *threo* ratio of arylglycerol- $\beta$ -aryl ether structure (E/T ratio) is regulated. E/T ratio in a DHP synthesized by the stepwise addition method (Zutropfverfahren) was 3 : 1, whereas that in a DHP synthesized by the one time addition method (Zurufverfahren) was about 1 : 1. E/T ratio in MWLs extracted from stepwisely milled wood meal increased with the increase in milling time, indicating that E/T ratio in secondary wall lignin is higher than that in compound middle lamella lignin. On the basis of these results, we concluded that in a endwisely polymerized lignin (secondary wall lignin), *erythro* type of arylglycerol- $\beta$ -aryl ether structure is preferentially formed, and that in a bulk polymer type lignin (compound middle lamella lignin) *threo* type becomes relatively important.

1993-106

デヒドロジコニフェリルアルコールの光学分割と絶対配置の決定

平井伸博\*<sup>1</sup>、宇田川裕晃\*<sup>1</sup>、山室宗弘\*<sup>1</sup>、加藤昌芳\*<sup>1</sup>、小清水弘一\*<sup>1</sup>、岡本昌彦\*<sup>2</sup>

\*<sup>1</sup>京都大学農学部, \*<sup>1</sup>住友化学株式会社

Optical resolution and absolute configuration of dehydrodiconiferyl alcohol

Nobuhiro Hirai\*<sup>1</sup>, Hiroaki Udagawa\*<sup>1</sup>, Munehiro Yamamuro\*<sup>1</sup>, Masayoshi Katoh\*<sup>1</sup>, Koichi Koshimizu\*<sup>1</sup>, Masahiko Okamoto\*<sup>2</sup>

\*<sup>1</sup>Faculty of Agriculture, Kyoto University, \*<sup>2</sup>Sumitomo Chemical Co., Ltd.

Abstract: The absolute configuration of dehydrodiconiferyl alcohol was elucidated by a chemical degradation. (+)-Dehydrodiconiferyl alcohol was prepared by optical resolution of the racemate with HPLC. The value of specific rotation was  $+63.3^\circ$ , suggesting that the natural (+)-dehydrodiconiferyl alcohol isolated from milk thistle ( $[\alpha]_D +10.9^\circ$ ) was not optically pure. (+)-Dehydrodiconiferyl alcohol was degraded to methylsuccinic acid via several steps. The methylsuccinic acid was (R)-(+)-enantiomer, the optical purity of which was confirmed by HPLC after derivatization. This showed that the absolute configuration of C-2 of (+)-dehydrodiconiferyl alcohol was S. Since H-2 and H-3 of dehydrodiconiferyl alcohol is trans, the absolute configuration of C-3 is inevitably R. Thus (+)-dehydrodiconiferyl alcohol is 2S and 3R.

1993-107

リグニン、フミン酸の酸化還元的性質 -ESRによる解析

鬼木隆幸

九州歯科大学

Redox properties of humic acid and lignin-Electron Spin resonance study

Takayuki Oniki

Kyushu Dental College

Abstract: Electron spin resonance (ESR) spectra of humic acids and lignin were measured at pH 13.0 under argon atmosphere or after air bubbling with or without redox reagents. ESR signal intensities of humic acids increased with elapsed time, whereas those of lignins decreased. The signals of humic acids decreased by oxidation with  $O_2$  or  $K_3[Fe(CN)_6]$  but original signals were recovered as time elapsed. The signal of lignins increased by the oxidation. The intensities of humic acids increased by reduction with a small amount of  $Na_2S_2O_4$  but decreased with a large amount of  $Na_2S_2O_4$ . The intensities of lignins decreased with a small amount of  $Na_2S_2O_4$ . Lignins were found to be a more reduced state than humic acids.

1993-108

コブシ細胞壁形成過程におけるモノリグノールグルコシドの挙動

松井直之<sup>\*1</sup>、福島和彦<sup>\*1</sup>、安田征市<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>1</sup>名大農, <sup>2</sup>USDA 林産物研

Behavior of monolignol glucosides during cell wall formation of magnolia.

Naoyuki Matsui<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Seiiti Yasuda<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Aoyama University, <sup>\*2</sup>United States Dept. of Agriculture, Forest Products Laboratory, U.S.A.

Abstract: To examine the behavior of glucose residue of monolignol glucosides in cell wall lignification, coniferin- $[Glc-6-^3H, \beta-^{14}C]$  was administered to magnolia two-years old shoot. After 3 hours or 7 days feeding, coniferin and syringin were isolated from the sap and each radioactivity was measured. The  $^3H$ -activity was observed not only in coniferin, but in syringin. It suggests the introduction of methoxyl group may occur in the state of monolignol glucosides. The decrease of  $^3H$  (glucose) to  $^{14}C$  (lignols) in monolignol glucosides was little at the end of 3 hours feeding, and increased corresponding to the length of feeding period. The ratio of  $^3H$ -decrease of monolignol glucosides in phloem region was larger than that in newly formed xylem region.

1993-109

Expression of brown midrib mutations on grass lignin.

B. Chabbert, M.T. Tollier and B. Monties

Laboratoire de Chimie Biologique, INRA

**Abstract:** Studies were conducted to characterize cell wall phenolic composition in diverse genotypes of grasses, including bmr6 and bmr12 sorghum lines, and bm1, bm2, bm3 maize lines and their normal counterparts. All brown midrib genotypes contained lower lignin content and alkali-labile p-coumaric acid. The monomer composition of lignin was differently altered according to the bm(r) gene. The occurrence of 5-hydroxyguaiacyl was shown in the alkyl aryl ether structures of bmr12 lignin of sorghum as previously reported for bm3 maize mutants. In these plants, the non-condensed lignin structures incorporated a low proportion of syringyl unit in contrast to the maize bm2 lignin which contained less guaiacyl moieties than normal lignin. Furthermore, bmr6 sorghum incorporated cinnamaldehydes units in the lignin polymer. The variations in the relative proportions of guaiacyl and syringyl units indicated that the bm(r) mutations cause different lignin structural changes. Therefore, the phenotypically similar brown midrib plants originate from different modifications of the lignification pathway.

1993-110

ウド CAD アンチセンス遺伝子を導入したタバコの解析

日尾野隆<sup>\*1</sup>、柴田大輔<sup>\*1</sup>、河津 哲<sup>\*2</sup>、高部圭司<sup>\*3</sup>、樋口隆昌<sup>\*4</sup>

<sup>\*1</sup> 三井植物バイオ研究所, <sup>\*2</sup> 王子製紙株式会社, <sup>\*3</sup> 京都大学農学部、<sup>\*4</sup> 日本大学農獣医学部

Analysis of tobacco plants with an antisense cinnamyl alcohol dehydrogenase transgene from *Aralia cordata*.

Takashi Hibino<sup>\*1</sup>, Daisuke Shibata<sup>\*1</sup>, Tetsu Kawazu<sup>\*2</sup>, Keiji Takabe<sup>\*3</sup>, Takayoshi Higuchi<sup>\*4</sup>

<sup>\*1</sup>Mitsui Plant Biotechnology Research Institute, <sup>\*2</sup>Kameyama Breeding Station, Oji Paper Co. Ltd.,

<sup>\*3</sup>Faculty of Agriculture, Kyoto University, <sup>\*4</sup>College of Agriculture and Veterinary Medicine, Nihon University.

**Abstract:** Cinnamyl alcohol dehydrogenase (CAD) catalyzes the reduction of hydroxycinnamic aldehydes (para-coumaryl, coniferyl, and sinapyl) to the corresponding alcohols (monolignols) in lignin biosynthesis. Thus, CAD is an important target in genetic engineering to modify lignin content or quality. We tested CAD activity in some tobacco plants carrying an antisense gene constructed with *Aralia cordata* CAD cDNA. CAD activity of one of transgenic tobacco plants was decreased about 55 % in comparison with that of a normal tobacco plant. Observation of cross-sections of shoots stained for lignin by the phloroglucinol-HCl assay provided evidence that more aldehydes accumulate in the cell wall in the transgenic tobacco plant than in normal tobacco plants.

1993-111

シュート分化により誘導される交雑ヤマナラシおよびタバコの酸性ペルオキシダーゼアイソザイムの発現解析

刑部敬史<sup>\*1</sup>、松本康郎<sup>\*1</sup>、小山浩和<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、秦 邦男<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター <sup>\*3</sup> 日本製紙株式会社

Expression analysis of anionic peroxidases correlated with shoot forming in *Nicotiana tabacum* and *Populus kitakamiensis*.

Keishi Osakabe<sup>\*1</sup>, Yasuo Matsumoto<sup>\*1</sup>, Hirokazu Koyama<sup>\*1</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Kunio Hata<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Nippon Paper Co., Ltd.

We have analysed the expression of peroxidase isozymes correlated with shoot forming in *Nicotiana tabacum* and *Populus kitakamiensis*. Several anionic isozymes were found to express in the callus forming vegetative bud or regenerating shoot but not in callus or leaf tissue. We have already isolated *N. tabacum* genomic peroxidase clones (*poxA1* and *poxC1*) and *P. kitakamiensis* genomic

clone (prxA1). In this report, we have isolated two other novel peroxidase clones from *P. kitakamiensis* cDNA library. Using these peroxidase genes as probes, expression patterns of anionic peroxidases were examined by RNA blot analysis.

1993-112

#### 樹木フェニルアラニンアンモニアリアーゼ遺伝子群の構造と発現の解析

刑部祐里子<sup>\*1</sup>、大坪祐二<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、山田恵子<sup>\*1</sup>、海老沼宏安<sup>\*1</sup>、秦 邦男<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 日本製紙株式会社

Characterization and expression of phenylalanine ammonia-lyase genes from a woody plant (*Populus kitakamiensis*)

Yuriko Osakabe<sup>\*1</sup>, Yuji Ohtsubo<sup>\*1</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Keiko Yamada<sup>\*1</sup>, Hiroyasu Ebinuma<sup>\*1</sup>, Kunio Hata<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup> Nippon Paper Co., Ltd.

Abstract: Six independent phenylalanine ammonia-lyase (PAL) genes were isolated from a genomic library and a cDNA library constructed with mRNAs from the young stem tissue of a hybrid aspen, *Populus kitakamiensis*. The isolated PAL clones from the cDNA library were transcribed from one gene. The corresponding gene (*pal g1*) to the cDNA and four other genes were isolated from the genomic library. Most of PAL genes consist of two exons divided with one intron. Interestingly, *pal g2a* and *pal g2b* were isolated as one DNA fragment containing two tandemly oriented PAL genes. The expressions of these PAL genes in stem, leaf, and callus tissues were demonstrated by RNA blot analysis using gene-specific probes. It was defined that *pal g1* was mainly transcribed in the young stem tissue.

1993-113

#### リグニン生合成系に関与する OMT 酵素蛋白と遺伝子の単離

早川敏雄<sup>\*1</sup>、岡村慎仁<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、秦 邦男<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 日本製紙株式会社

Purification of *O*-methyltransferase (OMT) involved in the lignin biosynthesis and cDNA cloning.

Toshio Hayakawa<sup>\*1</sup>, Shinji Okamura<sup>\*1</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Kunio Hata<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Cooperative Research Center, Tokyo University of Agriculture and Technology, <sup>\*3</sup> Nippon Paper Co., Ltd.

Abstract: *O*-methyltransferase (OMT) is a key enzyme for determining aromatic ring structures in lignin. We obtained two OMT activities from a hybrid aspen, *Populus kitakamiensis*, by using anion exchange chromatography and affinity chromatography on *S*-adenosyl-L-homocystein-Sepharose 4B. The results of Southern hybridization for total DNA from *P. kitakamiensis* suggested that OMT was consisted of a small gene family. We isolated a DNA fragment encoding OMT from a cDNA library constructed with the stem RNA and it was very similar to OMT genes from aspen and poplar.

1993-114

#### *Pseudomonas paucimobilis* SYK-6 株のビフェニル環開裂酵素遺伝子の単離と解析

花城 薫<sup>\*1</sup>、片山義博<sup>\*2</sup>、笠原健秀<sup>\*1</sup>、政井英司<sup>\*3</sup>、川合伸也<sup>\*1</sup>、山崎真狩<sup>\*4</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究開発センター、<sup>\*3</sup> 新技術開発事業団微生物進化プロジェクト、<sup>\*4</sup> 東京大学農学部

Cloning and analysis of the genes of biphenyl ring fission from *Pseudomonas paucimobilis* SYK-6.  
Kaoru Hanashiro, Yoshihiro Katayama, Takehide Kasahara, Eiji Masai, Shinya Kawai, Makari Yamasaki,  
Noriyuki Morohoshi

\*<sup>1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Cooperative Research  
Center, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Microbial Evolution Project, JRDC

\*<sup>4</sup>Faculty of Agriculture, The University of Tokyo

Abstract: *Pseudomonas paucimobilis* SYE-6 grows on various lignin dimeric compounds as a  
sole carbon source. In particular, it is characteristic of this strain to degrade biphenyl compounds. We  
have already reported about the metabolism of biphenyl structure in lignin and cloning of 15-kbp  
EcoR I fragment which could restore the wild's phenotype of mutants. We explain that 15-kbp EcoR I  
fragment is related to degradation of biphenyl compounds.

1993-115

リグニンビフェニル型化合物の分解酵素遺伝子群の単離と解析 (脱メチル酵素遺伝子の単離と解  
析)

窪田祥子\*<sup>1</sup>、小尾高広\*<sup>1</sup>、片山義博\*<sup>2</sup>、川合伸也\*<sup>1</sup>、諸星紀幸\*<sup>1</sup>

\*<sup>1</sup>東京農工大学農学部、\*<sup>2</sup>東京農工大学共同研究開発センター

Cloning and analysis of the genes involved in degradation of biphenyl structure of lignin compounds.  
Cloning and analysis of the demethylase gene.

Sachiko Kubota\*<sup>1</sup>, Takahiro Obi\*<sup>1</sup>, Yoshihiro Katayama\*<sup>2</sup>, Shinya Kawai\*<sup>1</sup>, Noriyuki Morohoshi\*<sup>1</sup>

\*<sup>1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Cooperative Research  
Center,

Abstract: *Pseudomonas paucimobilis* SYK-6 is able to grow on DDVA and other various lignin  
dimeric compounds as a sole carbon source. To reveal of the specific reactions of lignin metabolism  
of microorganism, we investigate the metabolism of biphenyl compound DDVA by SKY-6. We have  
isolated the gene coding DDVA demethylase as a 30kb *Sa*/I DNA fragment (plasmid clone pDM22)  
from *Pseudomonas paucimobilis* SYK-6 chromosomal DNA. Here, we have isolated another clone  
which has a 6kb EcoR I fragment (plasmid clone pLE6), which is thought to be the same of the 6kb  
EcoR I fragment in pDM22.

1993-116

リグニンペルオキシダーゼによるチトクローム C の酸化

割石博之\*<sup>1</sup>、Michael H. Gold\*<sup>2</sup>

\*<sup>1</sup>九州大学農学部、\*<sup>2</sup>Oregon Graduate Institute

Oxidation of ferrocytochrome c by lignin peroxidase.

Hiroyuki Wariishi\*<sup>1</sup>, Michael H Gold\*<sup>2</sup>

\*<sup>1</sup>Faculty of Agriculture, Kyushu University, \*<sup>2</sup>Oregon Graduate Institute of Science and Technology

Abstract: The direct oxidation of ferrocytochrome c by lignin peroxidase (LiP) from the lignin  
degrading basidiomycete, *Phanerochaete chrysosporium*, was demonstrated. As with cytochrome c  
peroxidase reactions, LiP oxidation of ferrocytochrome c decreased as the ionic strength increased,  
implying the involvement of electrostatic interactions between the polymeric substrate and enzyme.  
The reaction product ferricytochrome c inhibited veratryl alcohol oxidation by LiP in a  
noncompetitive manner, suggesting that cytochrome c binds to LiP at a site different from the small  
aromatic substrate binding site. Recent crystallographic studies show that the heme is buried in the  
LiP protein and unavailable for direct interaction with polymeric substrates, suggesting that the  
electron transfer from ferrocytochrome c to LiP may occur via electron tunneling, as in the reaction  
of cytochrome c peroxidase with ferrocytochrome c. This observation of the direct oxidation of

ferrocytochrome c by LiP may serve as a useful model for probing the mechanism of electron transfer between the buried heme of the enzyme and polymeric substrates.

1993-117

有機溶媒中における化学修飾ペルオキシダーゼの反応

吉田晋一、渡辺隆司、本田与一、桑原正章

京都大学木質科学研究所

Reaction of chemically modified peroxidase in organic solvents.

Shinichi Yoshida, Takashi Watanabe, Yoichi Honda, Masaaki Kuwahara

Wood Research Institute. Kyoto University

Abstract: Lignin peroxidase (LiP) from *Phanerochaete chrysosporium* was chemically modified with methoxypolyethylene glycol-succinimidyl succinate (MPSS). Reaction products by the native and modified LiP in organic solvents were analyzed by g.l.c. 3,4,5-Trimethoxybenzyl alcohol (TMBA) was oxidized by the modified LiP in benzene, While the native LiP was inactive to TMBA in the organic solvent. Furthermore, it has been found that veratryl alcohol was more susceptible to the oxidation than TMBA in aqueous solutions, while the reverse substrate specificity was observed in the reactions in benzene. Oxidation activity of the modified LiP in benzene was 1/300 of that observed in aqueous solution.

1993-118

*Phanerochaete chrysosporium* の芳香環開裂酵素について(II)

中村雅哉、西田篤実、高野麻理子

森林総合研究所

Aromatic ring cleavage enzyme from *Phanerochaete chrysosporium*. II.

Masaya Nakamura, Atsumi Nishida, Mariko Takano

Forestry and Forest Products Research Institute

Abstract: In the metabolic pathway for vanillic acid degradation by *Phanerochaete chrysosporium*, it was shown that 1,2,4-tri-hydroxybenzen underwent aromatic ring-cleavage. However, ring-fission dioxygenase is very unstable so the purification of this enzyme is very difficult. In this study, we succeeded in the purification of 1,2,4-trihydroxybenzen (hydroxyquinol) 1,2-dioxygenase and clarified some enzymatic properties. The native molecular weight of this enzyme is 94,000 Dalton and subunit molecular weight are 40,000 and 52,000 Dalton by SDS-PAGE. In the kinetic analysis, Michaelis constant for 1,2,4-tri-hydroxybenzen equals  $7 \mu\text{M}$  and  $V_{\text{max}}$  equals 0.826.

1993-119

リグノスチルベン- $\alpha$ ,  $\beta$ -ジオキシゲナーゼの活性と鉄の関係(II)

鴨田重裕、佐分義正

東京大学農学部

The relation between activity and iron content of lignostilbene- $\alpha$ ,  $\beta$ -dioxygenase. II.

Shigehiro Kamoda, Yoshhasa Saburi

Faculty of Agriculture, the University of Tokyo

Abstract: Lignostilbene- $\alpha$ ,  $\beta$ -dioxygenase I (LSD-I), one of LSD isozymes, contained iron. Native LSD-I was almost colorless or pale yellow at high concentration. LSD-I did not show the heme typical absorption spectrum. LSD-I seemed to have nonheme iron. LSD-I was inactivated by  $\text{H}_2\text{O}_2$ , oxidizing agent, and was activated by hydroxylamine, reducing agent, o-phenanthroline, chelating agent for ferrous ion, inhibited the LSD reaction. Tiron, chelating agent for ferric ion, did

not inhibit the LSD reaction. LSD-I inactivated by H<sub>2</sub>O<sub>2</sub> was reactivated with ferrous ion and hydroxylamine. These results indicated that ferrous ion play the important role on the enzyme activity. Furthermore, linear relation was founded between the amounts of ferrous ion and activities. The maximum amount of iron seemed to be two atoms per one molecule of LSD-I.

1993-特別講演、

植物培養細胞の二次代謝機能 –シキミ酸経路由来の shikonin と berberine を例に

福井宏至

香川大学農学部

Invited Lecture: Secondary metabolism (shikonin and berberine) in cultured plant cells.

Hiroshi Fukui

Faculty of Agriculture, Kagawa University

1993-201

リグニンからのポリウレタン

菱山正二郎<sup>\*1</sup>、大原誠資<sup>\*1</sup>、秦野恭典<sup>\*1</sup>、須藤賢一<sup>\*2</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 群馬女子短期大学

Polyurethanes from lignin.

Shojiro Hishiyama<sup>\*1</sup>, Seiji Ohara<sup>\*1</sup>, Yasunori Hatano<sup>\*1</sup>, Kenichi Sudo<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Gunma Womens Junior College

Abstract: In order to prepare the polyurethane from lignin, lignin derivatives (I and II) were synthesized from steam-exploded lignin using glycerol  $\alpha$ -monochlorohydrin (GMH). NMR studies show that lignin derivative II possesses large amount of hydroxyl groups which have high reaction activity with isocyanate. Preparation of polyurethane films was accomplished from lignin derivative II using two kinds of isocyanate, hexamethylenediisocyanate (HDI) and diphenylmethanediisocyanate (MDI). Viscoelastic properties of these polyurethane films were investigated.

1993-202

リグニン樹脂接着剤の製造

島谷啓二、佐野嘉拓、笹谷宜志

北海道大学農学部

Preparation of lignin-based wood adhesives.

Keiji Shimatani, Yoshihiro Sano, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Abstract: The utilization of kraft lignin in the substrate of wood adhesives has been investigated. A mixture of kraft lignin and phenol (8:2) was hydroxymethylated under alkali conditions in order to produce phenol-lignin co-polymer (WI and WS). WI was recovered in a yield of 89% from the reaction mixture. Resorcinol terminated resins of the co-polymers (WI-R) were prepared by condensation of WI (100 parts) with resorcinol (ca 30 parts) in alkali solution at pH 11. An alkali solution of WI-R (40% solids) containing 5-10% of paraformaldehyde had a gelation time of 25 minutes at room temperature. The gelation times varied with amounts and kinds of cross-linking reagents suggesting that wood lignins may be utilized as a readily available and inexpensive substrate for cold-setting wood adhesives.

1993-203

膨潤-溶媒とプロセスによる高反応性リグニンの合成

松原正幸、船岡正光、阿部 勲

### 三重大学生物資源学部

Synthesis of highly reactive lignins by the swelling-solvation process.

Masayuki Mtsubara, Masamitsu Funaoka, Isao Abe

Faculty of Bioresources, Mie University

Abstract: The swelling-solvation process is a method for direct conversion of protolignin into functional lignophenol derivatives, which proceeds rapidly at room temperature. The key point of this process is to treat lignocellulosics with concentrated acid under the solvation of lignin with phenol derivatives. The resulting lignophenol derivatives have several distinctive properties which conventional lignins do not have: no conjugated system, light color, high protein adsorbing capacity, etc. In this presentation, the processes for synthesizing lignophenol derivatives having different reactivities and functions are discussed.

1993-204

隣接基関与反応を応用するリグノフェノール誘導体の分子構造変換

寶勝智貴、船岡正光、阿部 勲

三重大学生物資源学部

Structural conversion of lignophenol derivatives by neighbouring group participation.

Tomotaka Hosho, Masamitsu Funaoka, Isao Abe

Faculty of Bioresources, Mie University

Abstract: Lignophenol derivatives are directly derived from protolignin by the swelling-solvation process combining the solvation of lignin with phenol derivative and the swelling and dissolution of carbohydrates by concentrated acid. Lignophenol derivatives are not subjected to complicated structural modifications, retaining structural characteristics of original lignin, and highly phenolic, due to the cleavage of benzyl ether linkages and the phenolation at  $\alpha$ -positions (0.65mol/C<sub>9</sub> in softwood, 0.90mol/C<sub>9</sub> in hardwood). In the present work, the lignocresols were synthesized from spruce and birch by the S-S process, and their depolymerizations were carried out by the neighbouring group participation in alkaline systems, in order to control their reactivities and functions. Spruce lignocresol was depolymerized to Mw ca. 900 by the treatments with 2N NaOH or a mixture of NaOH and Na<sub>2</sub>S at 170 °C for 2 hours, while birch lignocresol to Mw ca. 600. When *p*-cresol was added in the reaction system, spruce lignocresol decreased to Mw ca. 600. Alkaline depolymerization mechanisms of lignophenol derivatives were discussed.

1993-205

リグノフェノール誘導体の構造とタンパク質に対するその機能

井岡浩之、関 範雄、中嶋礼子、三亀啓吾、○船岡正光、阿部 勲

三重大学生物資源学部

Affinity of lignophenol derivatives for proteins.

Hiroyuki Ioka, Norio Seki, Reiko Nakajima, Kei'ō Mikame, Masamitsu Funaoka, Isao Abe

Faculty of Bioresources, Mie University

Abstract: Lignophenol derivatives were synthesized from various lignocellulosics, using the swelling-solvation process, and their affinity for proteins was investigated. Lignophenol derivatives had much higher affinity for proteins, compared with conventional lignin preparations. The protein adsorbing capacities of lignophenol derivatives differed with their originating species and increased with increasing basicity of phenol derivatives. The adsorption of protein on lignophenol derivatives rapidly took place at the initial step of treatment, after which the amount increased gradually with time. The maximum adsorption was achieved at isoelectric points of proteins. Proteins immobilized on lignophenol derivatives were not desorbed at any pH.

1993-206

リグニンの水素化分解 –触媒等の検討–

小山 実

物質工学工業技術研究所

Hydrocracking of lignin. –Search for catalysts and reaction conditions.

Makoto Koyama

National Institute of Materials and Chemical Research

Abstract: Hydrocracking of a kraft lignin (KL) was conducted in order to search the catalysts and reaction conditions as the purpose to rise monophenol yield and promote the monomerization of KL. The searched catalysts were as follows; solid acids (smectites, aluminosilicates, Al-pillared smectites, composite metal oxides, zeolites and titanium oxides), alumina, metal oxides and metal.

1993-特別講演、

樹木抽出成分 –フェニルプロパン誘導体–

笹谷宜志

北海道大学農学部

Invited Lecture: Wood extractives. –Phenylpropane derivatives.

Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Abstract: In numerous wood extractives, typical phenylpropane derivatives are lignans. They include those based on the new definition, namely neolignans. This paper summarizes the chemical structures of lignans and neolignans in larch *Larix leptolepis* Gord., fir *Abies sachalinensis* Masters, willows *Chosenia arbutifolia* A. Skvortz. and *Salix sachalinensis* Fr. Schm. Among them, trimeric and tetrameric derivatives were involved in addition to dimeric ones. It is presumed that there is intimate relation between lignans and Brauns' lignin (BL). Also, the biological activities of lignans will be dealt with only briefly here.

1993-207

稲ワラ・ソーダ蒸解黒液リグニンの分散剤としての利用

中野準三<sup>\*1</sup>、北仲由美子<sup>\*1</sup>、矢田英律<sup>\*1</sup>、石津 敦<sup>\*2</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 東京大学農学部

Utilization of rice straw soda lignin from pulping black liquor as dispersant.

Junzo Nakano<sup>\*1</sup>, Yumiko Kitanaka<sup>\*1</sup>, Hidenori Yada<sup>\*1</sup>, Atsushi Ishizu<sup>\*2</sup>

<sup>\*1</sup>Faculty of Engineering, Fukui Institute of Technology, <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Abstract: Soda lignin was isolated from the pulping black liquor of rice straw, then was sulfomethylated (SWL). The dispersibility of kaolin suspension and the setting of mortar with SWL were measured in contrast with wood lignosulfonate. The effects of dispersing additives were also tested with various carboxylic acids. The results are summarized as follows: (1) Dispersibility with rice straw SWL is efficient for concrete production. (2) Among the additives used here, sugar carboxylic acids are better than other carboxylic acid, and glucaric acid is superior than gluconic acid. (3) In order to simplify the sulfomethylation, lignin in black liquor was directly sulfomethylated after the acidification with dil. sulfurous acid. The dispersibility is poor comparing with that of purified SWL. The setting of mortar takes a long time.

1993-208

## リグニングラフトポリマーのセメント粒子への分散性と粘稠性

矢口 稔<sup>\*1</sup>, 大田晃<sup>\*1</sup>, 田中義夫<sup>\*1</sup>, 瓜生敏之<sup>\*2</sup>

<sup>\*1</sup> 株式会社エヌエヌビー, <sup>\*2</sup> 東京大学生産研究所

The dispersibility and viscosity of lignin graft polymer to cement particles.

Minoru Yaguchi<sup>\*1</sup>, Akira Ohta<sup>\*1</sup>, Yoshio Tanaka<sup>\*1</sup>, Toshiyuki Uryu<sup>\*2</sup>

<sup>\*1</sup>NMB Co., Lt d. <sup>\*2</sup> Institute of Industrial Science, the University of Tokyo

Keywords: lignin graft polymer, lignosulfonates, cement particles, dispersing agent, viscosity

Abstract: In this study, the synthesis of lignin graft polymer provides high-dispersibility and moderate viscosity for cement particles was investigated. Acrylamide (AM) and acrylamide methylpropansulfonate (AMPS) were grafted to lignin sulfonate (LSA) for which AM provides the viscosity and AMPS provides the high dispersibility. Various lignin graft polymers (LGP) were evaluated dispersibility and viscosity in cement mortar testings. It was found that LGP provided the high-dispersibility and the moderate viscosity to the cement particles.

1993-209

## 常圧酢酸パルプ化

金野晴男、佐野嘉拓、笹谷宜志

北海道大学農学部

Acetic acid pulping at atmospheric pressure.

Haruo Konno, Yoshihiro Sano, Takashi Sasaya

Faculty of Agriculture, Hokkaido University

Abstract: Atmospheric pulping of commercial hardwood chips of Hokkaido in a boiling aqueous AcOH with a small amount of sulfuric acid were carried out either in a batch system or in a mimetic continuous-extraction system. The continuous extraction conditions used for the chips were the optimum conditions for separating into each of the main components as quantitatively as possible. By the continuous extraction in a boiling 95% AcOH with 0.32% sulfuric acid, the chips yielded 44.6% of screened pulp with Klason lignin of 6.9%, 1.8% of reject, 16.9% of reducing sugars (14.1% of xylose) and 19.0% of AcOH lignin based on o.d. chips, respectively.

1993-210

## リグニンモデル化合物のオルガノソルブパルプ化処理における $\beta$ -O-4 結合の開裂機構(II)-キノンメチド生成速度に対する有機溶媒の効果

高橋一郎、坂井克己

九州大学農学部

The  $\beta$ -O-4 bond cleavage mechanism during organosolv pulping treatments of lignin model compound. I. - The effect of organic solvent on rate of quinone methide formation-

Ichirou Takahashi, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: The  $\beta$ -O-4 bonds in lignin and its model compounds were cleaved to give eugenol and/or isoeugenol during an organosolv pulping treatment with bisulfite at 160 °C. It was found that this reaction which proceeds *via* a quinone methide intermediate was seriously influenced by concentration and inductivity of organic solvents. Consequently we presumed that the rate-determining step is an ionic reaction. In order to investigate the effect of solvent on rate of quinone methide formation, a lignin model compound shown in Fig. 1 was subjected to an alcohol-phosphate buffer treatment in aqueous ethanol of various concentration at relatively low temperatures. The rate constants and activation parameters were calculated for *erythro* form to *threo* form. The conversion rate was affected seriously by solvent concentration. This result suggests that the

rate-determining step of this reaction is not the  $\beta$ -O-4 bond cleavage process, but the quinone methide formation process.

1993-211

パルプ漂白菌によるリグニンモデル物質の変換

飯森武志, 金子令治, 吉川宏, 町田誠, 吉岡英敏, 村上邦睦

日本製紙株式会社

Transformation of lignin model compounds by pulp-bleaching fungi.

Takeshi Iimori, Reiji Kaneko, Hiroshi Yoshikawa, Makoto Machida, Hidetoshi Yoshioka, Kunichika Murakami

Nippon Paper Industries Co., Ltd.

Keywords: pulp-bleaching fungus, oxygen-bleached pulp, lignin degradation fungus, enzyme activity

Abstract: We have already reported a new pulp-bleaching fungus, namely SKB-1152, which could increase the brightness of oxygen-bleached kraft pulp (OKP) to over 80%. In the present work, we investigated the change of three lignin model compounds (veratryl alcohol: VE, veratric aldehyde : VEA, veratric acid : VEacid) when these compounds was added to the OKP in bleaching. After incubation, culture filtrate were analyzed by HPLC. VE was oxidized to VEA and VEA was consumed in the treatment by SKB-1152. However, when VEA and VEacid were added, these compounds were reduced to VE respectively. Resulting, produced VE was oxidized to VEA again and finally consumed. Further, we reported the enzyme activity in culture filtrate.

1993-212

機械パルプの微生物処理に関する研究(XI) 光退色を抑制する菌とモデル化合物との反応性について

谷口新吾、武田早苗、橘 燦郎、伊藤和貴、沖 妙

愛媛大学農学部

Studies on biological treatment of mechanical pulps. XI. Reactivity between lignin model compounds and extracellular crude enzymes solution from fungi having ability for depression of color reversion of mechanical pulps.

Shingo Taniguchi, Sanae Takeda, Sanro Tachibana, Kazutaka Itoh, Tae Oki

Faculty of Agriculture, Ehime University

Abstract: Reactions between the lignin model compounds having functional groups for color reversion and the crude enzymes solution from six wood-rotting fungi having ability for depression of color reversion of mechanical pulps were examined. The model compounds used were coniferyl-aldehyde methy wther (1),  $\alpha$ -(2-methoxyphenoxy)- $\beta$ -hydroxypropioquaiacone (2), and methoxy-p-quinone (3). The compound (3) was most reactive to the crude enzymes solution in the three compounds, the compound (1) was next to the compound (3), and the compound (2) was less reactive. Main reaction of each compound was reductive reactions, but some oxidative reactions was also occurred. When the compound (3) was treated with the crude enzymes solution, main reaction was reduction of quinone to the corresponding hydroquinone and followed by methylation of the phenolic hydroxyl group generated. Based on the results of the reactivity between the model compounds and the crude enzymes solution, reduction of quinone and followed by protection of the phenolic hydroxyl group generated seem to contribute mainly to the depression of color reversion of mechanical pulps.

1993-213

リグニン分解菌によるクラフトパルプ漂白廃液の処理(VI)グルコノ- $\delta$ -ラクトン添加による処理性向上の機構について

李 宣鎬、近藤隆一郎、坂井克己

九州大学農学部

Decolorization of kraft bleaching effluent by lignin-degrading fungi. VI.

The mechanism of the decolorization of E1 effluent by an addition of glucono- $\delta$ -lactone.

Seon-Ho Lee, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: In a previous report, we observed that the addition of glucono- $\delta$ -lactone to the E1 effluent showed great decolorization during a short treatment period. In the present study, we have attempted to clarify the mechanism of decolorization by the addition of glucono- $\delta$ -lactone. When the aqueous solutions of glucose and glucono- $\delta$ -lactone were treated with *Coriolus versicolor*, most of the glucose was consumed and the glucono- $\delta$ -lactone was converted a part into gluconic acid remaining in the cultivation medium. The pH of the effluent With the glucono- $\delta$ -lactone was decreased from an initial pH of 4.5 to 3.6, although the pH of the effluent without any additives was increased gradually during fungal treatment. From the results, we assume that the effect of the glucono- $\delta$ -lactone on the great decolorization of E1 effluent was due to the some morphological change of the mycelium of the *C. versicolor* by the gradual decrease of pH.

1993-214

白色腐朽菌のリグニン分解に関与する酵素系に関する研究(II)クラフトパルプのバイオブリーチングに及ぼす金属塩の影響

平井浩文、近藤隆一郎、坂井克己

九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi. I.

Effects of metal salts on biological bleaching of kraft pulp.

Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We obtained several new isolates which showed higher ligninolytic activity and selectivity than typical lignin-degrading fungi, *Phanerochaete chrysosporium* and *Coriolus versicolor*. In the present work, we applied these new isolates to bleaching of the kraft pulp, and determined ligninolytic enzyme activities in these bleaching cultures. Manganese peroxidase (MnP) was dominant in most strains which could bleach the kraft pulp, and the higher brightness increase of fungal treated pulp was observed, the higher MnP activity was detected in the culture. If metal ions were removed from the kraft pulp with an acid treatment, biological bleaching of the pulp hardly showed brightness increase, and ligninolytic enzyme activity in the culture sharply decreased. These results suggest that metal ions in the kraft pulp played an important role in biological bleaching of the kraft pulp by white-rot fungi.

1993-215

リグニンの酵素分解に関する研究(IV) メンブランフィルターを用いた培養系におけるクラフトパルプの *in vitro* ブリーチング

近藤隆一郎、蔵敷賢二、坂井克己

九州大学農学部

In vitro bleaching of haft pulp by extracellular enzymes excreted from white-rot fungi in a cultivating system using a membrane filter.

Ryuichiro Kondo, Kenji Kurashiki, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: To clarify the role of the excreted extracellular enzymes during long-term incubation in biobleaching with white-rot fungi, we have developed a cultivation system using a membrane filter which can prevent the direct contact between hyphae and kraft pulp, but allows extracellular enzymes to attack the kraft pulp. The fungus YK-624 brightened the pulp 21.4 points to 54.0% brightness after 5-days *in vitro* treatment, which was significantly higher than *Phanerochaete chrysosporium* and *Coriolus versicolor* did during 7-days treatment. This results indicate that cell-free, membrane-filtered components from the *in vitro* biobleaching system are capable of delignifying unbleached kraft pulp. Obvious candidates for filterable reagents capable of delignifying and bleaching kraft pulp are peroxidase and phenoloxidase proteins. Secreted manganese peroxidase activity in the filterable components was substantial during the fungus YK-624 *in vitro* biobleaching. A positive correlation between the level of manganese peroxidase and brightening of the pulp was observed.

1993-216

亜硝酸前処理を用いるクラフトパルプ酸素漂白法とその漂白機構(2) アカマツパルプの亜硝酸処理とリグニンモデル化合物の反応

大井 洋、岸野正典、山口 彰

筑波大学農林工学系

A pretreatment with nitrous acid for oxygen bleaching of kraft pulp and its bleaching mechanism. II. Nitrous acid treatment of akamatsu pulp and reactions of lignin model compounds.

Hiroshi Ohi, Masanori Kishino, Akira Yamaguchi

Institute of Agriculture and Forest Engineering, University of Tsukuba

Abstract: To clarify the conditions of nitrous acid pretreatment for softwoods pulp, akamatsu kraft pulp (kappa number: 26, viscosity: 3lcP) at medium consistency was treated under various conditions. Kappa number of the pulp decreased to 13.5 under the condition of 0.3% nitrite, 4% nitric acid, 90 °C and 3 hours. Secondly we discussed about the bleaching mechanism based on reactions of non-phenolic lignin model compounds. When 1-(3,4-dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)-propan-1-ol was treated in the nitric acid solution without nitrite at 90 °C, it was stable even after 3 hours, which changed into an its stereo chemical isomer. More than 90% of the model was recovered. On the other hands, the model was clearly decomposed when it was treated with the nitrite and nitric acid, we identified 35% of veratraldehyde and 6% of 4-nitroveratrole from the model. It was found that a main reaction is the cleavage of a C $\alpha$ -C $\beta$  bond.

1993-217

酸処理を用いたクラフトパルプの無塩素漂白 -漂白機構-

池田 努<sup>\*1</sup>、真柄謙吾<sup>\*2</sup>、富村洋一<sup>\*2</sup>、細谷修二<sup>\*2</sup>

<sup>\*1</sup> 筑波大学農林工学系、<sup>\*2</sup> 森林総合研究所

Non-chlorine bleaching by acid treatment of kraft pulp. -Bleaching mechanism-

Tsutomu Ikeda<sup>\*1</sup>, Kengo Magara<sup>\*2</sup>, Yoichi Tomimura<sup>\*2</sup>, Shuji Hosoya<sup>\*2</sup>

<sup>\*1</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba, <sup>\*2</sup>Forestry and Forest Products Research Institute

Abstract: It was reported in our previous paper that beech and red pine kraft pulp were successfully delignified by sulfuric acid treatment. with a small amount of sodium nitrate and sodium nitrite followed by caustic extraction. In this paper, the structure of the lignin dissolved by acid treatment or caustic extraction were characterized by elemental analysis UV, IR, NMR, and GPC to

understand the delignification mechanism. Carbohydrate analysis of the pulp and the bleach effluent were also performed by using liquid chromatography to see the degradation of cellulose and hemicellulose during bleaching.

1993-218

酸素アルカリ漂白過程における多糖類の分解機構(2)―糖分解がリグニン反応に依存する系での反応選択性の向上―

安本光夫、松本雄二、石津 敦

東京大学農学部

Dependence of carbohydrate degradation on reaction of lignin during oxygen bleaching.

Mitsuo Yasumoto, Yuji Matsumoto, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo

Abstract: During oxygen bleaching, the degradation of carbohydrate depends on the reaction of lignin. Therefore, mechanistic studies such as degradation pathway of carbohydrates, factors affecting reaction selectivity, or protective effect of additives have to be performed in a system where carbohydrate degradation is hardly observed if lignin is absent. In our model system, methyl- $\beta$ -glucopyranoside (MGP) is not degraded when either vanillyl alcohol (VA) or oxygen is not present. Effects of oxygen pressure, magnesium to iron ratio, and methanol addition on the reaction rate of both MGP and VA, and on the reaction selectivity between MGP and VA were examined in this model system. Results suggested that degradation products of lignin peroxides rather than hydrogenperoxide or superoxide anion have a significant effect on the degradation of carbohydrate.

1993-219

The Contribution of high molecular lignosulfonate to the powerful bacterial cellulose production by *Acetobacter xylinum* ATCC 10245

S. Premjet、大谷慶人、鮫島一彦

高知大学農学部

Abstract: The high molecular lignosulfonate fraction and the low molecular lignosulfonate and carbohydrate mixture fraction were obtained through gel-filtration and a 80% ethanol precipitation method from the commercial sulfite pulping waste fraction (named CP powder). The media with high molecular lignosulfonate fraction showed better yields than those with the low molecular carbohydrate rich fractions. The elimination of carbohydrates, cations and low molecular fraction from the whole CP powder showed no negative effect on the powerful cellulose production. The powerful cellulose production was also observed by the addition of commercially pure sodium lignosulfonate. The contribution of the dispersing nature of the lignosulfonate was compared with synthetic dispersant and natural digitonin but they showed only slight effects on cellulose production.

1993-220

微粉碎セルロースの生成に及ぼす因子

遠藤貴士、北川良一、細川 純、壁谷 洋、西山昌史

四国工業試験所

Factors for production of fine-grinding cellulose.

Takashi Endo, Ryouichi Kitagawa, Jun Hosokawa, Hiroshi Kabeya, Masashi Nishiyama

Government Industrial Research Institute, Shikoku

Abstract: Air-dried or vacuum-dried CF11 (Whatman) was ground in a vibratory ball mill under several conditions, and then the obtained powders were characterized. In case of both air-dried and

vacuum-dried CF11 at room temperature, the particle size of powders became small and the crystallinity was decreased with grinding time. However, the degree of polymerization was not significantly reduced. In vacuum-dried CF11, the particle size was much smaller than in air-dried one. The particle distribution was same in both air-dried and vacuum-dried CF11 grinding at -100 °C, and the particle size of obtained powders was small. However, the crystallinity from air-dried CF11 was slightly decreased. Addition of organic solvents such as acetone on CF11 was effective in forming fine particles. In particular, fine particles were formed from dried CF11. For fine-grinding of cellulose, the absorbed water significantly effects on the production of powder. The absorbed water causes agglomeration of the particles and plasticizing of cellulose.

## 第 39 回 (1994.10.12-13)福岡リ-セントホテル

1994-101

熱分解ガスクロマトグラフィーによる広葉樹型リグニンの分析(II) 日本産広葉樹の分析

和泉明子、黒田健一、山口 彰

筑波大学農林工学系

Analysis of hardwood lignin by pyrolysis-gas chromatography. II. Analysis of Japanese hardwoods.

Akiko Izumi, Kenichi Kuroda, Akira Yamaguchi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Several Japanese hardwoods were analyzed by pyrolysis combined with gas chromatography (Py-GC). The yields of pyrolysis products were about half of those on nitrobenzene oxidation. The ratios of syringyl-derived pyrolysis products to guaiacyl-derived pyrolysis products were in agreement with the ratios of the syringaldehyde yields to the vanillin yields on nitrobenzene oxidation.

1994-102

熱分解ガスクロマトグラフィーによるイネ中の桂皮酸類の分析

黒田健一<sup>\*1</sup>、鈴木亜樹<sup>\*2</sup>

<sup>\*1</sup> 筑波大学農林工学系、<sup>\*2</sup> 筑波大学農林学系

Analysis of cinnamic acids in rice (*Oryza sativa* L.) by pyrolysis-gas chromatography.

Kenichi Kuroda<sup>\*1</sup>, Aki Suzuki<sup>\*2</sup>

<sup>\*1</sup> Institute of Agricultural and Forest Engineering, University of Tsukuba, <sup>\*2</sup> Institute of Agriculture and Forest, University of Tsukuba

Abstract: Pyrolysis derivatisation using tetramethylammonium hydroxide (TMAH), a thermally assisted hydrolysis and methylation method, was effectively used to identify cinnamic acids in paddy rice (*Oryza sativa* L.). Rice and its lignin produced 4-methoxy and 3,4-dimethoxycinnamic acid methyl esters as the main products on pyrolysis in the presence of TMAH., 3,4,5-trimethoxy-cinnamic acid methyl ester was absent. This report describes furthermore the determination of p-coumaric and ferulic acids in rice on the basis of the yields of 4-vinylphenol and 4-vinylguaiacol produced by the conventional pyrolysis-gas chromatography method (Py-GC). The amounts of p-coumaric and ferulic acids determined by Py-GC were in good agreement with those determined by a combination of alkaline hydrolysis and high temperature.

1994-103

Sorghum, pearl millet および maize の brown midrib mutant stem 細胞壁のリグニンおよびヒドロキ

## シ桂皮酸

Thi Bach Tuyet Lam<sup>\*1</sup>、飯山賢治<sup>\*1\*2</sup>、Bruce A. Stone<sup>\*1</sup>

<sup>\*1</sup>La Trobe 大学生化学科、<sup>\*2</sup> 東京大学農学部

Lignin and hydroxycinnamic acids in walls of brown midrib mutants of sorghum, pearl millet and maize stems

Thi Bach Tuyet Lam<sup>\*1</sup>, Kenji Iiyama<sup>\*1\*2</sup>, Bruce A. Stone<sup>\*1</sup>

<sup>\*1</sup>School of Biochemistry, La Trobe University, <sup>\*2</sup>Faculty of Agriculture, the University of Tokyo

Abstract: The brown-midrib (*bmr*) mutants have been found or induced in maize, sorghum, pearl millet and hybrid of sorghum × sudangrass. We discussed the characteristics of stem walls of *bmr* mutants of sorghum (two mutants, *Sorghum bicolor*), pearl millet (*Pennisetum glaucum*) and maize (*Zea mays*) focusing on linkage types of hydroxycinnamic acids to wall polymers and on lignin structural feature. Lignin content of all mutants determined using acid detergent lignin (ADL) procedure was significantly lower than that of normal counterparts, however there are no significant differences in lignin content determined by acetyl bromide procedure between *bmr* and normal strains, suggesting the incomplete polymerization of lignin molecules during lignification in *bmr* mutants. No etherified *p*-coumaric acids were found in all samples tested except on normal strain of pearl millet, the amounts of etherified ferulic acid in *bmr* mutants, which probably form ester-ether bridges between lignin and polysaccharides, were not as much as those of normal counterparts. The low content of the bridges in *bmr* mutants may contribute to the high rumen digestibilities.

1994-104

小麦 straw およびクスノキから抽出したリグニンの ESR

鬼木隆幸、高浜有明夫

九州歯科大学

Electron spin resonance study on lignins from wheat straw and camphor tree.

Takayuki Oniki, Umeo Takahama

Kyushu Dental College

Abstract: Milled straw or milled wood lignins and dioxane lignins were isolated successively from wheat straw and camphor tree. Saponification and acidolysis were used to release ester and ether linkages, respectively, between lignins and polymetic compounds. Electron spin resonance (ESR) spectra of the lignins isolated from each steps were measured at pH 13.0 or 12.5 under argon atmosphere or after air-bubbling in solutions. When air was bubbled in solutions, milled wood lignin from camphor tree showed an ESR signal due to 4-hydroxyphenyl group, while dioxane lignin showed ESR signals due to 3-methoxy-4-hydroxyphenyl (guaiacyl) group and 3,5-dimethoxy-4-hydroxyphenyl (syringyl) group. Wheat straw lignin showed a guaiacyl signal and a slight amount of syringyl signal by the air oxidation. The results confirm that lignins are polymerized with successive, sinapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol when three precursors present simultaneously in a cell.

1994-105

白色腐朽菌のリグニン分解に関与する酵素系に関する研究(IV)～白色腐朽菌の還元能について

平井浩文、近藤隆一郎、坂井克己

九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi. IV. Reducing ability of white-rot fungi.

Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: To clarify reducing ability of white-rot fungi, we used 6 tetrazorium salts which were

well-known as dehydrogenase-detectable agents. We examined the effect of various culture conditions on fungal reducing and oxidizing activity which were detected by colorization of the tetrazorium salts and the decolorization of Poly R-478, respectively. The highest level of reducing activity of white-rot fungi was detected in nutrient-rich conditions although the decolorization of Poly R-478 was observed in nutrient-poor conditions.

1994-106

組み換え DNA によるマンガンペルオキシダーゼ変異株の作成とその諸性質

岸克行<sup>\*1</sup>、Margo Kusters<sup>\*1</sup>、Mary B. Mayfield<sup>\*1</sup>、Taina Lundell<sup>\*2</sup>、Margaret Alic<sup>\*1</sup>、Michael H. Gold<sup>\*1</sup>,  
<sup>\*1</sup>Oregon Graduate Institute, <sup>\*2</sup> Helsinki University

Homologous expression and site-directed mutagenesis of recombinant manganese peroxidase in *Phanerochaete chrysosporium*.

Katsuyuki Kishi<sup>\*1</sup>, Margo Kusters<sup>\*1</sup>, Mary B. Mayfield<sup>\*1</sup>, Taina Lundell<sup>\*2</sup>, Margaret Alic<sup>\*1</sup>, Michael H. Gold<sup>\*1</sup>

<sup>\*1</sup>Dept. of Chemistry, Biochemistry and Molecular Biology, Oregon Graduate Institute of Science and Technology, <sup>\*2</sup>Dept. of Applied Chemistry and Microbiology, University of Helsinki

Abstract: Homologous expression and site-directed mutagenesis on Mn<sup>II</sup> ligands of manganese peroxidase (MnP) in *Phanerochaete chrysosporium* were performed using glyceraldehyde-3-phosphate dehydrogenase (*gpd*) primary metabolic promoter and polymerase chain reaction (PCR). The recombinant proteins were expressed and secreted under primary metabolic growth conditions. The Mr and absorption spectra of the recombinant MnP proteins were essentially identical to the wild type MnP. Steady state kinetic values for the oxidation of Mn<sup>II</sup> by recombinant wild type MnP and wild type MnP were also very similar. In contrast, the mutation at Mn<sup>II</sup> binding site resulted in markedly lower affinity and reactivity for Mn<sup>II</sup>.

1994-107

リグノスチルベン- $\alpha$ ,  $\beta$ -ジオキシゲナーゼアイソザイム遺伝子のクローニング

鴨田重裕、佐分義正

東京大学農学部

Cloning of a lignostilbene- $\alpha$ ,  $\beta$ -dioxygenase isozyme gene from *Pseudomonas paucimobilis* TMY1009.

Shigehiro Kamoda, Yoshimasa Saburi

Faculty of Agriculture, the University of Tokyo

Abstract: The gene of lignostilbene- $\alpha$ ,  $\beta$ -dioxygenase I (LSD-I), one of LSD isozymes, has been cloned and expressed in *E. coli*. Since there has been no other gene of LSD isozyme around LSD-I gene, genomic library was newly constructed. Detection of LSD isozyme gene was done with universal probe for  $\alpha$ ,  $\beta$ ,  $\gamma$  subunits, which compose LSD isozymes. The positive clone was analyzed by southern blot hybridization. The *Bam*HI-*Hind*III 4.2kb fragment, containing LSD isozyme gene, was subcloned in pUC118. The gene was expressed in *E. coli* by the use of *lac* promoter. The product was purified in the purity showing single band on PAGE. And it was identified as LSD-III on native-PAGE and reversed-phase HPLC by comparison with LSD-I. Furthermore the nucleotide sequence of the gene accorded with the amino acid sequences of two peptides from digested  $\beta$  subunits.

1994-108

樹木 OMT 遺伝子の構造とその発現様式の解析

早川敏雄<sup>\*1</sup>、南藤和也<sup>\*1</sup>、岡村慎仁<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 東京農工大学共同研究センター

Structures and expression analysis of O-methyltransferase genes from woody plant.

Toshio Hayakawa<sup>\*1</sup>, Kazuya Nantou<sup>\*1</sup>, Shinji Okamura<sup>\*1</sup>, Shinya Kawai,<sup>\*1</sup> Yoshihiro Katayama<sup>\*2</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology

Abstract: We isolated two genes encoding O-Methyltransferase from *Populus kitakamiensis*. The Genomic clone g26 consists of four exons divided with three introns. And another clone, g25 consists of five exons divided with four introns and it shared higher homology with OMT cDNA from *P. kitakamiensis*. RNA blot analysis using gene-specific probes shows that the cDNA accumulates in young stem tissue, but g26 expresses in young leaf. The difference of expression pattern of genes demonstrates that OMT genes are developmentally regulated in the tissue-specific manners.

1994-109

PAL 活性の阻害は二次壁の木化にどのような影響を及ぼすのか？ ヒヤクニチソウ単離葉肉細胞培養系を用いて

中島 仁、高部圭司、佐伯 浩  
京都大学農学部

Inhibition of PAL activity by 2-aminoindan-2-phosphonic acid (AIP) caused the depression of lignin content of secondary wall thickening isolated *Zinnia* mesophyll cell.

Jin Nakashima, Keiji Takabe, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Abstract: Isolated mesophyll cells from the first leaves of *Zinnia elegans* L. cv. Canary Bird can be induced to differentiate into tracheary elements, which can give us a lot of biochemical events during the course of secondary thickening and lignification. The influence of AIP, an inhibitor of PAL on lignin formation was observed under a TEM and an UV microscope. At 96 hr, the differentiation into tracheary elements had almost finished, the secondary walls were lignified completely and showed the electron opaque material covered the fibrillar texture observed at 72 hr. These walls gave the absorption maxima about 280nm. Secondary walls inhibited PAL activity by AIP at 100 μM presented greatly different images as if they were cracked. They showed weak UV absorption and quite different UV absorption spectra. At 54 hr of culture, coniferyl alcohol at 100 μM were administered after inhibition of PAL activity by AIP, then the secondary walls were given the UV absorption maxima as much as the secondary walls normally cultured, indicating that the secondary walls were artificially lignified by the exogenous monolignol.

1994-110

モノリグノールグルコシドの樹幹内分布

福島和彦、田口小百合、松井直之、安田征市  
名古屋大学農学部

Distribution of monolignol glucosides in tree.

Kazuhiko Fukushima, Sayuri Taguchi, Naoyuki Mstsui, Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: Quantitative analyses were made on monolignol glucosides in 50% EtOH extracts from different tissue fractions of *Pinus thunbergii*, *Ginkgo biloba* and *Magnolia kobus* in May, June and August. In ginkgo and pine, coniferin existed mainly in the xylem, and the content was highest in May and lowest in August. In magnolia, large amount of coniferin and syringin was contained even in the bark. and the content of syringin in August was much higher than that in other season. As the distance from tip became longer, the syringin/coniferin ratio became higher, especially in the bark.

1994-111

*Arctium lappa* のリグナン生合成酵素

梅澤俊明、島田幹夫

京都大学木質科学研究所

Lignan synthesis by cell-free extracts of *Arctium lappa*.

Toshiaki Umezawa, mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Cell free extracts from *Arctium lappa*. catalyzed the formation of secoisolariciresinol and lariciresinol, when incubated with coniferyl alcohol in the presence of NADPH and H<sub>2</sub>O<sub>2</sub>. Since *A. lappa* grows very well, the plant can be used as a plant material for the study of lignan synthesizing enzymes.

1994-112

(+)-*Erythro*-(4,7-dihydroxy-3-methoxy-1''-allyl-3',5'-dimethoxy)-8-O-4'-neolignan の生物変換とその変換物の抗菌活性

宮沢三雄、○笠原博幸、亀岡 弘

近畿大学理工学部

Biotransformation and antibacterial activity of (+)-*erythro*-(4,7-dihydroxy-3-methoxy-1''-allyl-3',5'-dimethoxy)-8-O-4'-neolignan.

Mitsuo Miyazawa, Hiroyuki Kasahara, Hiromu Kameoka

Faculty of Science and Engineering, Kinki University

Abstract: The biotransformation of an acyclic neolignan, (+)-*erythro*-(4,7-dihydroxy-3-methoxy-1''-allyl-3',5'-dimethoxy)-8-O-4'-neolignan (**1**) in rat and fecal intestinal bacteria *in vitro* have been investigated. The sole metabolic product which excreted to feces (>98%) and urine (<2%) was identified as (+)-(4-hydroxy-3-methoxy-1'-allyl-3',5'-dimethoxy)-8-O-4'-neolignan (**2**) by the spectroscopic methods. Although rat and fecal intestinal bacteria could transform **1** to **2**, several tested microbes which can oxidize lignans and terpenoids could not transform **1**. The antibacterial activities of **1** and **2** were also investigated and revealed that both compounds showed to be antibacterial against several microbes.

1994-特別講演

フェニールプロパノイドと植物保護

谷口東二

九州大学農学部

Invited Lecture: The role of phenylpropanoids in plant protection and plant growth regulation.

Eiji Taniguchi

Faculty of Agriculture, Kyushu University

Abstract: A wide variety of phenylpropanoids, including flavonoids and tannins etc., is considered as very important ecochemicals in the environmental ecology. For example, the flavic acid, producing from the plant residues in the soil and partially from lignin-like materials, may take a role of iron-transportation from terrestrial to aquatic environment, where a rich biosphere is brought in by nourishing algae. In plant-parasite relationship, a sort of flavonoids has been revealed to be the signal compound of host plant for the parasite, and some of phytoalexins are old-known pterocarpanoids. Allelopathy is also largely caused by phenylpropanoids and their related compounds. From the chemo-ecological point of view, the importance of phenylpropanoids for plant protection and regulation will be discussed by presenting two brief stories concerning with an

insecticidal neolignan of the genus *Phryma* and an auxin-transport inhibitor as a chalcone analog.

1994-201

常温硬化クラフトリグニン接着剤の製造に関する研究

島谷啓二<sup>\*1\*2</sup>、佐野嘉拓<sup>\*1</sup>

<sup>\*1</sup>北海道大学農学部、<sup>\*2</sup>本州製紙株式会社

Preparation of kraft lignin-based cold setting adhesives.

Keiji Shimatani<sup>\*1</sup>, Yoshihiro Sano<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Honshu Paper Co. Ltd.

Abstract: The utilization of softwood kraft lignin in one of the main substrate of cold setting wood adhesives was investigated. Kraft lignin, formaldehyde-phenol-kraft lignin copolymer (LP-resin) and resorcinol-terminated LP-resin (LPR-resin) were prepared as described in the 38th Lignin Symposium (Takamatsu). When 5-10% methanol were added to the LPR-resin solution with a solid content of 45% containing small amounts of paraformaldehyde, the mixture developed the excellent strength properties for cold-setting wood adhesives. Furthermore, LP-, LPR- and resorcinol-formaldehyde-resins were characterized by thermal analyses.

1994-202

リグニン及び糖蜜含有型ポリウレタンフォームの物性

廣瀬重雄<sup>\*1</sup>、渡嘉敷唯章<sup>\*2</sup>、畠山兵衛<sup>\*1</sup>

<sup>\*1</sup>物質研研究所、<sup>\*2</sup>トロピカルテクノセンター

Thermal and mechanical properties of polyurethanes containing lignin and saccharides.

Shigeo Hirose<sup>\*1</sup>, Tadaaki Tokashiki,<sup>\*2</sup> Hyoe Hatakeyama<sup>\*1</sup>

<sup>\*1</sup>National Institute of Materials and Chemical Research, <sup>\*2</sup>Tropical Technology Center Ltd.

Abstract: Polyurethane (PU) foams were prepared by the following procedures. An ethylene glycol (EG) solution of kraft lignin (KL) was mixed with polyethylene glycol (PEG), and then the obtained solution was reacted with diphenylmethane diisocyanate (MDI) in the presence of small amounts of water, silicone surfactant and tin catalyst. PU's containing molasses (MOL) were also prepared according to the above procedures. Thermal properties of PU's were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). Mechanical properties were also studied by compression tests. The effect of the addition of KL, MOL and EG to PU's on physical properties were studied.

1994-203

未晒し酢酸パルプの化学修飾による分子会合体の調製(I) 残存リグニンをコアとする誘導体のセルフアッセンブリー

橋田 光、浦木康光、佐野嘉拓

北海道大学農学部

Preparation of unbleached acetic acid pulp derivatives to form self-aggregates in water by chemical modification. I. Self-assembly of the pulp derivatives centered around residual lignin as cores.

Koh Hashida, Yasumitsu Uraki, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Self-assembly or aggregation of polymer amphiphiles and hydrophobically associating water-soluble polymers is of great interest with respect to biological application and novel industrial importance. In this study, the preparation of self-aggregates in water from acetic acid pulp (AWP), which contained larger amount of lignin than unbleached kraft pulp, by chemical modification was investigated to develop new functional materials from lignocellulose. Hydroxypropyl (HP)-AWP was

indicated to form the aggregates in aqueous solution by transmission electron microscopic observation. On the other hand, HP-bleached AWP and commercial HP-cellulose were not found the phenomena. Furthermore, carboxymethyl-AWP did not also form the aggregate. These suggested that the AWP derivatives involving hydrophilically nonionic functional group self-assembled in water as cores of the hydrophobically residual lignin.

1994-204

化学変性した工業リグニン中のフェノールカルボン酸型構造の抗菌活性

中野準三、山田まゆみ、草桶秀夫

福井工業大学工学部

Antibiotic activity of phenol carboxylic acid type structure in chemically modified industrial lignin.

Junzo Nakano, Mayumi Yamada, Hideo Kusaoke

Faculty of Engineering, Fukui Institute of Technology

Abstract: (1) The antibiotic activity of phenol carboxylic acid changes with the species of micro-organisms. The activity of ester is higher than that of free carboxyl group. Methoxyl group gives negative effect toward the activity. The relative position of phenolic hydroxyl and carboxyl groups on aromatic nucleus does not give the remarkable effect toward the activity. (2) In order to give the activity to industrial lignin, the introduction of phenol carboxylic type structure has been tried by the use of sodium sulfide treatment and caustic fusion. Within the limits of this experiment so far, the ethanol soluble fraction after the fractionation of caustic fused lignin shows comparatively high antibiotic activity.

1994-205

*Phanerochaete sordida* YK-624 株の産生するマンガンペルオキシダーゼによるクラフトパルプの漂白

原園幸一、近藤隆一郎、坂井克己

九州大学農学部

Bleaching of kraft pulp with manganese peroxidase secreted from *Phanerochaete sordida* YK-624.

Koichi Harazono, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We have previously reported that bleaching of hardwood kraft pulp with isolated manganese peroxidase (MnP) from *Phanerochaete sordida* YK-624 is possible. In the present study, supplementary experiments in various conditions were carried out to improve the method of bleaching with MnP. An optimum pH for enzyme treatment was 4.5. A maximum activity was observed when a temperature was 45°C. In various organic acid buffers (50 mM and pH 4.5), malonate functioned most effectively as an Mn<sup>3+</sup> chelator during bleaching of pulp with MnP. A surfactant was an important factor on enzyme bleaching. Enzyme treatments with H<sub>2</sub>O<sub>2</sub>-generating enzyme, glucose oxidase, had a similar effect on pulp brightness and bleachability as those with H<sub>2</sub>O<sub>2</sub> added directly. The pulp treated with MnP had strength properties comparable with those for unbleached hardwood kraft pulp.

1994-206

An initial evaluation of the role of lignin-carbohydrate complexes in the xylanase prebleaching of kraft pulps.

Shinzo Yokota<sup>\*1</sup>, Ken K.Y. Wong<sup>\*2</sup>, John N. Saddler<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Utsunomiya University, <sup>\*2</sup>Faculty of Forestry, University of British Columbia

Abstract: The molecular weight distribution of lignin- and xylan-containing macromolecules,

that have been isolated from kraft pulps derived from aspen and spruce, was determined using size exclusion chromatography under highly alkaline conditions. A UV-vis monitor and a pulsed amperometric detector were used to monitor the elution of lignin and carbohydrates, respectively. The change in molecular weight, as a result of treatment with xylanase and acid was evaluated in order to examine the role of lignin-carbohydrate complexes in the xylanase prebleaching of kraft pulp. The results indicated that xylanase could decrease the molecular weight distribution of the UV-absorbing material in xylan-rich fractions obtained from kraft pulp.

1994-207

クラフトパルプの着色性キシラン画分の変質と微生物分解

三亀啓吾、渡辺隆司、本田与一、桑原正章

京都大学木質科学研究所

Fractionation and microbial degradation of chromophoric xylan fractions from kraft pulp.

Keigo Mikame, Takashi Watanabe, Yoichi Honda, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: Unbleached kraft pulp (UKP) was degraded by a cellulase/ xylanase-bioreactor. Water-soluble chromophoric xylan was separated from the UKP by silica gel column chromatography. The fraction was characterized as follows; 1) This fraction contained more than 40% of unremovable inorganic atoms including Si, Na and S, together with non-branched xylan chain. 2) In the NMR spectrum, signals originating from olefinic carbons and methoxyl group were below background noise, suggesting that the major chromogen in this fraction is not a typical residual lignin. 3) The xylanase-resistant fraction was more effectively decolorized by microflora from soils rather than selected white-rot fungi which effectively decolorize the intact unbleached kraft pulp itself.

1994-208

酸素-アルカリ漂白過程における多糖類の分解機構(3) 酸素圧の反応選択性への影響

横山朝哉、安本光夫、松本雄二、飯塚堯介

東京大学農学部

Dependence of carbohydrate degradation on reaction of lignin during oxygen bleaching. III. Effect of oxygen pressure on the reaction selectivity.

Tomoya Yokoyama, Mitsuo Yasumoto, Yuji Matsumoto, Gyosuke Meshitsuka

Faculty of Agriculture, The University of Tokyo

Abstract: A kinetic investigation was performed on the oxygen-alkali treatment of the mixture of carbohydrate model compound, methyl  $\beta$ -D-glucopyranoside (Me $\beta$ G) and lignin model compound, 2,4,6-trimethylphenol (TMPH). The whole degradation pathway of TMPH was expressed by a following simple formula.

$-d[\text{TMPH}]/dt = k[\text{TMPH}]^n$  [TMPH]: concentration of TMPH n: reaction order k: reaction constant  
The amount of degraded MePG is dependent on the amount of degraded TMPH and expressed roughly by a following simple formula.

MePG degradation (mol) = A x TMPH degradation (mol) A : reaction selectivity constant

1994-209

リグニンによるセルロースのオゾン分解促進

真柄謙吾<sup>\*1</sup>、富村洋一<sup>\*1</sup>、細谷修二<sup>\*1</sup>、島田謹爾<sup>\*1</sup>、池田 努<sup>\*2</sup>

<sup>\*1</sup> 森林総合研究所, <sup>\*2</sup> 筑波大学農林工学系

Accelerated degradation of cellulose by the presence of lignin during ozonolysis.

Kengo Magara<sup>\*1</sup>, Yoichi Tomimura<sup>\*1</sup>, Shuji hsoya<sup>\*1</sup>, Einji Shimada<sup>\*1</sup>, Tsutomu Ikeda<sup>\*2</sup>

\*<sup>1</sup>Forestry and Forest Products Research Institute, \*<sup>2</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: To clarify the influence of residual lignin in the kraft pulp on the degradation of cellulose, cellobiose was treated with ozone in the presence of vanillyl alcohol. When cellobiose alone was ozonized, the cellobiose was degraded linearly with the increase in supplied ozone. When cellobiose was ozonized in the presence of vanillyl alcohol, the coexisted vanillyl alcohol was completely consumed at the initial period of ozonolysis. As for the degradation of cellobiose, more degradation of the cellobiose was observed in the presence of vanillyl alcohol than its absence until ozone supply reached about 6 mmol per one mol of cellobiose. Most of the supplied ozone within this period has been consumed by the reaction with vanillyl alcohol, and the amount of ozone to attack cellobiose should be much smaller. However, the cellobiose was degraded more readily in the presence of vanillyl alcohol than in vanillyl alcohol free condition. So that we concluded that organic ozonides or hydroxy radicals formed from the reaction of vanillyl alcohol and ozone accelerated the degradation of cellobiose.

1994-210

漂白過程で生じる高分子塩素化リグニンの構造

新谷博幸、松本雄二、飯塚堯介

東京大学農学部

Structure of high molecular weight chlorolignin produced by bleaching.

Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka

Faculty of Agriculture, the University of Tokyo

Abstract: Three types kraft pulp (unbleached softwood kraft pulp, unbleached hardwood kraft pulp and oxygen prebleached hardwood kraft pulp) were chlorinated at various levels of chlorine ratio (0.1 - 0.3), and residual chlorolignins in pulps were extracted in high yields with aqueous dioxane. Extracted chlorolignins were treated by aqueous alkali under a similar condition as E1-stage of bleaching. Structural features of extracted chlorolignins and their alkali-treated products were analyzed by <sup>1</sup>H-NMR spectroscopy. These analytical results revealed that chlorolignins have structures which are quite different from usual lignin structures. Namely, only few aromatic structures are present in chlorolignins. Instead of this, chlorolignins are very rich in methyl, methylene and methine structures.

1994-211

北海道産広葉樹の連続常圧酢酸パルプ化 - 酢酸パルプの漂白について -

金野晴男、佐野嘉拓

北海道大学農学部

Acetic acid pulping of commercial hardwood chips in Hokkaido at atmospheric pressure with continuous extraction. - Bleaching of acetic acid pulp -.

Haruo Konno, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: To establish the bleaching methods of acetic acid pulp with non-chlorine reagents, the pulps were prepared by extracting commercial chips of hardwood grown in Hokkaido with boiling 95% aqueous acetic acid containing 0.32% H<sub>2</sub>SO<sub>4</sub> continuously. The pulps were bleached in PA (peracetic acid), PA-P (hydrogen peroxide) and O (oxygen)-PA-P sequence. The pulps were bleached at 62.9%, 77.9% and 90.2% brightness by using 5%PA(70°C,30min)-3%PA (70°C, 90min), 5%PA-3%PA-P (2% pH11, 70°C, 2h) and O (7%NaOH, 110°C, 60min)-5%PA (70°C, 60min)-P, respectively. The bleached pulps were characterized by K-values, viscosity and strength properties.

1994-212

ラジオトレーサー法によるクラフトパルプ化中のキシランの挙動の解明

今井貴規<sup>\*1</sup>、安田征市<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup>名古屋大学農学部, <sup>\*2</sup>USDA 林産物研究所

Behavior of xylan during kraft cooking studied by radiotracer technique.

Takanori Imai<sup>\*1</sup>, Seiiti Yasuda<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>United States Department of Agriculture, Forest Products Laboratory

Abstract: To examine the behavior of xylan during kraft cooking by radiotracer method, the wood meal in which xylan was radio-labeled selectively by feeding myo-inositol-[2-<sup>3</sup>H] as a precursor to plant was treated under kraft cooking condition. Radioactivities of pulp and cooking black liquor obtained at various cooking stages were determined. The results showed that dissolution of xylan was remarkable during heat-up period and more than 70% of xylan was dissolved at this stage, and suggested that about 10% of the dissolved xylan was reabsorbed on pulp fiber and this part amounts to about 25% of xylan remaining in pulp.

1994-213

リグニン誘導体添加によるバクテリアセルロース膜生産性の改善

鮫島一彦、シリポン・プレムジェット、大谷慶人

高知大学農学部

Improvement of the bacterial cellulose production efficiency with the addition of lignin derivatives.

Kazuhiko Sameshima, Siripong Prenjet, Yoshito Ohtani

Faculty of Agriculture, Kochi University

Abstract: In the previous papers we have demonstrated that the addition of lignosulfonate to a bacterial cellulose medium remarkably enhanced the efficiency of the cellulose production by *Acetobacter xylinum* ATCC 10245. The highest cellulose membrane yield was 389% on the standard Hestrin-Schramm medium. In this paper the effect of the addition of kraft lignin samples has been investigated. The addition of pine kraft lignin increased the cellulose membrane yield (max. 139%) but that of birch kraft lignin affected adversely. The reason for this phenomena might have to do with the lignin structure difference and could be a clue to find a better medium for the cellulose production.

1994-P101

白色腐朽菌ベッコウタケの染料脱色能及びリグニン分解能

遠藤陽子、割石博之、大賀祥治、田中浩雄

九州大学農学部

Decolorization of polymeric dye and degradation of lignin by the white-rot basidiomycete *Fomitella fraxinea*.

Yoko Endo, Hiroyuki Wariishi, Shoji Ohga, Hiroo Tanaka

Faculty of Agriculture, Kyushu University

Abstract: Effective decolorization of polymeric dye, Poly-R by the white-rot basidiomycete *Fomitella fraxinea* was demonstrated under high nutrient carbon-high nutrient nitrogen (HCHN) conditions. This fungus also exhibited the ability to oxidatively degrade either phenolic or nonphenolic lignin model compounds under HCHN conditions. Under these conditions only laccase activity was observed, so far. The influence of the atmosphere and pH (4.5-6.5) on physiological phenomena of *F. fraxinea* was relatively minor compared to those of *Phanerochaete chrysosporium*.

1994-P102

白色腐朽菌による色素の分解

桑原正章<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>、井上千景<sup>\*2</sup>、本田与一<sup>\*1</sup>

<sup>\*1</sup> 京都大学木質研究所、<sup>\*2</sup> 近畿大学農学部

Masaaki Kuwahara<sup>\*1</sup>, Takashi Watanabe<sup>\*1</sup>, Chikage Inoue<sup>\*2</sup>, Yoichi Honda<sup>\*1</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University

<sup>\*2</sup>Faculty of Agriculture, Kinki University

Abstract: Degradation of dyes by various basidionycetes was examined. Several fungi *Phanerochaete crysosporium*, *Bjerkandera adusta*, *Coriolus versicolor*, *C. hirsutus*, *C. consors*, *C. vellerus*, decolorized Azur B, Orange II, Congo red, Tropaeolin O and other dyes, which were added into Kirk's low nitrogen medium. However, the rate of the degradation differed in fungal strains.

1994-P103

リグニン生分解に関する研究(II) –バイオブリーチング時に産生される還元系酵素について–  
片桐誠之、堤 祐司、西田友昭

静岡大学農学部

Extracellular reductive enzyme produced during biobleaching of kraft pulp by white-rot fungi.

Nobuyuki Katagiri, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: The role of reductive enzyme for the biobleaching of kraft pulp by *Phanerochaete crysosporium* and *Coriolus versicolor* was investigated in solid-state fermentation system with low nitrogen-high carbon and high nitrogen high carbon media. The profiles of manganese peroxidase (MnP) and reductive enzyme productions during the biobleaching were very different each other, suggesting the complementary function of both enzymes for the lignin degradation. Though a positive relationship between cumulative MnP activity and brightness increase was observed, any positive correlation was not observed in case of cumulative reductive enzyme activity. This result suggests that reductive enzyme may not be involved in the biobleaching of kraft pulp.

1994-P104

クラフトパルプ漂白能力を持つ木材腐朽菌のスクリーニング

高野麻理子、西田篤実、中村雅哉

森林総合研究所

Screening of wood rotting fungi for kraft pulp biobleaching.

Mariko Takano, Atsumi Nishida, Masaya Nakamura

Forestry and Forest Products Research Institute

Abstract: Many studies about biobleaching processes are proceeding to develop new chlorine-free bleaching systems. But more efforts will be needed to overcome remaining problems for practical use. We selected several wood rotting fungi for kraft pulp biobleaching using two screening methods, Poly-R decolorization test and phenol coloradon test. 7 Fungi selected by Poly-R decolorization test show kraft pulp biobleaching ability. After 10 days treatment, the most effective fungus was able to increase the brightness from 28 to 54 and decrease kappa number from 15.7 to 6.1. 2 Fungi selected by phenol coloration test were able to increase the brightness of oxygen-alkali bleached pulp but not unbleached kraft pulp.

1994-P105

機械パルプの光による色戻りを抑制する菌のスクリーニング

河村佳枝、伊藤和貴、沖 妙、橘 燦朗

## 愛媛大学農学部

Screening of fungi on depression of color reversion of mechanical pulps.

Yoshie Kawamura, Kazutaka Itoh, Tae Oki, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Screening of fungi having depression of light-induced color reversion of mechanical pulps was carried out by using 2,6-dichloroindophenol and methoxy-*p*-quinone as an indicator for estimation of ability of depression of the-color reversion. First, we tried tile screening of fungi having reducing ability of 2,6-dichloroindophenol from soils in our university forest and 67 fungi were found on Czapek-Dox agar plates. In the second step, each 67 fungi was incubated in a liquid medium containing methoxy-*p*-quinone and 20 fungi having ability of decoloration of the quinone were obtained. In the third step, reactivity between each an extracellular crude enzymes from the 20 fungi and methoxy-*p*-quinone was measured and screened fungi having higher reactivity. By using this method, we obtained a fungus which was called 501 had higher ability for depression of the color reversion. The fungus could be depressed 47 % of the color reversion of thermomechanical pulps.

## 1994-P106

Compositional changes in compost during conventional and environmentally controlled composting and growth of *Agaricus bisporus*.

Kenji Iiyama<sup>\*1\*3</sup>, Thi Bach Tuyet Lam<sup>\*1</sup>, Barry J. Macauley<sup>\*2</sup>, Bruce A. Stone<sup>\*1</sup>

<sup>\*1</sup>Schools of Biochemistry and <sup>\*2</sup>Microbiology, La Trobe University, Australia

<sup>\*3</sup>Department of Forest Products, the University of Tokyo

Abstract: Samples from conventional, "cold" and "hot" environmentally controlled composts ("cold" and "hot" EC) taken at various stages of composting and mushroom (*Agaricus bisporus*) growth were analyzed for changes in extractives, neutral sugar composition, lignin concentration, and lignin structural features. Variable amounts of extraneous inorganic solids in the form of fine sandy particles were removed by sedimentation of the samples in a CCl<sub>4</sub>-CH<sub>2</sub>Br<sub>2</sub> mixture. During composting, about two-thirds of the initial wall polysaccharides were consumed by compost microorganisms, and only 13-16% of the total polysaccharides were used during mushroom production. The relative lignin content of composts as measured by acetyl bromide procedure increased, both during composting and mushroom growth, and the chemical structure of lignin was altered by condensation and oxidation reactions.

## 1994-P107

*Eucalyptus camaldulensis* および *E. globulus* におけるリグニン S/G 比樹間内変異

小名俊博、園田哲也、柴田 勝

新王子製紙株式会社 林木育種研究所

With-in tree variation of lignin S/G ratio in *Eucalyptus camaldulensis* and *E. globulus*.

Toshihiro Ona, Tetsuya Sonoda, Masaru Shibata

New Oji Institute For Forest Tree Improvement

Abstract: With-in tree variation of lignin S/G ratio was analyzed for *Eucalyptus camaldulensis* and *E. globulus* from Western Australia by using thioacidolysis method, as a link or quality breeding program. Furthermore, whole-tree values of S/G ratio and suitable sampling heights were examined from the results of each position. As a result, the differences between species and trees were recognized.

## 1994-P108

クラフトパルプの亜硝酸処理における脱リグニン機構(2) –亜硝酸処理における LCC モデル化合物の反応–

岸野正典、大井 洋、黒田健一、山口 彰

筑波大学農林工学系

Mechanism of delignification during nitrous acid treatment of kraft pulp. II. Reaction of LCC model compound during nitrous acid treatment.

Masanori Kishino, Hiroshi Ohi, Kenichi Kuroda, Akira Yamaguchi

Institute of Agricultural and Forest Engineering, The University of Tsukuba

Abstract: Much attention has been paid to nitrous acid treatment of kraft pulp as one of the non-chlorine bleaching. A nonphenolic lignin-carbohydrate complex (LCC) structure is one of the important residual lignin structures of kraft pulp. To discuss the mechanism of delignification during nitrous acid treatment, veratrylglycerol- $\beta$ -guaiacyl ether (VG) and its  $\alpha$ -ethyl ether (VGE, as an LCC model compound) were used. The reaction products observed at 90°C suggested that the following reactions occur in the models: (1) cleavage of the C $\alpha$ -C $\beta$  bond, (2) acid-hydrolysis at an  $\alpha$ -ethyl ether (in the case of the VGE experiment). Furthermore, the identification of several unknown peaks was attempted and it is assumed that one of the unknown peaks is corresponding to a compound with carboxylic acid.

1994-P109

ベンジルエーテル結合の選択的開裂によるクラフトパルプ残存リグニンの性状の検討

木村尚代、飯塚堯介

東京大学農学部

Characterization of residual lignin in kraft pulp by selective cleavage with pivaloyl iodide.

Hisayo Kimura, Gyosuke Meshitsuka

Faculty of Agriculture, the University of Tokyo

Abstract: In recent years, it has been claimed that chlorine bleaching produces various organic chlorinated compounds causing environmental problems. Therefore, the development of pollution-free bleaching is one of the most important subjects for the pulping industry. Many studies have been reported on the chemical structures of residual lignin for the better understanding of inhibiting factors for the delignification. In this report, by the use of pivaloyl iodide (one of HASB reagents) for the selective cleavage of benzyl ether bonds under mild conditions, we tried to evaluate the contribution of benzyl ether bonds to the residual nature of lignin in kraft pulp and to characterize the lignin fraction released from kraft pulp by this treatment.

1994-P110

熱分解ガスクロマトグラフィーによるクラフトパルプ残存リグニンの構造解析 –漂白処理における変化–

田中潤治、和泉明子、大井 洋、黒田健一、山口 彰

筑波大学農林工学系

Structural analysis of residual lignin in kraft pulp by pyrolysis-gas chromatography. Changes of residual lignin during chlorine bleaching.

Junji Tanaka, Akiko Izumi, Hiroshi Ohi, Kenichi Kuroda, Akira Yamaguchi

Institute of Agricultural and Forest Engineering, The University of Tsukuba

Abstract: Pyrolysis-gas chromatography (Py-GC) provides useful complementary information about lignin structures to chemical degradation methods, using small amounts of samples without any sample pretreatment. Unbleached hardwood kraft pulp (LUKP) and oxygen-bleached hardwood kraft pulp (LOKP) were chlorinated at various chlorine ratios (1–5% on Pulp), and were extracted

with sodium hydroxide solution. Chlorinated kraft pulps before and after the alkali extraction were subjected to Py-GC, and structural changes of lignin in kraft pulp were studied.

1994-P111

酢酸リグニンを原料とする炭素繊維の調製(3) -酢酸リグニンの溶融性-

久保智史、沢田雅博、浦木康光、佐野嘉拓

北海道大学農学部

Preparation of carbon fiber from acetic acid lignin. III. -Fusibility of acetic acid lignin-.

Satoshi Kubo, Masahiro Sawada, Yasumitu Uraki, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Thermal properties, especially fusibility, of acetic acid lignin (AWL) were investigated by thermomechanical analysis (TMA). On the TMA measurement of fractionated birch (B)-AWL, the fractions with less than 1,000 of molecular weight (Mw) indicated the clearly fusion state, while other fractions having larger a than original B-AWL did not fuse. Therefore, the fusibility of B-AWL was caused by low molecular weight fractions. However, abies (A)-AWL was not fused probably due to condensation of aromatic nucleus. These results suggest that the fusibility of AWL depends on not only acetylation of hydroxyl groups but also molecular structures such as condensation.

Furthermore, we examined the thermal properties of industrial kraft lignin (KPL) blended with AWL.

The glass-transition temperature of KPL was decreased by the addition of AWL remarkably. These results indicate that KPL may be used as thermal molding materials by blending with a small amount of AWL.

1994-P201

未晒し酢酸パルプの化学修飾による分子会合体の調製(II) ~ゲスト分子との相互作用~

橋田 光、浦木康光、佐野嘉拓

北海道大学農学部

Preparation of unbleached acetic acid pulp derivatives to form self-aggregates in water by chemical modification. I. - Interaction between pulp derivatives and guest molecules.

Koh Hashida, Yasumitu Uraki, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Uptake of hydrophobic fluorescence reagents as guest molecules to self-aggregates of hydroxypropylated AWP (HP-AWP) was investigated to clarify the conjugation of the aggregates with water-insoluble materials. HP-AWP was found to have obvious transition concentration at 1.27 mg/ml corresponding to the critical micell concentration, and to form extremely hydrophobic regions in the aggregates, which was suggested by both of the remarkably shift of maximum emission wavelength and the enhancement of emission intensity. However, other derivatives having no self-assembly, HP-cellulose and carboxymethyl-cellulose, scarcely form the hydrophobic region. This suggested that the aggregates of HP-AWP took in the hydrophobic guest molecules in the hydrophobic regions which were probably formed by residual lignin in HP-AWP.

1994-P202

フェニルクマラン型二量体の配糖体化

渡辺雄<sup>\*1</sup>、棚橋光彦<sup>\*1</sup>、重松幹二<sup>\*1</sup>、篠田善彦<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学農学部, <sup>\*2</sup> 岐阜大学連農

Glycosylation of phenylcoumaran type dimer.

Yuichi Watanabe<sup>\*1</sup>, Mitsuhiro Tanahashi<sup>\*1</sup>, Mikiji Shigematsu<sup>\*1</sup>, Yoshihiko Shinoda<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Gifu University, <sup>\*2</sup> The United Graduate School of Agricultural Science, Gifu

University

Abstract: Phenylcoumaran glycoside was synthesized by linking the phenolic hydroxyl group of dehydrodiconiferylalcohol with  $\alpha$ -bromo-saccharides (glucose, galactose and xylose). The effects of the protecting groups on the yields were investigated. The glucosylation yield was increased from 30.7 % to 46.8 % by changing the protecting group of glucose from acetyl to pivaloyl. In the case of pivaloyl derivatives of galactose and xylose, the yields were 23.40% and 68.0%, respectively. For the synthesis of this phenylcoumaran glycoside, a new synthetic route was attempted with a phenylcoumaran type dimer derived from dehydrogenation of ethylferulate.

1994-P203

リグニン前駆体とヘミセルロースの親和性

杉野秀明、重松幹二、棚橋光彦、(岐大連農)篠田善彦

岐阜大学農学部

Affinities between lignin precursors and hemicelluloses.

Hideaki Sugino<sup>\*1</sup>, Mikiji Shigematsu<sup>\*1</sup>, Mitsuhiko Tanahashi<sup>\*1</sup>, Yoshihiko Shinoda<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Gifu University, <sup>\*2</sup>The United Graduate School of Agricultural Science, Gifu University

Abstract: In plant cell wall, a lignin is deposited in the matrix of polysaccharides through the lignification process. In this study, the binding of lignin precursors (*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) to hemicelluloses (from softwood and hardwood, and citrus pectin) were observed by ultrafiltration of the mixed solutions to examine the affinities between lignin precursors and hemicelluloses. As a result, the binding of lignin precursor to hemicellulose was observed in all pairs. It shows that the attractive interaction exists between them.

1994-P204

ラマン散乱スペクトルによる木材と竹のリグニン解析

武井利之、加藤紀子、飯島倫明、桧垣宮都

東京農業大学農学部

Raman spectroscopic identification of wood and bamboo lignin.

Tosiyuki Takei, Noriko Kato, Tomoaki Iijima, Miyato Higaki

Faculty of Agriculture, Tokyo University of Agriculture

Abstract: Fundamental conditions to record near-infrared excited fourier-transform Raman spectra from wood meal samples were researched. Favorable Raman spectra were obtained between 150mW to 200mW of laser power with more than 100 times scanning, The size of meal samples between 20 to 200 mesh, has not affected the spectra. Under these conditions Raman spectra were recorded from meal samples and holocellulose of *Fagus crenata* B.I., *Cryptomeria japonica* D, Don and *Phyllostachys pubescens* Mazel as a typical hardwood, softwood and bamboo respectively. The Raman band intensity of *F. crenata* and *C. japonica* were decreased by the delignification process, at the wave number of 1660  $\text{cm}^{-1}$ , 1600  $\text{cm}^{-1}$ , 1460  $\text{cm}^{-1}$ , 1330  $\text{cm}^{-1}$ , 1030  $\text{cm}^{-1}$  and 800  $\text{cm}^{-1}$ . In the case of *P. pubescens*, extremely strong bands observed at the wave number of 1630 and 1604  $\text{cm}^{-1}$ , and their intensity were decreased by alkaline-treatment. By the delignification process of *P. pubescens* the same bands as so *F. crenata* and *C. japonica* but 1660  $\text{cm}^{-1}$ , and the bands at 1630  $\text{cm}^{-1}$  and 1424  $\text{cm}^{-1}$  were decreased. This result indicate that these Raman bands decreased by the delignification process were those of lignin origin. It was suggested that by recording Raman spectra from wood meal sample, the information of native state lignin were obtained directly and easily.

1994-P205

## リグニンモデルの一電子酸化

服部和生、高谷政広、浜田良三、岡本 忠

近畿大学農学部

One electron oxidation of lignin models.

Kazuo Hattori, Masahiro Takatani, Ryoza Hamada, Tadashi Okamoto

Faculty of Agriculture, Kinki University

Abstract: To study the mechanism of alkaline nitrobenzene oxidation of lignin, oxidation of some lignin models, derivatives of cinnamic acid, was examined by using nitrobenzene or some oxidizing agents such as CAN and MnO<sub>2</sub>. Obtained results support a mechanism of initial oxidative decarboxylation, succeeding hydration of a side-chain double bond, and oxidation of the generated benzylic alcohol. Although one-electron-transfer mechanism is important in the oxidation step, quinone methide intermediate is also necessary because it accelerates hydration of the aryl-conjugated double bond under alkaline conditions.

## 1994-P206

ユーカリ属の組織化学的方法によるリグニン分析(III) -抽出条件の決定-

渡辺陽子<sup>\*1</sup>、小島康夫<sup>\*1</sup>、船田 良<sup>\*1</sup>、深沢和三<sup>\*1</sup>、小名俊博<sup>\*2</sup>、浅田隆之<sup>\*2</sup>

<sup>\*1</sup>北海道大学農学部、<sup>\*2</sup>新王子製紙株式会社林木育種研究所

Lignin analysis of Eucalyptus by histochemical methods. III. - Evaluation of the methods of alkali extraction in removing polyphenols.

Yoko Watanabe<sup>\*1</sup>, Yasuo Kojima<sup>\*1</sup>, Ryo Funada<sup>\*1</sup>, Kazumi Fukazawa<sup>\*1</sup>, Toshihiro Ona<sup>\*2</sup>, Takayuki Asada<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Shin Oji Institute for Forest Tree Improvement,

Abstract: Lignin analysis of Eucalyptus have been done by histochemical methods. However, Eucalyptus species contain a lot of polyphenols which influence on lignin analysis and thus it is required to remove those polyphenols prior to analysis of lignin. In this study, the effect of polyphenols on lignin analysis by histochemical methods were evaluated using alkali extracted samples. Specimen (cross sections and wood meals) of two Eucalyptus species were extracted by given alkali conditions and then they were analyzed by chemical and histochemical methods. It appeared that those alkali extractives contained guaiacyl type polyphenols and affected considerably on lignin analysis, especially in vessel walls and ray cells, by histochemical methods.

## 1994-P207

ポプラ早生樹リグニソの化学構造について -ヒドロキシ芳香族酸類のリグニンに対する結合様式

金 泳信<sup>\*1</sup>、飯山賢治<sup>\*1</sup>、倉橋昭夫<sup>\*2</sup>、飯塚堯介<sup>\*1</sup>

<sup>\*1</sup>東京大学農学部、<sup>\*2</sup>東京大学北海道演習林

Structural feature of lignin in fast-grow and native aspen woods: Linkage types of hydroxybenzoic and hydroxycinnamic acids.

Youngsin Kim<sup>\*1</sup>, Kenji Iiyama<sup>\*1</sup>, Akio Kurahashi<sup>\*2</sup>, Gyosuke Mochizuki<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*2</sup>University Forest, the University of Tokyo

Keywords: MWL, LCC, vanillic acid, syringic acid, syringaldehyde, *p*-coumaric acid, ferulic acid, cell wall, GC-MS

## 1994-P208

交雑ヤマナラシ (*Populus kitakamiensis*) シンナミルアルコールデヒドロゲナーゼ (CAD) 遺伝子の単離および解析

小園聖治<sup>\*1</sup>、刑部敬史<sup>\*1</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>

\*<sup>1</sup> 東京農工大学農学部、\*<sup>2</sup> 東京農工大学共同研究開発センター

Isolation and characterisation of genes encoding cinnamyl alcohol dehydrogenase from hybrid aspen (*Populus kitakamiensis*).

Shoji Oguni\*<sup>1</sup>, Keisi Osakabe\*<sup>1</sup>, Shinya Kawai\*<sup>1</sup>, Yoshihiro Katayama\*<sup>2</sup>, Noriyuki Mrohosi\*<sup>1</sup>

\*<sup>1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology

Abstract: To change the quality and quantity of lignin, we isolated a partial gene encoding cinnamyl alcohol dehydrogenase (CAD) from hybrid aspen (*Populus kitakamiensis*) by polymerase chain reaction (PCR) method. The nucleotide sequence was analyzed and used as a probe of Southern and Northern analysis and cDNA isolation. Results showed that there was a small number of genes for CAD in the genome and CAD genes expressed in the upper and lower stem and weakly expressed in leaves. Screening of  $\lambda$  gt 10 cDNA library, one CAD cDNA clone (1.4 Kbp) was isolated and characterized.

1994-P209

交雑ヤマナラシ・キクカミハクヨウの茎において発現するペルオキシダーゼアイソザイム遺伝子群の発現様式の解析

刑部敬史\*<sup>1</sup>、小山浩和\*<sup>1</sup>、川合伸也\*<sup>1</sup>、片山義博\*<sup>2</sup>、諸星紀幸\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学農学部、\*<sup>2</sup> 東京農工大学共同研究開発センター

Molecular cloning of anionic peroxidases from *Populus kitakamiensis* and Inhibition of peroxidase expression by using antisense RNA method.

Keisi Osakabe\*<sup>1</sup>, Hirokazu Koyama\*<sup>1</sup>, Shinya Kawai\*<sup>1</sup>, Yoshihiro Katayama\*<sup>2</sup>, Noriyuki Mrohosi\*<sup>1</sup>

\*<sup>1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology,

Abstract: Agrobacterium-mediated gene transformation and plant regeneration from transformed tissue were established for hybrid aspen, *Populus kitakamiensis* (*P. sieboldii* X *P. grandidentata*). Using this system, antisense *prxA1* gene driven by *prxA1* promoter that was introduced into aspen. The peroxidase activities of transformed callus were about 2-5 fold decreased. We have already isolated three cDNAs that encode anionic peroxidase from *P. kitakamiensis*. In this report, we have two genomic DNAs corresponding to the cDNAs and a novel genomic DNA that encodes anionic peroxidase. The pattern of expression of the peroxidase genes in several plant organs is discussed.

1994-P210

樹木フェニルアラニンアンモニアリアーゼ (PAL) の発現解析

刑部祐里子\*<sup>1</sup>、北村宗子\*<sup>1</sup>、川合伸也\*<sup>1</sup>、片山義博\*<sup>2</sup>、諸星紀幸\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学農学部、\*<sup>2</sup> 東京農工大学共同研究開発センター

Characterization and Expression of Phenylalanine Ammonia-Lyase from *Populus kitakamiensis*/S  
Yuriko Osakabe\*<sup>1</sup>, Hiroko Kitamura\*<sup>1</sup>, Shinya Kawai\*<sup>1</sup>, Yoshihiro Katayama\*<sup>2</sup>, Noriyuki Mrohosi\*<sup>1</sup>

\*<sup>1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology,

Abstract: In *Populus kitakamiensis*, the genes for phenylalanine ammonia-lyase (PAL) form a small gene family. Southern blot analysis indicated that PAL family was consisted with at least six members. We then isolated and characterized six PAL genes, HPAL13, *pal g1*, *pal g2a*, *pal g2b*, *pal g3*, and *pal g4*, from genome of *Populus kitakamiensis*. Furthermore, the PAL protein was isolated from the stem tissue, and analyzed using anion-exchange chromatography and 2-D gel electrophoresis detected by immuno blot. Results indicated that Mr identical with PAL subunits was 75,000 and five subunits differing pI values were observed in the whole stem tissue. Results from Northern blot

analysis suggested that *pal g1* was expressed in the young tissues near the shoot bud and *pal g2* gene-group was mainly expressed in lower stems. Thus, the expression of each PAL gene (or gene-class) from *Populus kitakamiensis* was tissue-specific and altered with the stem growth. In *Populus kitakamiensis* PAL play the important roles that are classified two groups in the function of the stem.

1994-P211

カワラタケラッカーゼアイソザイムの解析

三園順子<sup>\*1</sup>、飯村洋介<sup>\*2</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*3</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup>東京農工大学農学部、<sup>\*2</sup>通産省工業技術院資源環境技術総合研究所、<sup>\*3</sup>東京農工大学共同研究開発センター

Characterization of laccase isoenzymes from *Coriolus versicolor*.

Junko Mikuni<sup>\*1</sup>, Yousuke Iimura<sup>\*1</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Noriyuki Mrohosi<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Cooperative Research Center, Tokyo University of Agriculture and Technology,

Abstract: Extracellular laccase is commonly produced by wood-degrading white-rot fungi. Our previous studies cleared the genetic and enzymic properties of Laccase III from *Coriolus versicolor*, and showed this enzyme was concerned in lignin biodegradation. In order to define the inherent and physiological role of laccase, we present to characterize the other laccase isoenzymes. Laccase I was little adsorbed on ion exchanger, thus it is considered to have a weak surface charge. So this enzyme was separated by preparative electrophoresis system, the Rotofor cell (BIO-RAD). As genetic characterization, we determined the DNA sequence of *CVLG1*.

1994-P212

担子菌のプロトプラスト調製および細胞融合によって誘導されたラッカーゼ欠損株の安定性

江口文陽、楡垣宮都

東京農業大学

The stability of laccase-less mutants induced by preparation of protoplasts and cell fusion of Basidiomycetes.

Fumio Eguchi, Miyato Higaki

Faculty of Agriculture, Tokyo University of Agriculture,

Abstract: Protoplasts were prepared from the mycelia of basidiomycetes; *P. ostreatus*, *P. sajor-caju* and *P. eryngii*. In the regenerated mycelia from them, some mutants lacking laccase were induced. These mutants had no decoloring activity for carminic acid and Remazol brilliant blue R, both of which are decolorized by the parent strains. Some fusion strains with no laccase activity were produced by individual electric fusion between these laccase-less mutants or the strains with and without the laccase activity. These laccase-less mutants were successively cultured on an agar plate and 3 months, growth alteration was observed in some of their mycelia. Laccase activity of these mycelia were determined and some strains were found to have lower activities of the enzyme than the parent strains. In order to examine the possibility that the culture conditions of mycelia have caused this phenomenal, an investigation of changes in laccase activity of mycelia were made by the freeze stock method at -80 °C and under the culture conditions using a liquid or agar medium. These results indicate that the laccase activity and the growth of mycelia were more stable for the freeze stock method.

1994-特別寄稿

「リグニン討論会の発足の頃」

## 第 40 回 (1995.10.12-13) つくば 研究交流センター

1995-101

樹木のフェニルプロパノイド生合成系のチトクロム P-450 遺伝子の解析

盛 有子<sup>\*1</sup>、川合伸也<sup>\*2</sup>、Zhan Xiang Can<sup>\*2</sup>、塩川貴広<sup>\*2</sup>、片山義博<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院生物システム応用科学研究所、<sup>\*2</sup>東京農工大学大農学部

Molecular cloning and heterologous expression of cytochrome P-450 from a woody plant (*Populus kitakamiensis*).

Ariko Mori<sup>\*1</sup>, Sinya Kawai<sup>\*2</sup>, Zhan Xiang Can<sup>\*2</sup>, Takahiro Shiokawa<sup>\*2</sup>, Yoshihiro Katayama<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>

<sup>\*1</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: In higher plants, some cytochrome P-450 enzymes are concerned with biosynthesis of phenylpropanoids. One of them, cinnamic acid 4-hydroxylase (CA4H), catalyzes the formation of *p*-coumaric acid from *trans*-cinnamic acid. The other enzyme, ferulic acid 5-hydroxylase (FA5H), catalyzes the formation of 5-hydroxyferulic acid from ferulic acid. CA4H and FA5H provide precursors for the biosynthesis of secondary metabolites, such as lignin. CA4H gene (*cyp73a*, *cyp73b*, and *cyp73c*) were isolated from *Populus kitakamiensis*, and have been determined the nucleotide sequences of their ORFs and promoter regions. Each of them has two introns. In the promoter regions of *cyp73a* and *cyp73b*, there are many *cis*-element-like sequences that are conserved in promoters of genes involved in phenylpropanoid biosynthesis. We also isolated a cDNA (*cyp73a*) from a *P. kitakamiensis* cDNA library constructed with mRNAs of the upper part of the stem. Using this cDNA clone, we constructed CA4H expression plasmids for heterologous expression in yeast.

1995-102

樹木酸性ペルオキシターゼ遺伝子の組織特異的発現様式の解析

手嶋克介<sup>\*1</sup>、刑部敬史<sup>\*2</sup>、川合伸也<sup>\*2</sup>、片山義博<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、海老沼宏安<sup>\*3</sup>

<sup>\*1</sup>東京農工大学大学院生物システム応用科学研究所、<sup>\*2</sup>東京農工大学大農学部、<sup>\*3</sup>日本製紙株式会社中央研究所

Tissue specific expression patterns of anionic peroxidase genes from *Populus kitakamiensis*.

Katsusuke Teshima<sup>\*1</sup>, Keishi Osakabe<sup>\*2</sup>, Sinya Kawai<sup>\*2</sup>, Yoshihiro Katayama<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Hiroyasu Ebinuma<sup>\*3</sup>

<sup>\*1</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Nippon Paper Industries.

Abstract: We have isolated three cDNAs (*pA2a*, *pA2b* and *pA3*) and four genomic DNAs (*prxA1*, *prxA2b*, *prxA3*, and *prxA4a*) for anionic peroxidases from *Populus kitakamiensis* and analyzed their expression patterns by using Northern blotting. The results suggested that each gene is under different regulation. *prxA3a* and *prxA4a* are the genes that encode anionic isoenzymes, which specifically express in stems. To identify the regulation of each gene, we analyzed the developmental expression of GUS activity in transgenic tobacco plants containing the *prxA3a*- or *prxA4a*-promoter and GUS gene fusion. The GUS activity under the control of the *prxA3a* promoter (1.0 kbp) was histochemically detected in xylem and phloem tissues in which lignin is vigorously synthesized. In the

other hand, the *prx44a* promoter (1.1kbp) had transcriptional activity only in the auxiliary bud and leaf trace. In order to determine *cis*-acting elements which regulate complicated patterns of *prx43a* expression, we constructed the 5 - deleted series of the promoter fragment with GUS gene and transformed plants with them.

1995-103

酵素ラッカーゼによるコニフェリルアルコール、イソオイゲノールの重合反応

柴 忠裕、肖 玲、宮腰哲雄

明治大学理工学部

Polymerization of coniferyl alcohol and isoeugenol by laccases.

Tadahiro Shiba, Xiao Ling, Tetsuo Miyakoshi

Department of Industrial Chemistry, Meiji University

Abstract: In this paper, we wish to report dehydrogenative polymerization of isoeugenol and coniferyl alcohol by various laccases and peroxidase. Urushi laccase oxidized isoeugenol very slowly. Dimer (1), (2a,2b), tetramer (3) and oligomer were produced, but no dehydrogenative polymer (DHP). Fungal laccase oxidized the substrate faster than urushi laccase. Peroxidase from horseradish oxidized isoeugenol even slower than the fungal laccase in the presence of hydrogen peroxide. Compared to urushi laccase, fungal laccases oxidized coniferyl alcohol faster under the same reaction conditions. Dehydrogenative polymer obtained enzymic reaction of coniferyl alcohol and isoeugenol have been characterized by NMR analysis.

1995-104

*Arctium lappa* によるセコイソラリシレジノールの生合成

梅澤俊明、島田幹夫

京都大学木質科学研究所

Biosynthesis of secoisolariciresinols in *Arctium lappa*.

Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Cell-free extracts from *Arctium lappa* L. cv. *kobarutogokuwase* catalyzed the enantio-selective formation of (+)-secoisolariciresinol. Then incubated with coniferyl alcohol in the presence of NADPH and H<sub>2</sub>O<sub>2</sub>. The stereochemical mechanisms sharply contrasts with that in (-)-secoisolariciresinol formation from coniferyl alcohol by enzymes of *Forsythia* plants.

1995-105

リグニン化学構造の不均一性 -エーテル結合の部分的開裂によって生成する低分子量リグニン区分の性状-

大熊啓映子、飯塚堯介

東京大学農学生命科学研究科

Heterogeneity of lignin structure. -Properties of low molecular weight lignin formed by limited ether bonds cleavage.

Keko Ohkuma, Gyosuke Meshitsuka

Graduate School of Agriculture and Agricultural Life Sciences, the University of Tokyo

Abstract: The authors have been investigating the structural heterogeneity of lignin, in particular, heterogeneous distribution of bonding structures and aromatic structures. In this context, a  $\beta$ -O-4 rich end-wise lignin fraction was found in the low molecular weight fraction of birch periodate lignin and phenylcoumaran rich lignin fraction was found in a very low yield in the TMSiI-depolymerized fraction. In this paper, a periodate lignin prepared from diazomethane-

methylated wood meal was partially depolymerized by TMSiI and the low molecular weight fractions extracted by dioxane/water (9/1) were characterized. It was found that the low molecular weight fractions were rich in  $\beta$ -O-4 linkage and syringyl unit. This was particularly characteristic for the acetone soluble fractions.

1995-106

リグニンの酸化過程におけるシリングルおよびグアイアシルカルボニルラジカルの生成機構—特異的シリングルおよびグアイアシル末端基の定量—

鬼木隆季、高浜有明夫

九州歯科大学一般教育部

Production mechanism of syringyl carbonyl and guaiacyl carbonyl radicals by oxidations of lignin. —Determination of syringyl and guaiacyl end-groups the bonding type of which are specific.

T. Oniki, U. Takahama

Kyushu Dental College

Abstract: Electron spin resonance spectra of dioxane lignins from various plants were measured at pH 13 in the presence of oxidants. Hardwood lignin and true grass lignins showed signals due to syringyl carbonyl and guaiacyl carbonyl radicals, and softwood lignins showed only very weak guaiacyl carbonyl signal. These radicals were thought to be produced by oxidative C $\alpha$ -C $\beta$  cleavage in lignins. The signal intensity was found to be due to the types of linkages of end-groups.

1995-107

DHP および  $\beta$ -O-4 型リグニンモデル化合物の熱分解生成物

黒田健一

筑波大学農林工学系

Comparative study of pyrolysis products of DHP and  $\beta$ -O-4 lignin model compounds.

Kenichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: This paper describes the contributions of the  $\beta$ -O-4 substructure in lignin to the pyrograms of lignocellulosic materials. Two  $\beta$ -O-4 type lignin model compounds, guaiacylglycerol- $\beta$ -guaiacyl ether (GGG) and guaiacylglycerol- $\beta$ -coniferyl ether (GGC), were pyrolyzed at 500 °C for 4 s. The products were compared with those of a dehydrogenation polymer of coniferyl alcohol (DHP). The primary products of GGG were guaiacylvinylketone and (*E*)-coniferyl alcohol, together with guaiacol released by the cleavage of the  $\beta$ -ether bond. 4-Methylguaiacol, 4-vinylguaiacol, ioseugenol and dihydroconiferyl alcohol, the major products of DHP, were obtained in very small levels. GGC produced dihydroconiferyl alcohol, coniferaldehyde and (*E*)-coniferyl alcohol in considerable levels. Unlike GGG, GGC contributed to the formation of guaiacol, 4-methylguaiacol, 4-vinylguaiacol and ioseugenol. The pyrolysis products from the model compounds suggest that coniferyl alcohol end-groups in lignin are related to the formation of dihydroconiferyl alcohol.

1995-108

クラフトパルプの亜硝酸処理における脱リグニン機構(3)—非フェノール性  $\beta$ -5 型および  $\beta$ -O-4 型リグニンモデル化合物における C $\alpha$ -C $\beta$  結合の関裂—

岸野正典、大井 洋、山口 彰

筑波大学農林工学系

Mechanism of delignification during nitrous acid treatment of kraft pulp. III. Cleavage of C $\alpha$ -C $\beta$  bond in nonphenolic  $\beta$ -5 type and  $\beta$ -O-4 type lignin model compounds.

Masanori Kishino, Hiroshi Ohi, Akira Yamaguchi

Institute of Agricultural and Forest Engineering, The University of Tsukuba

Abstract: The C $\alpha$ -C $\beta$  cleavage has been reported as one of the main reactions during the nitrous acid treatment of nonphenolic  $\beta$ -O-4 type lignin model compounds. The mechanism of C $\alpha$ -C $\beta$  cleavage was discussed using a nonphenolic  $\beta$ -5 type lignin model compound and nonphenolic  $\beta$ -O-4 type lignin model compounds in which deuterium was substituted for C $\alpha$ -hydrogen. The C $\alpha$ -C $\beta$  bond in coumaran ring of dehydrodiisoeugenol methyl ether was cleaved giving veratraldehyde in a high yield. Thus, the cleavage of the C $\alpha$ -C $\beta$  bond in the nonphenolic  $\beta$ -5 type lignin model compound was one of the main reactions, and it was the same as in nonphenolic  $\beta$ -O-4 type lignin model compounds. Veratrylglycerol- $\beta$ -guaiacyl ether which had a deuterium at the C $\alpha$  position gave veratraldehyde having deuterium. The abstraction of hydrogen was not observed during the nitrous acid treatment.

1995-109

塩素漂白過程における酸化反応の役割

幸田圭一、新谷博幸、松本雄二、飯塚堯介

東京大学農学部

Role of oxidation reaction in the chlorine bleaching process.

Keiichi Koda, Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agriculture and Agricultural Life Science, the University of Tokyo,

Abstract: New calculation method was proposed for the evaluation of oxidation reaction and substitution reaction during chlorine bleaching. New calculation method proved that more than half of the chlorine was consumed by oxidation reaction during chlorine bleaching. As an average, about 4 electrons were abstracted from one lignin structural unit. This result coincides with our former results that chlorinated lignin contains only few aromatic structures. When oxidation reaction was depressed, delignification did not proceed effectively.

1995-110

ラジオトレーサー法によるクラフトパルプ化中のペクチンおよびキシランの挙動の解明

今井貴規<sup>\*1</sup>、後藤任孝<sup>\*1</sup>、松村浩如<sup>\*1</sup>、安田征市<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup>名古屋大学農学部、<sup>\*2</sup>USDA 林産物研究所

Behavior of pectin and xylan during kraft pulping studied by radiotracer technique

Takanori Imai<sup>\*1</sup>, Hideyuki Goto<sup>\*1</sup>, Hiroyuki Matsumura<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Aoyama University, <sup>\*2</sup>United States Dept. of Agriculture, Forest Products Laboratory

Abstract: Pectin and xylan were labeled with <sup>14</sup>C and <sup>3</sup>H respectively by administration of D-glucuronic acid-[6-<sup>14</sup>C] and *myo*-inositol-[2-<sup>3</sup>H] to a growing stem of magnolia. The doubly radio-labeled wood tissue was treated under kraft cooking conditions, and radioactivities of pulps and cooking black liquors were determined at various stages of cooking. The results showed that xylan was dissolved rapidly during heat-up stage, whereas pectin could not be dissolved easily at the early stage of cooking. Readsorption of xylan on pulp was demonstrated at the late stage, whereas that of pectin was not observed.

1995-111

アバカ・ケナフの酵素処理

上垣勇吾、伊藤和貴、沖 妙、橘 燦郎

愛媛大学農学部

Enzyme treatment of non-woody fiber, abaca and kenaf.

Yuugo Uegaki, Kazutaka Itoh, Tae Oki, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Treatment of the pulps prepared from non-woody plants, abaca and kenaf with two commercially available pectinases containing CMC-ase, xylanase and  $\beta$ -glucosidase was conducted to investigate the effect of the pulp properties on the pectinase treatment. We found that parenchyma cells in the pulps were removed by the treatment with pectinases. We also found that physical properties, water retention value and pulp strength were improved by the treatment with pectinases.

1995-112

フェノール酸化試薬によるリグニン酸化過程における分子状酸素の役割 –モデル実験–

森下智之、松本雄二、飯塚堯介

東京大学農学部

Model experiment on the role of molecular oxygen during oxidation reaction of lignin by phenol oxidizing reagents.

Tomoyuki Morishita, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agriculture and Agricultural Life Science, the University of Tokyo

Abstract: When vanillyl alcohol (VA) was oxidized by laccase under pressurized oxygen (3 atm), reaction products become more hydrophilic than those obtained by the oxidation under normal pressure.  $^1\text{H-NMR}$  analysis suggested that oxidation products of VA by Mn(III) under pressurized oxygen had a different structural feature from those obtained under anaerobic condition. These results revealed that oxygen can be incorporated in the reaction of phenolic compounds with one electron oxidizing reagents. When methyl- $\beta$ -D-glucopyranoside (MGP) was subjected to Mn(III) oxidation together with homovanillic acid, no active species harmful to MGP was produced.

1995-113

常圧酢酸パルプ化に関する研究 – $\beta$ -O-4 型エーテル結合の反応性–

榎 牧子、佐野嘉拓

北海道大学農学部

Acetic acid pulping of wood at atmospheric pressure. – Reactivity of  $\beta$ -aryl ether linkages.

Makiko Enoki, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: To explain the reaction mechanism of delignification by aqueous AcOH containing a small amount of HCl or H<sub>2</sub>SO<sub>4</sub> (acetolysis), guaiacylglycerol- $\beta$ -guaiacyl ether (GOG) and veratrylglycerol- $\beta$ -guaiacyl ether (VOG) were refluxed in 70–95% AcOH with HCl or H<sub>2</sub>SO<sub>4</sub>.  $\beta$ -Ethers by acetolysis were cleaved much more readily by acetolysis than acidolysis. R-GOG and R-VOG with  $\gamma$ -CH<sub>3</sub> were prepared from GOG and VOG by tosylation, iodination and finally reduction. R-GOG and R-VOG produced guaiacol and corresponding aryl acetone as main products indicating that acetolysis for protolignin modified terminal CH<sub>2</sub>OH groups in lignin to CH<sub>3</sub> groups is a new degradation method for the investigation on the chemical structure of lignin.

1995-特別講演

遺伝子の世界からみた生命の不思議 –つくば高血圧マウスとつくば低血圧マウスの創作–

村上和雄

筑波大学応用生物化学科

Invited Lecture: Tsukuba hypertensive mice and Tsukuba hypotensive mice.

Kazuo Murakami

Institute of Applied Biochemistry, University of Tsukuba

Abstract: We have constructed the chimeric renin-angiotensin cascade in mice comprising both human renin and human angiotensinogen as well as the endogenous angiotensin-converting enzyme and angiotensin II receptor by crossmating separate lines of transgenic mice carrying either the human renin or human angiotensinogen genes. Although each single gene carrier did not develop hypertension despite the observed normal tissue specific expression of the transgenes, dual gene strains exhibited a chronically sustained increase in blood pressure (BP). The systolic BP was  $130 \pm 7$  mmHg. We named the hypertensive mice as "Tsukuba Hypertensive Mice". On the other hand, we generated angiotensinogen-deficient mice by homologous recombination in mouse embryonic stem cells. These mice do not produce angiotensinogen in the liver, resulting in the complete loss of plasma immunoreactive angiotensin I. The systolic blood pressure of the homozygous mutant mice was  $66.9 \pm 4.1$  mmHg, significantly lower than that of wild-type mice ( $100.4 \pm 4.4$  mmHg). We named the hypotensive mice as "Tsukuba Hypotensive Mice".

1995-201

白色腐朽菌の産生するマンガンペルオキシダーゼの諸特性について

原園幸一、近藤隆一郎、坂井克己

九州大学農学部

Comparison of properties of manganese peroxidases from some white rot fungi.

Koichi Harazono, Ryuichiro Rondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: Properties of partially purified manganese peroxidases (MnPs) from liquid cultures of white rot fungi, the fungus YK-505, *Phanerochaete sordida* YK-624 and *Phanerochaete chrysosporium* were compared. Properties of MnP from *P. sordida* YK-624 were similar to those of MnP from *P. chrysosporium*, while MnP from YK-505 had different properties from those produced by two other fungi. MnP from YK-505 adsorbed onto a hardwood kraft pulp. MnPs from *P. sordida* YK-624 and *P. chrysosporium* did not significantly adsorb onto the pulp. MnP from YK-505 was superior to MnPs from *P. sordida* YK-624 and *P. chrysosporium* in stabilities against high temperature and high concentration of H<sub>2</sub>O<sub>2</sub>.

1995-202

アルカリ性木粉培地に生育する微生物が生産するフェノールオキシダーゼについて

国沢直子、近藤隆一郎、坂井克己

九州大学農学部

Characterization of phenoloxidases from new isolates which can grow on alkaline wood meal media.

Naoko Kunizawa, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We found several fungi producing extracellular phenol oxidases on alkaline wood meal media. These crude phenol oxidases had optimal pH near neutral when guaiacol was used as a substrate. These enzymes were produced well on alkaline wood meal media, but hardly on well-known laccase-inducing media. Active fractions were obtained by ion-exchange chromatography, and the fractions revealed several bands of activity at pH 4.6 and 8 on non-denaturing PAGE, but culture filtrate of *Coriolus versicolor* revealed active bands only at pH 4 and 6.

1995-203

カワラタケラッカーゼアイソザイムの解析

三国順子<sup>\*1</sup>、中村雅哉<sup>\*2</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*3</sup>、諸星紀幸<sup>\*3</sup>

<sup>\*1</sup>東京農工大学農学部、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>東京農工大学生物システム応用科学科

Characterization of laccase isoenzymes from *Coriolus versicolor*.

Junko Mikuni<sup>\*1</sup>, Masaya Nakamura<sup>\*2</sup>, Shinya Kawai<sup>\*1</sup>, Yosbihiro Katayama<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Forestry and Forest Products Research Institute, <sup>\*3</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology

Abstract: Our previous studies showed laccase III concerned in lignin biodegradation, and cleared the properties of this enzyme genetically and enzymatically. In order to define the inherent and physiological role of laccase, we present to characterize the other laccase isoenzymes. As genetic characterization, we sequenced another laccase gene and named CVLG1, previously. In this study, the origin of Laccase III gene and CVLG1 were confirmed by Southern hybridization. Two Pst I DNA fragments were hybridized by probe a and b, respectively. These four fragments were analyzed.

1995-204

土壤微生物 *Pseudomonas paucimobilis* SYK-6 のリグニン・ビフェニル特異的脱メチル化酵素遺伝子に関する研究

東 素夫<sup>\*1</sup>、笠原健秀<sup>\*2</sup>、小尾高広<sup>\*2</sup>、片山義博<sup>\*1</sup>、川合伸也<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>

<sup>\*1</sup>東京農工大学生物システム応用科学科、<sup>\*2</sup>東京農工大学農学部

Analysis of the lignin-biphenyl specific demethylase gene from *Pseudomonas paucimobilis* SYK-6.

Motoo Higashi, Takehide Kasahara, Takahiro Obi, Yoshihiro Katayama, Shinya Kawai, Noriyuki Morohoshi

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract; *Pseudomonas paucimobilis* SYK-6 is able to grow on DDVA and other various lignin dimeric compounds as a sole carbon source. To study of the specific reactions of lignin degradation by the microorganism, we investigate the degradation of the biphenyl compound, DDVA, by *P. paucimobilis* SYK-6. In our study, we analyzed the demethylation of DDVA, which is the first step of DDVA degradation. We isolated a deficient mutant (NT-1) for DDVA demethylation, and the 6kbp-fragment from *P. paucimobilis* SYK-6 chromosomal DNA, which complemented DDVA demethylation for NT-1. Here we report characteristics of this 6kbp-fragment.

1995-205

土壤微生物 *Pseudomonas paucimobilis* SYK-6 のリグニン・ビフェニル特異的環開裂酵素遺伝子の構造と機能に関する研究

片山義博<sup>\*1</sup>、花城 薫<sup>\*1</sup>、川合伸也<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>、江頭 崇<sup>\*3</sup>、彭 学、金原和秀<sup>\*4</sup>、政井英司<sup>\*3</sup>、福田雅夫<sup>\*4</sup>、矢野圭司<sup>\*4</sup>

<sup>\*1</sup>東京農工大学大学院生物システム応用科学科、<sup>\*2</sup>東京農工大学農学部、<sup>\*3</sup>長岡技術科学大学、<sup>\*4</sup>新技術事業団

Cloning and characterization of the gene encoding novel ring cleavage enzyme for lignin biphenyl compound in *Pseudomonas paucimobilis* SYK-6.

Yoshirou Katayama, Kaoru Hanashiro, Shinya Kawai, Noriyuki Morohoshi

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Nagaoka University of Technology, <sup>\*4</sup>Research Development Cooperation.

Abstract: The soil bacterium, *Pseudomonas paucimobilis* SYK-6 is able to degrade various

types of dimeric lignin compounds such as biphenyl,  $\beta$ -aryl ether, phenylcoumaran etc. Here, we reported molecular cloning of the gene encoding ring cleavage enzyme for lignin biphenyl. The 1.5 Kbp DNA fragment which maintained the ring cleavage activity was identified by subcloning and sequencing. An open reading frame encoding 334 amino acid was identified which designated lig Z. The lig Z gene was expressed in *E. coli* and the characterization of this enzyme was carried out. The enzymatic activity was observed only when OHDDVA (2,2',3-trihydroxy-3'-methoxy-5,5'-dicarboxybiphenyl) was used as substrate but not for protocatechuate, 3-methylgallic acid and 2,3-dihydroxybiphenyl.

1995-206

$\alpha$  位にカルボニル基を有する難分解性  $\beta$ -O-4 型リグニンモデル化合物のマンガン及びシユウ酸による分解

近藤 登、服部武文、島田幹夫  
京都大学木質科学研究所

A novel MnP-mimetic breakdown of recalcitrant nonphenolic lignin model compounds with two electron pulling groups in the presence of Mn(III) and oxalate.

Noboru Kondo, Takefumi Hattori, Mikio Shimada  
Wood Research Institute, Kyoto University

Abstract: Nonphenolic dimeric lignin model compounds with two electron-pulling groups such as 1-(4-ethoxy-3-methoxyphenyl)-2-(4-formyl-2-methoxyphenoxy)-1-ethanone (I) was broken down with Mn(III) in the presence of oxalate and dimethyl sulfoxide (DMSO), yielding the C $\alpha$ -C $\beta$  bond cleavage and C $\beta$ -ether bond cleavage products such as 4-O-ethylvanillic acid (II) and vanillin (III), respectively. In this case, one atom of dioxygen has been demonstrated to be incorporated into the product (II). Almost no cleavage reaction occurred in the control systems without either Mn(III), oxalate or DMSO. Possible mechanisms for these unprecedented degradation of lignin models are discussed.

1995-207

担子菌由来リグニン分解酵素の有機溶媒中における反応

吉田晋一、渡辺隆司、本田与一、桑原正章  
京都大学木質科学研究所

Reaction of ligninolytic enzymes from basidiomycete in organic solvents.

Shinichi Yoshida, Takashi Watanabe, Yoichi Honda, Masaaki Kuwahara  
Wood Research Institute, Kyoto University

Abstract: Oxidation of aromatic compounds by lignin peroxidase (LiP) of *Phanerochaete chrysosporium* was examined in organic solvents. LiP exhibited high activity of 3,3'-dimethoxybenzidine oxidation in several 70% aqueous solutions of water-miscible solvents including ethylene glycol, diethylene glycol, methylcellosolve, and acetone. LiP catalyzed the oxidation of several phenolics and aromatic amine including 3,3'-dimethoxybenzidine, catechol,  $\sigma$ -phenylenediamine and  $\sigma$ -aminophenol in 70% aqueous ethylene glycol solution. UV/VIS absorption analysis suggested the formation of an intermediary charge-transfer complex in the reaction in water, whereas the presence of this complex was not shown in the 70% aqueous ethylene glycol media. Electron spin resonance (ESR) analysis demonstrated that the reaction proceeded *via* the cation radical of 3,3'-dimethoxybenzidine both in water and 70% aqueous ethylene glycol solution.

1995-208

リグニン生分解に関する研究(IV) 一針葉樹および広葉樹クラフトパルプのバイオブリーチングに

おけるマンガンペルオキシダーゼとリグニン分解の関係—

片桐誠之、江原克信、堤 祐司、西田友昭

静岡大学農学部

Studies on lignin biodegradation. IV. The relationship between manganese peroxidase and delignification on biobleaching of softwood and hardwood kraft pulp.

Nobuyuki Katagiri, Katsunobu Ehara, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: The relationship between MnP and delignification on biobleaching of softwood (SWKP) and hardwood kraft pulp (HWKP) was investigated. The treatment of SWKP and HWKP with partially purified MnP supports that MnP can bleach SWKP and HWKP, and lignin loss of SWKP and HWKP by MnP is nearly same level. In the biobleaching of HWKP, there was a linear relationship between brightness increase (lignin loss) and cumulative activity of MnP produced by *Phanerochaete chrysosporium*, *Trametes versicolor* and IZU-154. In the biobleaching of SWKP, though lignin loss was same level, cumulative activity of MnP produced by *Phanerochaete chrysosporium* was much less than by IZU-154. These results suggest that other enzymes may contribute to delignification of SWKP during treatment with *P. chrysosporium*.

1995-209

白色腐朽菌のリグニン分解に関与する酵素系に関する研究(VII)—クラフトパルプのバイオブリーチングにおける白色腐朽菌の還元能の役割—

平井浩文、北濱 孝、近藤隆一郎、坂井克己

九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi. VII. The role of reducing abilities of white-rot fungi during biological bleaching of kraft pulp.

Hirofumi Hirai, Takashi Kitahama, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We examined biological bleaching of unbleached hardwood kraft pulp (UKP) with *Phanerochaete sordida* YK-624 and *Phlebia* sp. YK-63. *P. sordida* YK-624 secreted oxalate during the biological bleaching of UKP under the condition of the initial culture pH 7.0, and then the culture pH was dropped to about 5.0. After 2 days incubation, the culture pH being dropped, the brightness increase of fungal-treated UKP and MnP production were observed. *Phlebia* sp. YK-663 could not bleach UKP at initial culture pH 7.0, and neither the drop of pH nor MnP production were observed. Mn<sup>2+</sup> ion was detected in UKPs which were brightened by each fungus although *Phlebia* sp. YK-663 could not reduce manganese dioxide present in UKP under the initial culture pH 7.0. It is expected that the ability of dropping culture pH and MnO<sub>2</sub>-reducing ability are necessary to delignify residual lignin in UKP, and that these abilities were related to the reducing ability detected with tetrazolium salts.

1995-210

MnSO<sub>4</sub>無添加系でのマンガンペルオキシダーゼによるクラフトパルプの漂白

原園幸一、近藤隆一郎、坂井克己

九州大学農学部

Bleaching of kraft pulp with manganese peroxidase without addition of MnSO<sub>4</sub>.

Koichi Harazono, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: *In vitro* bleaching of an unbleached hardwood kraft pulp was performed with partially purified manganese peroxidase (MnP) from the fungus *Phanerochaete sordida* YK-624 without the

addition of MnSO<sub>4</sub> in the presence of some organic acids. When the pulp was treated without the addition of MnSO<sub>4</sub>, the pulp brightness increased by about 10 points in the presence of 2 mM oxalate while the brightness did not significantly increase in the presence of 50 mM malonate, a good Mn<sup>3+</sup> chelator. Oxalate reduced MnO<sub>2</sub> which had been existed in the pulp or produced from Mn<sup>2+</sup> by the oxidation with MnP, and supplied Mn<sup>2+</sup> to MnP system. It can be concluded that bleaching of hardwood kraft pulp with MnP by the effective use of manganese originally present in the pulp was possible in the presence of oxalate, a good Mn<sup>3+</sup> chelator and MnO<sub>2</sub>-reducing agent.

1995-211

PEG および PEG-PPG 系リグニン/糖ベースポリウレタンの熱分析

畠山兵衛<sup>\*1</sup>、伊豆田良信<sup>\*1</sup>、河崎将也<sup>\*1</sup>、中野準三<sup>\*1</sup>、小橋川健<sup>\*2</sup>、照屋輝一<sup>\*2</sup>、廣瀬重雄<sup>\*3</sup>、  
畠山立子<sup>\*3</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> トロピカルテクノセンター、<sup>\*3</sup> 物質研究所

Thermal analysis of polyurethanes from PEG- and PEG-PPG-/lignin and saccharide systems. Hyoe Hatakeyama<sup>\*1</sup>, Yoshinobu Izuta<sup>\*1</sup>, Masaya Kawasaki<sup>\*1</sup>, Junzo Nakano<sup>\*1</sup>, Ken Kobashigawa<sup>\*2</sup>, Kiichi Teruya<sup>\*2</sup>, Shigeo Hirose<sup>\*3</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Fukui Institute of Technology, <sup>\*2</sup>Tropical Technology Center Ltd., <sup>\*3</sup>National Institute of Materials and Chemical Research

Abstract: Polyurethane (PU) foams were prepared by the following procedures. A 50 wt% solution of kraft lignin (KL) in polyethylene glycol 200 (PEG, m.w. 200) was mixed with PEG 200, and then the obtained solution was reacted with diphenylmethane diisocyanate (MDI) in the presence of small amounts of water, silicone surfactant and tin catalyst. PU foams were also prepared using a PEG- polypropylene glycol (PPG) copolymer instead of PEG 200 in the above process. Furthermore, PU's containing molasses (MOL) were also prepared according to the above procedures. The thermal properties of PU's were studied by differential scanning calorimetry (DSC), thermogravimetry (TG) and TG-infrared spectrometry (FTIR). The influence of the addition of KL and MOL to PU's on thermal properties were studied.

1995-212

リン酸化によるリグノセルロースのヒドロゲル化

斉藤直人<sup>\*1</sup>、青山政和<sup>\*1</sup>、清水祐一<sup>\*2</sup>、高井光男<sup>\*3</sup>、林 治助<sup>\*3</sup>

<sup>\*1</sup> 北海道立林産試験場、<sup>\*2</sup> 苫小牧工業高等専門学校、<sup>\*3</sup> 北海道大学大学院工学研究科

Hydrogelation of lignocellulosic materials by phosphorylation.

Naoto Saito<sup>\*1</sup>, Masakazu Aoyama<sup>\*1</sup>, Yuichi Shimizu<sup>\*2</sup>, Mitsuo Takai<sup>\*3</sup>, Jisuke Hayashi<sup>\*3</sup>

<sup>\*1</sup>Hokkaido Forest Products Reserach Institute, <sup>\*2</sup>Tomkomai National College of Technology, <sup>\*3</sup>Graduate School of Hokkaido University

Abstract: To investigate the swelling mechanism with crystalline and fine structures, the chlorite-treated woodmeal and the ramie fiber were pretreated with hydrochloric acid or sodium hydroxide and by intensive milling. The phosphorylated product obtained from the milled ramie showed the water absorbency 17 (g H<sub>2</sub>O/g). The treatment with HCl or NaOH being followed by phosphorylation decreased the water absorbency of the product prepared from the woodmeal. The phosphorylated product was identical with Cellulose I regarding the crystalline structure. Consequently, the phosphorylation occurs on the finer structure unit such as microfibril. The stronger hydrogen bond between microfibrils of the ramie decreases the water absorbency of the product.

1995-213

## ベンジル化木材の単独発泡における含有 LCC の効果

平岡俊治<sup>\*1</sup>、上田昌見<sup>\*1</sup>、高見泰博<sup>\*1</sup>、越島哲夫<sup>\*2</sup>

<sup>\*1</sup> 日本化学機械製造株式会社, <sup>\*2</sup> 近畿大学農学部

Effects of lignin-carbohydrate complexes on foaming of benzylated wood without adding plasticizers. Toshiharu Hiraoka<sup>\*1</sup>, Masami Ueda<sup>\*1</sup>, Yasuhiro Takami<sup>\*1</sup>, Tetsuo Koshijima<sup>\*2</sup>

<sup>\*1</sup>Japan Chemical Engineering & Machinery Co. Ltd., <sup>\*2</sup>Faculty of Agriculture, Kinki University

Abstract: Researches have been done aiming to make a degradable foam from benzylated wood. As a result we have found that it is possible to produce a expandable benzylated wood without adding any of plasticizers or other polymers and also it is necessary for the benzylated wood to retain more than 70% of the LCC in the original wood in order to accomplish ten to twenty times foaming. There was direct proportional relationship between the foaming extents and LCC contents of the resin up to nine-teen times of foaming extent. What kinds of effects of lignin have been brought on physical properties of the final products also have been investigated.

1995-P01

## モノグリノールグルコシドの樹幹内分布と季節変動

田口小百合、福島和彦、安田征市

名古屋大学農学部

Distribution and seasonal changes of monolignol glucosides in *Magnolia kobus*.

Sayuri Taguchi, Kazuhiko Fukushima and Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: Monolignol glucosides (MLG), coniferin (CF) and syringin (SY), existed in the xylem and the bark of *Magnolia kobus* in different season were determined quantitatively. The proportion of SY in the bark were much higher compared with that in the xylem. The concentration of CF was a higher value in lignifying season. But even in a resting stage, SY content in the bark was very high. In lignifying season, MLG in the outer bark was almost syringin, on the contrary, in the cambial zone and differentiating xylem was almost coniferin. It seems that CF existing in the xylem is related to the lignification of stem. But there is no relationship between SY content and lignification of xylem in magnolia shoot.

1995-P02

## 芳香環 3 位あるいは 5 位に水酸基を導入したモノグリノールグルコシドのコブシ樹幹内での挙動

松井直之<sup>\*1</sup>、福島和彦<sup>\*1</sup>、安田征市<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup> 名古屋大学農学部、<sup>\*2</sup> USDA 林産物研究所

Behavior of monolignol glucoside derivatives which contains hydroxyl group on aromatic ring 3- or 5-position in magnolia shoot

Naoyuki Matsui<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Nagoya University, <sup>\*2</sup>United States Dept. of Agriculture, Forest Products Laboratory, U.S.A.

Abstract: The feeding of hydroxylated monolignol glucoside to magnolia shoot revealed that these derivatives can be used as precursors of coniferin and syringin, and the structural conversion proceeds mostly to the direction of the increase of methoxyl groups. The mechanism of the conversion seems to need a temporary removal of glucose residue, in spite of our previous result [1]. By the further study using variously labeled coniferin, it became clear the conversion from coniferin to syringin is achieved at the stage of monolignols, not their glucoside.

1995-P03

交雑ヤマナラシ キタカミハクヨウから単離した OMT 遺伝子の解析

早川敏雄<sup>\*1</sup>、吉澤たまか<sup>\*1</sup>、川合伸也<sup>\*1</sup>

高塚慎司<sup>\*2</sup>、片山義博<sup>\*2</sup>、諸星紀幸<sup>\*2</sup>

<sup>\*1</sup>東京農工大農、<sup>\*2</sup>東京農工大生物システム応用科学研究科

Analysis of genes for OMT that were isolated from a hybrid aspen, *Populus kitakamiensis*.

Toshihiro Hayakawa<sup>\*1</sup>, Tamaka Yoshizawa<sup>\*1</sup>, Shinya Kawa<sup>\*1</sup>, Shinji Takatsuka<sup>\*2</sup>, Yoshihiro Katayama<sup>\*2</sup>, Noriyuki Morohoshi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Graduate school of BASE, Tokyo University of Agriculture and Technology

Abstract: *O*-methyl transferase (OMT) plays an important role in monolignol biosynthesis. Genomic Southern blot analysis suggested that the genes for OMT formed a small gene family in *Populus kitakamiensis*. We have isolated two genes, *homt1* and *homt3*, from the genome of *P. kitakamiensis*. Two OMT isoenzymes have been isolated from stems of *P. kitakamiensis*. They differed from one another in substrate specificity. It is important to clarify the relationship between the genes and isoenzymes. We attempted to express the genes in *E. coli* cells and *P. kitakamiensis*. On the other hand, an antisense gene for OMT was introduced into tobacco and the transformants were regenerated into plants.

1995-P04

ゴマ (*Sesamum indicum*) のフロフラン型リグナンの生合成

片山健至、池西康晴

香川大学農学部

Biosynthesis of furofuran lignans in sesame (*Sesamum indicum*).

Takeshi Katayama, Yasuharu Ikenishi

Faculty of Agriculture, Kagawa University

Abstract: Sesame seeds contain furofuran lignans such as (+)-sesamin and (+)-pinoresinol, which are widely distributed in higher plants. To investigate biosynthesis of the furofuran lignans in sesame (*Sesamum indicum*), [8-<sup>14</sup>C]coniferyl alcohol was fed to excised stems of sesame and [8-<sup>14</sup>C]coniferyl alcohol was incubated with insoluble residue from stems and capsules, upon removal of soluble enzymes, in the absence of cofactor and in the presence of NAD-malate or aqueous KI. Following [8-<sup>14</sup>C]coniferyl alcohol administration to excised shoots for 3 hr, radio-labeled pinoresinol was formed more in stems than in leaves. The (+)/(-) ratio was 42-46 : 58-54. Radio-activities for sesamin and sesamolin were the same as background level. Enzymatic [8,8'-<sup>14</sup>C]pinoresinol formation with the insoluble residue was found in each incubation condition. The addition of NAD-malate enhanced the pinoresinol formation.

1995-P05

カラスザンショウ (*Zanthoxylum ailanthoides*) のリグナンの生合成と立体化学

正岡 武、片山健至

香川大学農学部

Lignans biosynthesis and stereochemistry of *Zanthoxylum ailanthoides*.

Takeshi Kasaoka, Takeshi Katayama

Faculty of Agriculture, Kagawa University

Abstract: Administration of [8-<sup>14</sup>C]coniferyl alcohol to an excised shoot of *Zanthoxylum ailanthoides* resulted in a conversion of pinoresinol (almost racemic), (-)-lariciresinol (71% ee), and (+)-secoisolariciresinol (56% ee). (±)-[8,8'-<sup>14</sup>C]pinoresinols were incubated for 1 hr with cell-free extracts from *Z. ailanthoides* in the presence of NADPH. Both [8,8'-<sup>14</sup>C]lariciresinol and [8,8'-<sup>14</sup>C]

secoisolariciresinol were detected as (+)-forms. Time-course experiments (5, 20min, 1 hr) using the cell-free extracts [10–80% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, precipitate under the same condition as above showed formations of lariciresinol and secoisolariciresinol were linear over the time period, corresponding a linear depletion of pinoresinol.

1995-P06

反芻家畜の消化作用により可溶化したイネ科牧草リグニンの特性

渡辺隆司<sup>\*1</sup>、近藤恒夫<sup>\*2</sup>、大下友子<sup>\*2</sup>、久馬 忠<sup>\*2</sup>、本田与一<sup>\*1</sup>、桑原正章<sup>\*1</sup>

<sup>\*1</sup> 京都大学木質科学研究所、<sup>\*2</sup> 東北農業試験所

Structural characteristics of soluble lignin fractions released by digestion in ruminant animal from forage grasses.

Takashi Watanabe<sup>\*1</sup>, Tsuneo Kondo<sup>\*2</sup>, Tomoko Ohshita<sup>\*2</sup>, Tadashi Kyuma<sup>\*2</sup>, Yoichi Honda<sup>\*1</sup>, Masaaki Kuwahara

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Tohoku National Agricultural Experiment Station

Abstract: Faecal soluble lignin (FSL), extracted from the faeces of sheep that received orchard grass and timothy, were compared with 90% dioxane-soluble lignins released by ball milling (MHL) and by subsequent enzymatic hydrolysis (EHL) from the same grasses. FSL contained much less carbohydrate and esterified *p*-coumaric and ferulic acids than MHL and EHL. Molecular weight of FSL was much smaller than those of MHL and EHL. The molar ratio of syringaldehyde to vanillin produced by nitrobenzene-oxidation was higher for FSL than for MHL and EHL. Results indicated that syringyl-rich lignin fragments with less phenolic acid esters were released by digestion in sheep from the forage grasses.

1995-P07

白色腐朽菌のリグニン分解に関与する酵素系に関する研究(VIII)–*Phanerochaete sordida* YK-624株によるベラトリルアルコールの生産について–

平井浩文、近藤隆一郎、坂井克己

九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi. VIII. Production of veratryl alcohol by *Phanerochaete sordida* YK-624.

Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Dept. of Forest Products, Kyushu University

Abstract: To clarify the production of veratryl alcohol (VA) by *Phanerochaete sordida* YK-624 under the nutrient-rich conditions, where the reduction of tetrazolium salts was induced and no lignin peroxidase activity was detected, the pathway for VA biosynthesis was examined by the addition of cinnamic acid (Cacid) as the precursor of VA to potato-dextrose media. (pH 7.0). Cacid was transformed to cinnamaldehyde (Cald), cinnamyl alcohol (CA), benzaldehyde (Bald), and benzyl alcohol (BA) by *P. sordida* YK-624, and no benzoate was detected. It was suggested that the pathway for VA biosynthesis in *P. sordida* YK-624 differed from the pathway proposed by Jensen *et al.* *Phlebia* sp. YK-663. which showed lower tetrazolium salts-reducing activity than *P. sordida* YK-624 and hardly produced VA under ligninolytic or nutrient-rich conditions, transformed Cacid to Cald and CA, but Bald and BA were hardly detected.

1995-P08

リグノスチルベン- $\alpha, \beta$ -ジオキシゲナーゼアイソザイム I および III のキメラ酵素の基質特異性(II)

鴨田重裕、佐分義正

東京大学農学部

Substrate specificities of chimera enzymes of lignostilbene- $\alpha$ . $\beta$ -dioxygenase isozyme I and III. (II)  
Shigehiro Kamoda, Yoshimasa Saburi  
Faculty of Agriculture, the University of Tokyo

Abstract: *Pseudomonas paucimobilis* TMY1009 produced at least four lignostilbene- $\alpha$ , $\beta$ -dioxygenase (LSD) isozymes. LSD-I and -III were composed of two homogeneous  $\alpha$  and  $\beta$  subunits, respectively. LSD-I degraded 4, 2'-dihydroxy-3, 3'-dimethoxy-5-(2''-carboxyvinyl) stilbene ( $\beta$ -5 stilbene) very slowly. It seemed to be specific for 4, 4'-dihydroxy-3, 3'-dimethoxystilbene ( $\beta$ -1 stilbene). The other hand, LSD-III degraded  $\beta$ -5 stilbene better than  $\beta$ -1 stilbene. The gene of LSD-I (*IsdA*) and -III (*IsdB*) were cloned and sequenced. These two isozymes share 69% amino acid sequence identity, yet differ markedly with respect to their substrate specificities. Chimeric LSD consisting of either the N-terminal fragment of  $\alpha$  subunit fused with the C-terminal fragment of  $\beta$  subunit or the inverse pair. Chimera  $\alpha$  158  $\beta$  includes the 158 N-terminal residues of  $\alpha$  subunit fused to the complementary part of the  $\beta$  subunit sequence. Chimera  $\beta$  158  $\alpha$ ,  $\beta$  356  $\alpha$  and  $\alpha$  407  $\beta$  were designed in the same way. Analyses on Km and specific activities for two stilbenes indicated that chimera  $\alpha$  158  $\beta$  and  $\beta$  158  $\alpha$  have the same substrate specificities as LSD-III ( $\beta$  subunit) and LSD-I ( $\alpha$  subunit), respectively. As concerns  $\beta$  356  $\alpha$  and  $\alpha$  407  $\beta$ , no activity was detected. Further investigation is required.

1995-P09

種々の培養条件下における白色腐朽菌 *Phanerochaete chrysosporium* のフェニルアラニンアンモニアリアーゼ (PAL) 活性

服部武文、島田幹夫

京都大学木質科学研究所

The detection of PAL activity in *Phanerochaete chrysosporium* grown in the four different cultures.  
Takefumi Hattori, Mikio Shimada

Wood Research Institute. Kyoto University

Abstract: The activities of L-phenylalanine ammonia-lyase extracted from *Phanerochaete chrysosporium* which had been grown in the four different cultures (HC-LN, HC-HN, LC-MN, and LC-HN) were assayed. The PAL activity and the concentration of veratryl alcohol in the culture fluid were greater in HC-LN culture than in HC-HN culture. Furthermore, the PAL activities were detected in both of LC-MN and LC-HN cultures during a short period after the mycelial growth reached the peak. However, in HC-LN culture, PAL activity was detected before the mycelial growth peaked and maintained for another 6 days at higher level.

1995-P10

PEGに結合させたリグニンモデル化合物の白色腐朽菌及びその酵素による分解

河合真吾<sup>\*1</sup>、Ken Jensen<sup>\*2</sup>、Wuli Bao<sup>\*2</sup>、Ken Hammel<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学農学部、<sup>\*2</sup> USDA 林産物研究所

Fungal and enzymic oxidation of PEG-linked lignin model compound.

Shingo Kawai<sup>\*1</sup>、Kenneth A. Jensen<sup>\*2</sup>, Jr., Wuli Bao<sup>\*2</sup>、Kenneth E. Hammel<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Gifu University, <sup>\*2</sup> USDA Forest Products Laboratory

Abstract: We prepared a lignin model in which  $\beta$ -O-4 dimers were covalently attached to 8000 MW polyethylene glycol (PEG). The PEG-linked model was mineralized extensively in liquid medium and in solid wood cultures of the white-rot fungus *Phanerochaete chrysosporium*. GPC showed that *P. chrysosporium* degraded the PEG-linked model by cleaving its lignin dimer substructure rather than its PEG moiety. C $\alpha$ -C $\beta$  cleavage was the major fate of the PEG-linked model after incubation with *P. chrysosporium* and also after oxidation with its lignin peroxidase. The brown-rot fungus

*Gloeophyllum trabeum* was unable to degrade the PEG-linked model efficiently.

1995-P11

白色腐朽菌カワラタケのシュウ酸合成酵素の部分精製

三井香代子、服部武文、島田幹夫

京都大学木質科学研究所

Partial purification of glyoxylate oxidase from the white-rot basidiomycete *Coriolus versicolor*.

Kayoko Mii, Takefumi Hattori, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: The glyoxylate oxidase which catalyses oxidation of glyoxylate to form oxalate was partially purified from the homogenate of a white-rot basidiomycete *Coriolus versicolor*. The glyoxylate oxidase was purified by combination of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> precipitation, DEAE-Biogel A chromatography and Sephadex G-150 gel filtration. Three isozymes were detected by DEAE-Biogel A chromatography.

1995-P12

白色腐朽菌 *Phanerochaete chrysosporium* の核酸要求性変異株の単離とその相補遺伝子の取得

中村雅哉、西田篤実、高野麻理子

森林総合研究所

Isolation of uracil auxotrophic mutants from *Phanerochaete chrysosporium*.

Masaya Nakamura, Atsumi Nishuda, Mariko Takano

Forestry and Forest Products Reserach Institute

Abstract: Uracil auxotrophic mutants of the white-rot fungus *Phanerochaete chrysosporium* using a positive screening procedure with 5-fluoro orotic acid. Mutants deficient for the orotidin-5'-phosphate decarboxylase (*pyr 4* mutants) and for the orotate phosphoribosyl transferase (*pyr 2* mutants) have been characterized by enzyme assays. The *pyr 4* gene was screened from a *P. chrysosporium* genomic library using the *Aspegillus nidulans pyr 4* gene as a probe. The *pyr 2* gene was amplified from *P. chrysosporium* genomic DNA by PCR using the *pyr 2* specific primers.

1995-P13

クラフト蒸解条件の酸素酸化漂白への影響 -蒸解条件による酸素酸化したパルプ中残留リグニンの構造変化

陳 嘉義、清水祐一、高井光男、林 治助

北海道大学大学院工学研究科

Effect of kraft cooking conditions on efficiency of oxygen delignification. -The structure characteristics of residual lignin in the oxygen delignified pulp.

J.-Y. Chen, Yuichi Shimizu, Mitsuo Takai, Jisuke Hayashi

Graduate School or Engineering, Hokkaido University

1995-P14

リグニンスルホン酸添加バクテリアセルロース製造における菌株、炭素源の選択

恩地真一、大谷慶人、鮫鳥一彦

高知大学農学部

Selection of strain of *Acetobacter xylinum* and carbon source in cultuer medium with lignosulfonate for production of bacterial cellulose.

Shinichi Onji, Yoshito Ohotani, Kazuhiko Sameshima

Faculty of Agriculture, Kochi Univercity

Abstract: We have found that the cellulose yields of seven different strains of *Acetobacter xylinum* increased by the addition of lignosulfonate from sulfite pulping waste 2% glucose medium. In this study, we studied whether cellulose yield of each strain could be increased or not with different carbon source with or without lignosulfonate. We used Fructose, Glycerol, Saccharose, Xlose and Lactic acid as carbon source. The results indicated that cellulose yields of each strain of *A. xylinum* are not always increased by the use of different carbon source. The selections of strain and carbon source are very important to secure the cellulose yield.

1995-P15

熱分解ガスクロマトグラフィーによる広葉樹型リグニンの分析(III)ークラフト蒸解およびパルプ漂白による熱分解物の変化ー

和泉明子、田中潤治、大井 洋、黒田健一、山口 彰

筑波大学農林工学系

Analysis of hardwood lignin by pyrolysis-gas chromatography. III. Changes of pyrolysis products by kraft cooking and pulp bleaching.

Akiko Izumi, Junji Tanaka, Hiroshi Ohi, Ken-ichi Kuroda, Akira Yamaguchi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Several Japanese hardwood kraft pulps were analyzed by pyrolysis combined with gas chromatography (Py-GC). The major pyrolysis products were guaiacol, 4-methylguaiacol, 4-vinylguaiacol, *trans*-isoeugenol, coniferylaldehyde, syringol, 4-methylsyringol, 4-vinylsyringol, *trans*-4-propenylsyringol, sinapaldehyde. The ratios of syringyl-derived pyrolysis products to guaiacyl-derived pyrolysis products were decreased by kraft cooking. The yields of pyrolysis products from lignin in chlorinated kraft pulp were small, and the chlorinated-derived pyrolysis products were rarely detected.

1995-P16

ケナフ靱皮部の酸素パルプ化

敖日格勒、佐野嘉拓

北海道大学農学部

Oxygen pulping of kenaf bast.

Aorigele, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Oxygen pulping of kenaf bast was carried out with 10%–20% NaOH of o.d. bast at 110 °C and 7 kg/cm<sup>2</sup> of O<sub>2</sub> pressure for 60–120 min. Products were separated into pulp-1 (long fiber pulp), pulp-2 (screened pulp), fines (epidermis part) and a reaction liquor. After boiling with 50–70% AcOH, pulp-1 was further delignified and yielded the bast pulp. Satisfactory bast pulps with much greater delignification and physical properties were obtained in yields of 48%–56% when bast was subjected to oxygen pulping with 15% NaOH for 60–120 min, followed by boiling in aqueous AcOH. The reaction liquor was separated into three main fractions according to the fractional precipitate procedure and so on in order to analyze chemical properties and utilize as raw materials for biomass conversion.

1995-P17

酢酸リグニンを原料とする炭素繊維の調製(5)ー針葉樹酢酸リグニンの炭素繊維化ー

久保智史、石川直哉、浦木康光、佐野嘉拓

北海道大学農学部

Preparation of carbon fiber from acetic acid lignin (5) –preparation of carbon fiber from softwood

acetic acid lignin-

Satoshi Kubo, Naoya Ishikawa, Yasumitu Uraki, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Preparation of lignin fiber as precursors for carbon fibers from softwood acetic acid lignin (NAL) was obtained from todomatu wood (*Abies sachalinensis*) by aqueous AcOH pulping with 0.1% HCl at atmospheric pressure. NAL was infusible, though birch acetic acid lignin (BAL) was readily fusible without any chemical modification. However, F-2 which was precipitated from waste liquor by 70% aqueous AcOH and was obtained in a yield of 81% based on NAL, had fusibility and spinnability. Preparation of lignin fiber was achieved without thermal treatment, though the fiber had a rough surface and mechanical properties inferior to those for BAL fibers. F-2 was possible to undergo direct carbonization without thermal stabilization. Carbon fibers prepared from the lignin fibers of F-2 had worse mechanical properties compared with those for BAL fibers. The characterization of F-2 lignin fibers and carbon fibers seemed to be improved by addition of plasticizer for F-2 to have a lower fusible temperature for our handmade spinning apparatus.

1995-P18

Flavan-3,4-carbonate の開環重合による高重合度縮合型タンニンの合成とその機能

米田 聡、河本晴雄、中坪文明

京都大学農学部

Synthesis of high-molecular-weight condensed tannin by cationic ring-opening polymerization of flavan-3,4-carbonate and their function.

Satoshi Yoneda, Haruo Kawamoto, Fumiaki Nakatsubo

Faculty of Agriculture, Kyoto University

Abstract: In order to obtain high-molecular-weight condensed tannin, we synthesized newly flavan-3,4-carbonate and tried its cationic ring-opening polymerization with BF<sub>3</sub>-Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. The molecular-weight of polymers increased with an increase of reaction time, and the number-average degrees of polymerization (DP<sub>n</sub>) reached 47 after 264h. The protein-precipitating capacity was found to increase with an increase in the molecular weight of condensed tannin.

## 第 41 回 (1996.10.3-4) 名古屋大学農学部

1996-101

樹木の細胞壁リグニン生合成過程の免疫組織学的研究

増野洋子\*<sup>1</sup>、早川敏雄\*<sup>1</sup>、船田 良\*<sup>2</sup>、川合伸也\*<sup>3</sup>、諸星紀幸\*<sup>1</sup>、片山義博\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学大学院 BASE, \*<sup>2</sup> 北海道大大学農学部、\*<sup>3</sup> 東京農工大学農学部

Immunohistochemistry of biosynthesis of lignin in woody plants.

Yoko Mashino\*<sup>1</sup>, Toshio Hayakawa\*<sup>1</sup>, Ryo Funada\*<sup>2</sup>, Shinya Kawai\*<sup>2</sup>, Noriyuki Morohoshi\*<sup>1</sup>, Yoshihiro Katayama\*<sup>1</sup>

\*<sup>1</sup> Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, \*<sup>1</sup> Hokkaido University, \*<sup>3</sup> Tokyo University of Agriculture and Technology

Abstract: As protoxylem and metaxylem of angiosperms mature and develop, the elements with

more extensive secondary thickenings than that represented by a helix deposit the secondary wall in two stages. First, a helical framework is built (first-order secondary wall). Then, additional secondary wall material is laid down as sheets or strands or both between the gyres of the helix (second-order secondary wall). In this study, we report the intergrading of tracheary elements using by immuno-

histochemistry. We prepared antiserum for immunohistochemical analysis. Antiserums were raised against PAL, OMT, CAD, 4CL, and POX. The peptide in the expression vector pQE (QUIAGEN, Chatsworth, CA, USA) was expressed in *E. coli* cells. The ability of the antiserum to react with crude and purified protein from *P. kitakamiensis* was tested by Western immunoblotting. PAL OMT, CAD, 4CL and POX were localized specifically in cells of xylem, but not observed in parenchyma.

1996-102

樹木の桂皮酸 4-水酸化酵素遺伝子の発現様式の解析

塩川貴広<sup>\*1</sup>、片山義博<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、川合伸也<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE, <sup>\*2</sup> 東京農工大学農学部

Expression analysis of a cinnamic acid 4-hydroxylase gene from a hybrid aspen, *Populus kitakamiensis*.

Takahiro Shiokawa<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Shinya Kawai<sup>\*2</sup>,

<sup>\*1</sup>Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Tokyo University of Agriculture and Technology

Abstract: In higher plants, Cinnamic acid 4-hydroxylase (CA4H) is the second enzyme involved in phenylpropanoid biosynthesis and is a member of cytochrome P-450 superfamily. Three CA4H genes, *-cyp73a*, *cyp73b*, and *cnd cyp73c-*, and a cDNA clone of *cyp73a* were isolated from a genomic library and a cDNA library of a hybrid aspen; *Populus kitakamiensis*, *ctnd* were characterized. They might be interrupted by two introns, respectively. *cyp73a* and *cyp73b* were very similar each other not only in coding regions but also in non-coding regions. Southern blot analysis showed that four homologous genes for CA4H constructed a small gene family in the diploid genome of *P. kitakamiensis*. In the promoter regions, there were many common *cis*-element-like sequences in phenylpropanoid biosynthesis genes. Here, we report a tissue-specific expression manner of an aspen CA4H gene in transgenic tobacco plants. We made a *cyp73a* promoter-GUS gene fused construct. It was introduced to tobacco and aspen cells. The GUS activity in transgenic tobacco plants with the *cyp73a* promoter-GUS fusion gene was mainly detected in the vascular bundles and was strongly induced in a non-tissue-specific manner by wounding.

1996-103

樹木細胞壁形成におけるリグニンと糖代謝遺伝子の特徴

真壁和彦<sup>\*1</sup>、西窪伸之<sup>\*1</sup>、川合伸也<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE, <sup>\*2</sup> 東京農工大学農学部

Characteristics of genes related to lignin and sugar metabolism in plant cell wall formation.

Kazuhiko Makabe<sup>\*1</sup>, Nobuyuki Nishikubo<sup>\*1</sup>, Shinya Kawai<sup>\*2</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Tokyo University of Agriculture and Technology

Abstract: Lignin biosynthesis and carbohydrate chain biosynthesis are closely related to cell wall formation of plant. We constructed the cDNA library from the one year old stem of *Populus kitakamiensis*, which showed active cell wall thickness and lignification. We isolated the cDNA fragments of Sucrose synthase, UGPase and DAHP synthase from the cDNA library. Sucrose synthase and UGPase are related to sugar metabolism, and DAHP synthase is related to shikimic acid pathway and lignin biosynthesis. The nucleotide sequences and the deduced amino acid sequences of their DNA fragments showed that sucrose synthase and UGPase of *P. kitakamiensis* are similar to other higher plant.

1996-104

シナピルアルコールを用いた広葉樹細胞壁木化過程シミュレーション

伊藤岐仁、重松幹二、棚橋光彦

岐阜大学農学部

Modeling of hardwood lignification using sinapyl alcohol.

Michihito Itoh, Mikiji Shigematsu, Mitsuhiko Tanahashi

Faculty of Agriculture, Gifu University

Abstract: To be clear biosynthetic process and chemical structure of hardwood lignin, the effect of hydrophobicity of reaction media on dehydrogenative polymerization (DHP) of sinapyl alcohol was studied by using a horseradish peroxidase. First, to inhibit polymerization of sinapyl alcohol in water around the enzyme, the hydrophilic site of horseradish peroxidase was converted to be hydrophobic by modifying with methoxypolyethylene glycol succinimidyl succinate. Sinapyl alcohol was polymerized by the modified enzyme, and the products were analyzed by  $^1\text{H-NMR}$ . Second, considering the lignification model that sinapyl alcohol is polymerized by  $\beta$ -O-4 linkage to syringaresinol formed previously, syringaresinol was used as starting radical at DHP process of sinapyl alcohol. Third, to examine the effect of hydrophobic media, polymerization of sinapyl alcohol in polysaccharide solution or hydrophobic solvents was investigated by  $^1\text{H-NMR}$ . Further, structure of polymerized products of C  $\beta$ -labeled sinapyl alcohol ( $\text{HO-C}_6\text{H}_2(\text{OCH}_3)_2\text{-CH=C}^*\text{H-CH}_2\text{OH}$ ) was analyzed by  $^{13}\text{C-CP/MAS}$ .

1996-105

広葉樹の CAD 形質転換体における異常リグニンの化学的構造について

伊藤 隆<sup>\*1</sup>、河合真吾<sup>\*1</sup>、大橋英堆<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学農学部, <sup>\*2</sup> 京都大学名誉教授

Chemical study on abnormal hardwood lignin with antisense cinnamyl alcohol dehydrogenase (CAD) gene.

Takashi Ito<sup>\*1</sup>, Shingo Kawai<sup>\*1</sup>, Hideo Ohashi<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>The United Graduate School of Agriculture Science, Gifu University, <sup>\*2</sup>Professor emeritus of Kyoto University

Abstract: Various DHPs derived from mixtures of coniferyl aldehyde and sinapaldehyde with coniferyl and sinapyl alcohol were prepared for the model of the transgenic hardwood lignin. Fr-IR and UV analysis of the DHP showed that sinapaldehyde and sinapyl alcohol were effectively incorporated into these DHPs. However, GC-MS analyses of the thioacidolysis products of the DHPs showed that coniferyl aldehyde was significantly incorporated into the DHPs and end group via  $\beta$ -O-4 linkages, and the incorporation of sinapaldehyde into the DHPs as end group was very small. Therefore, the thioacidolysis products of sinapaldehyde were analyzed by GC-MS. The chromatogram gave a small peak of the extended product with relatively large amount of two new components derived from sinapaldehyde.

1996-106

カラスザンショウにおけるリグナン生合成

片山健至、正岡 武、杉本博之、瀧井忠人、大柿 篤

香川大学農学部

Biosynthesis of lignans in *Zanthoxylum ailanthoides*.

Takeshi Katayama, Takeshi Masaoka, Hiroyuki Sugimoto, Tadato Takii, Atsushi Ogaki

Faculty of Agriculture, Kagawa University

Abstract: Interestingly *Zanthoxylum ailanthoides* have (8*S*,8'*S*)-furofuran lignans such as

(-)-pinoresinol and (8*R*,8'*R*)-(-)-secoisolariciresinol. It was suggested that insoluble residue from *Z. ailanthoides* catalyzed enantioselective (-)-pinoresinol formation from coniferyl alcohol. Incubation of cell-free extracts from the plants with (±)-pinoresinols in the presence of NAD(P)H resulted in the enantiospecific formation of (+)-lariciresinol, whose configuration was identical with that of natural (-)-secoisolariciresinol. Following administration of [8-<sup>14</sup>C]coniferyl alcohol the radioactivities were incorporated in pinoresinol, lariciresinol and secoisolariciresinol with their (8*S*,8'*S*) enantiomer preferred. Following administration of [8,8'-<sup>14</sup>C] pinoresinol, the formation of radioactive lariciresinol and secoisolariciresinol was found again, although they were almost racemic. These facts suggested the presence of both biosynthetic pathways to (8*S*,8'*S*) and (8*R*,8'*R*) lignans in the plant.

1996-107

トチュウのリグナン・ネオリグナンの生合成と立体化学

片山健至、加登優樹、大柿 篤

香川大学農学部

Biosynthesis and stereochemistry of lignans and neolignans in *Eucommia ulmoides*.

Takeshi Katayama, Yuki Kado, Atsushi Ogaki

Faculty of Agriculture, Kagawa University

Abstract: *Eucommia ulmoides* contains diverse lignans and neolignans. To investigate their biosynthesis, [8-<sup>14</sup>C]coniferyl alcohol was fed to excised young shoots, and it was incubated with cell-free extracts of the plant in the presence of H<sub>2</sub>O<sub>2</sub> and with insoluble residue in the absence of cofactors. (+)-Pinoresinol formation was found in preference to the (-)-form in the feeding experiment. *Erythro*-isomer was more than the *threo* one in guaiacylglycerol-β-coniferyl ether obtained both in the feeding experiment and in the assay using the insoluble residue. (-)-Dehydrodiconiferyl alcohol and optically active *erythro* and *threo*-guaiacylglycerol-β-coniferyl ethers were formed in the assay using cell-free extracts in spite of their low enantiomeric excess (9-14%).

1996-108

*Wikstroemia sikokiana* から単離されたリグナンとその生合成経路について

奥西智哉、梅澤俊明、島田幹夫

京都大学木質科学研究所

A possible biosynthetic pathway of lignans in *Wikstroemia sikokiana*.

Tomoya Okunishi, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: [9,9-<sup>2</sup>H<sub>2</sub>OC<sup>2</sup>H<sub>3</sub>]Coniferyl alcohol, [9,9,9',9'-<sup>2</sup>H<sub>4</sub>]pinoresinol, [9,9,9',9'-<sup>2</sup>H<sub>4</sub>]lariciresinol and [9,9,9',9'-<sup>2</sup>H<sub>4</sub>]secoisolariciresinol were administered to *Wikstroemia sikokiana*, and incorporation of deuterium atoms into several lignans were observed. Based on the result, a possible biosynthetic pathway of lignans in *W. sikokiana* was proposed.

1996-109

*Eucalyptus camaldulensis* および *E. globulus* 各 2 個体の樹幹内変異を用いたリグニンの S/G 比とリグニン含有率の関係について

小名俊博、園田哲也、伊藤一弥、伊藤昌樹

王子製紙株式会社森林資源研究所

Relationship between lignin content and lignin S/G ratio in the same trunk sought by their within-tree variations in *Eucalyptus camaldulensis* and *E. globules*.

Toshihiro Ona, Tetsuya Sonoda, Kazuya Ito, Masaki Ito

Kameyama Research Center, Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: The relationship between extractives-free (EF) lignin content and lignin monomeric composition as syringyl/guaiacyl (S/G) ratio by thioacidolysis was examined. This was performed in the same trunk by their within-tree variations, which mean the investigation with the same genes, in *Eucalyptus camaldulensis* and *E. globules*. As results, each species had a high negative correlation between EF-lignin content and lignin S/G ratio although the difference between species and/or individuals was observed in the trend of within-tree variations of the wood properties. The relationship between EF-lignin content and lignin S/G ratio is considered to be caused from the difference in the fiber morphology from the relationship between lignin and EF-basic density which may relate to the fiber morphology.

1996-110

5-Hydroxyguaiacyl nuclei in native lignin.

Kenji Iiyama<sup>\*1</sup>, Satoshi Suzuki<sup>\*2</sup>, Thi Bach Tuyet Lam<sup>\*3</sup>

<sup>\*1</sup>Asian Natural Environmental Science Center, the University of Tokyo, <sup>\*2</sup>Graduate School of Agriculture and Life Science, the University of Tokyo, <sup>\*3</sup>School of Biochemistry, La Trobe University

1996-111

多糖類存在下におけるリグニンモデル物質の反応

大森茂俊<sup>\*1</sup>、青山政和<sup>\*2</sup>、榊原 彰<sup>\*3</sup>

<sup>\*1</sup>College of Environmental Science and Forestry, State University of New York, <sup>\*2</sup>北海道立林産試験場、<sup>\*3</sup>北海道大学名誉教授

Reaction of lignin model compounds in the presence of polysaccharides.

Shigetoshi Omori<sup>\*1</sup>, Masakazu Aoyama<sup>\*2</sup>, Akira Sakakibara<sup>\*3</sup>

<sup>\*1</sup>College of Environmental Science and Forestry, State University of New York, <sup>\*2</sup>Hokkaido Forest Products Research Institute, <sup>\*3</sup>Professor emeritus, Hokkaido University

Abstract: The lignin model compounds of  $\beta$ -O-4 type were treated in dioxane and water (1:1) mixture at 180°C for 20 min with and without spruce holocellulose. A model, guaiacylglycerol- $\beta$ -guaiacyl ether (1) gave  $\beta$ -I (8),  $\beta$ -5 (9),  $\beta$ - $\beta$  (10) dilignols and a trilignol (11) which are the products of recoupled radicals from homolysis of the model (1). However, when treated in the presence of holocellulose, these dimeric and trimeric compounds could not be detected. The results indicate that the polysaccharides act as hydrogen donor to stabilize the formed radicals before their coupling. The same results were also recognized in the case of other  $\beta$ -O-4 model compounds.

1996-112

分析的熱分析によるリグニンの分析 —熱分解生成物の起源構造について—

和泉明子、黒田健一

筑波大学農林工学系

Analytical pyrolysis of lignin : origins of pyrolysis products.

Akiko Izumi, Ken-ichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Lignin model compounds,  $\beta$ - $\beta$  and  $\beta$ -5 types, were pyrolyzed in the presence of tetramethylammonium hydroxide (TMAH) to obtain information on the lignin structure. Pinoresinol and syringaresinol yielded full methylated products as main products. The full methylated product ( $M^+$  400) of dehydrodiconiferyl alcohol was not observed. However, dehydrodiconiferyl alcohol showed the formation of three methylated products, which were isomers from their mass fragment

patterns ( $M^+ 370$ ). These methylated dimer products were also observed in the pyrolysis of hardwood type dehydrogenative polymers.

1996-113

熱分解-メチル化によるリグニンの分析:  $\beta$ -O-4 型構造由来の熱分解生成物

黒田健一

筑波大学農林工学系

Pyrolysis-gas chromatography analysis of lignin in the presence of tetra-methylammonium hydroxide:  $\beta$ -O-4 substructure-derived pyrolysis products.

Ken-ichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: To obtain pyrolysis fragments with information on the lignin structure, a dehydrogenation polymer of coniferyl alcohol was pyrolyzed in the presence of tetramethylammonium hydroxide (TMAH) at 500 °C for 4 s. A series of methylated products were swept on a gas chromatograph column. The products, such as (3,4-dimethoxyphenyl) methoxyethylenes and 1-(3,4-dimethoxy-phenyl)-1,2,3-trimethoxypropanes, derived from the  $\beta$ -O-4 building blocks were observed in the pyrolyzate. TMAH/pyrolysis of Japanese cedar and Japanese Douglas fir woods also produced these products. The sources of some products were explained on the basis of the TMAH/pyrolysis results of  $\beta$ -O-4 type lignin model compounds. Abundances of the  $\beta$ -O-4 building blocks in lignin were compared among the woods and several isolated lignins using the peak intensities of 1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropanes. Results showed that TMAH/pyrolysis offers much information on the  $\beta$ -O-4 lignin building blocks than conventional pyrolysis without TMAH.

1996-114

リグニンの  $\beta$ -O-4 構造の化学反応性(2)-ルイス酸触媒アセトリスによるリグニンの  $\beta$ -O-4 構造の定量-

小幡雅子、中坪文明

京都大学農学部

Chemical reactivity of  $\beta$ -O-4 substructures in lignins. -Quantitative analysis of  $\beta$ -O-4 structures in lignins by Lewis acid catalyzed acetolysis (LCA) -

Masako Obata, Fumiaki Nakatsubo

Faculty of Agriculture, Kyoto University

Abstract: In our recent investigation, Lewis acid catalyzed acetolysis (LCA) reaction has been shown to be a suitable degradation method for the analysis of  $\beta$ -O-4 substructures in lignins, for its characteristic reactivity and the simple experimental procedure. Here, we describe the synthesis of Hibbert's ketones in order to identify the degradation products, and discuss some structural aspects of *Eucalyptus globules* MWL from its LCA reaction products.

1996-115

機械パルプの光褪色におよぼすフェノール性水酸基の影響

足立幸雄、伊藤和貴、坪田弘志、沖 妙、橘 燦郎

愛媛大学農学部

Effect of phenolic hydroxyl groups in mechanical pulps on depression of color reversion of mechanical pulps.

Yukio Adachi, Kazutaka Itoh, Hiroshi Tsubota, Tae Oki, Sano Tachibana

Faculty of Agriculture, Ehime University

Abstract: In order to investigate the effect of phenolic hydroxyl groups in mechanical pulps on depression or light-induced color reversion of mechanical pulp, two types of mechanical pulp (thermomechanical pulp : TMP, groundwood pulp : GP) were acetylated, and examined to what extent the color reversion of the pulps was prevented by the acetylation. When about 11% of the phenolic hydroxy groups in unbleached GP and unbleached TMP were acetylated, the color reversion of the pulps were also completely depressed. On the other hand, when about 16% and 29% of the phenolic hydroxy groups in bleached GP and bleached TMP, respectively, were acetylated, the color reversion of the pulps were completely depressed. On the basis of these results, the phenolic hydroxyl groups in mechanical pulps seem to contribute mainly to the depression of the color reversion of mechanical pulps.

1996-116

バクテリアセルロース製造培地における緩衝液成分およびリグニンスルホン酸の役割

島本 明、Siripong Premjet、大谷慶人、鮫島一彦

高知大学農学部

Role of buffer components and lignosulfonate in the superior medium for bacterial cellulose production.

Akira Shimamoto, Siripong Premjet, Yoshito Ohtani, Kazuhiko Sameshima

Faculty of Agriculture, Kochi University

Abstract: We have already reported bacterial cellulose membrane yield is greatly increased by the addition of lignosulfonate to a standard cultivation medium. In this report we examined the relationship between concentration of buffer, yield of cellulose membrane and final pH of media to clarify the role of buffer components and lignosulfonate in the superior bacterial cellulose production medium. The results showed that the final pH values of media with lignosulfonate were slightly higher than those media without lignosulfonate but the cellulose yield increases were greater. Only citric acid was probed to be the effective component for the superior cellulose production system with lignosulfonate.

1996-特別講演

樹木系フェノールポリマーとエコテクノロジー

阿部 勲

三重大学生物資源学部

Woody phenolpolymers and ecotechnology.

Isao Abe

Faculty of Bioresources, Mie University

Abstract: The investigations on woody phenolpolymers, namely wood lignin and some bark proanthocyanidins (condensed tannins) I participated were summarized, and the forest ecotechnology concerning the specific species, which contained highly of condensed tannins in bark, was discussed.

1996-201

オイルパーム・フロンド爆砕パルプからのボードの調製と爆砕パルプ中のリグニンの性状

鈴木 聡<sup>\*1</sup>、新谷博幸<sup>\*1</sup>、朴 承栄<sup>\*1</sup>、Nikhom Laemsak<sup>\*1</sup>、大熊幹章<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学アジア生物資源環境研究センター

Preparation of binderless boards from steam exploded pulp of oil palm frond and structural characteristic of lignin in steam exploded pulp.

Satoshi Suzuki<sup>\*1</sup>, Hiroyuki Shintani<sup>\*1</sup>, Seung-Young Park<sup>\*1</sup>, Nikhom Laemsak<sup>\*1</sup>, Motoaki Okuma<sup>\*1</sup>,

Kenji Iiyama\*2

\*1Graduate School of Agricultural and Life Science, the University of Tokyo, \*2Asian Natural Environmental Science Center, the University of Tokyo

Abstract: The binderless boards were prepared from steam exploded (2.0–3.0MPa, 5–10min) pulps of oil palm frond. The strength of these boards met the requirements of the boards of JIS. To clarify the mechanism of the bonding of the binderless boards, oil palm frond, pulp and board were analyzed by the chemical and spectrometrical methods and pyrolysis–gas chromatography mass spectrometry. Björkman lignin from oil palm frond, and this lignin was characterized by the presence of significant amount of esterified *p*-hydroxybenzoic acid. Most ester bonds and  $\beta$ -O-4 bonds were cleaved during steam explosion process, and the other hand, guaiacyl units were condensed greatly, as revealed by <sup>1</sup>H and <sup>13</sup>C-NMR spectra. Moreover, the structural difference of the aromatic units between 2.5MPa and 3.0MPa exploded pulp, were observed in <sup>1</sup>H, <sup>13</sup>C-NMR and FTIR spectra. The ratios of syringyl derivatives to guaiacyl derivatives (S/G) from total ion pyrograms were decreased by hot pressing. As a result of the analytical pyrolysis, 5-hydroxymethylfurfural, derived from cellulose, was increased by the steam explosion especially 3.0MPa. Significant amount of furfural, derived from pentosan, was detected in the pulp steam exploded under the condition of 2.5MPa, and furfural was increased during hot pressing. These facts suggest that furfural is involved in the formation of binder together with lignin.

1996–202

蒸解黒液中のリグニンの性状に関する研究

岩瀬幸彦, 種田英孝, 井上敏雄

日本製紙株式会社

Studies on lignin in the kraft black liquor.

Yukihiko Iwase, Hidetaka Taneda, Toshio Inoue

Nippon Paper Industries Co., Ltd.

Abstract: We analyzed a black liquor to establish a method to determine a pulp yield. When the black liquor was acidified to separate lignin and other wood components, it was observed that kraft cooking with anthraquinone (AQ) increased the rate of precipitated lignin to the total lignin in the black liquor. Determinations of functional groups of precipitated lignin, "kraft lignin", and acid-soluble lignin, indicated that AQ did not give a significant influence to a character of kraft lignin, but did much to one of acid-soluble lignin. It would be suggested that AQ decreased the acid-solubility of lignin by preventing formation of lignin-carbohydrates-complex (LCC) containing carboxylic acids derived from carbohydrates degradation compounds.

1996–203

酸素–アルカリ漂白過程における多糖類の分解機構(6)–過酸化物の安定性と炭水化物分解の関連について–

横山朝哉、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Degradation mechanisms of carbohydrate during oxygen–alkali bleaching. VI. – Relationships between peroxide stability and carbohydrate degradation–

Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: A cellulose model compound, methyl  $\beta$ -D-glucopyranoside (MGP), was treated with an alkaline hydrogen peroxide solution in the presence or absence of metal ions, such as iron, manganese and magnesium, and the effect of these metal ions on the degradation of MGP was

examined. The results showed that the amount of degraded MGP at a certain consumption of hydrogen peroxide was strongly dependent on the metal ions. The addition of iron did not cause more MGP degradation than the case of no metal addition, and the less MGP degradation was observed when more magnesium was added together with iron. Contrarily, the addition of manganese caused only a little degradation of MGP though the rate of hydrogen peroxide degradation was very high, and the addition of magnesium together with manganese had no positive effect on the protection of MGP. The sole addition of magnesium had some positive effect on the protection of MGP but the complete protection of MGP was not obtained.

1996-204

リグニンおよび兼モデル化合物とオゾンとの直接の反応によるヒドロキシラジカルの生成  
スウェーデン王立工科大学

Martin Ragnar<sup>\*1</sup>, Tord Eriksson<sup>\*1</sup>, Torbjörn Reitberger<sup>\*2</sup>

Formation of hydroxyl radicals from direct ozone reactions with lignin and carbohydrate model compounds —A kinetic study

Martin Ragnar<sup>\*1</sup>, Tord Eriksson<sup>\*1</sup>, Torbjörn Reitberger<sup>\*2</sup>

<sup>\*1</sup>Department of Pulp and Paper Chemistry and Technology, Royal Institute of Technology,

<sup>\*2</sup>Department of Chemistry, Royal Institute of Technology, Sweden

Abstract: オゾンがリグニンモデル化合物と反応する際には、二重結合を酸化的に解裂する通常のイオニックな酸化反応のほかに、一電子的にフェノールを酸化してフェノキシラジカルを生成するラジカル的な反応が考えられる。その時に生じるオゾンの還元生成物は酸素とヒドロキシラジカルに分解するので、オゾン漂白中の多糖類分解の原因となることを明らかにした。このラジカル的な酸化反応の反応速度は、反応の相手方であるフェノールの酸化電位と直線的な相関を示す。反応 pH が高いと反応速度は急激に増大する。

1996-205

化学パルプの高収率化と無塩素漂白に関する研究、 亜硝酸処理におけるリグニンの反応  
大井 洋<sup>\*1</sup>、轟 英治<sup>\*1</sup>、具 延<sup>\*1</sup>、岸野正典<sup>\*1\*2</sup>

<sup>\*1</sup>筑波大学農林工学系、<sup>\*2</sup>北海道立林産試験場

Pretreatment for chemical pulping and non-chlorine bleaching reactions of lignin during nitrous acid treatment.

Hiroshi Ohi, Eiji Todoroki, Yan Ju, Masanori Kishino

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Nitrous acid treatment of kraft pulp has been proposed as a non-chlorine bleaching method. This treatment is also expected to be effective as a pretreatment for kraft pulping to increase the pulp yields. Behaviors of lignin degradation during the nitrous acid treatment were studied using beech wood meals and nonphenolic  $\beta$ -O-4 type lignin model compounds. The delignification during kraft pulping was accelerated by the pretreatment. By the nitrous acid treatment, veratrylglycerol- $\beta$ -syringyl ether (VS) and  $\alpha$ -ethyl ether of VS (VSE) were distinctly degraded through cleavage of their C $\alpha$ -C $\beta$  bonds giving veratraldehyde in a 51 and 47 mol% yields, respectively. Both erythro and threo of the lignin models were treated with nitric acid solution in the absence and presence of nitrite, and the degradation behaviors were discussed.

1996-206

白色腐朽菌によるポリエチレンの生分解(I)

飯吉由佳、堤 祐司、西田友昭

静岡大学農学部

Polyethylene biodegradation by white rot fungi.

Yuka Iiyoshi, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: Polyethylene (PE) biodegradation by white rot fungi, IZU-154, *Phanerochaete chrysosporium*, and *Trametes versicolor*, was investigated. PE was effectively biodegraded under the nutritional nitrogen- and/or carbon-limited culture condition, and IZU-154 showed the most significant PE biodegradation among three white rot fungi. The addition of manganese sulfate into nitrogen- and/or carbon-limited medium enhanced the PE biodegradability of white rot fungi. These results suggest that manganese peroxidase (MnP) plays a significant role in the PE biodegradation by white rot fungi, and *in vitro* PE biodegradation by isolated MnP supports this hypothesis.

1996-207

リグニン生分解に関する研究(VII) ～バイオブリーチングにおける針葉樹クラフトパルプ残留リグニンの構造変化～

片桐誠之、堤 祐司、西田友昭

静岡大学農学部

Studies on lignin biodegradation. VI. Changes in the residual lignin framework in softwood kraft pulp during biobleaching by *Phanerochaete chrysosporium* and manganese peroxidase.

Nobuyuki Katagiri, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: Softwood kraft pulp (SWKP) was treated with *Phanerochaete chrysosporium* or with its manganese peroxidase (MnP) under both conditions of which Mn(II) was added or not, and the residual lignin frameworks were compared among these treated pulps by the chemical analysis (nitrobenzene oxidation, acidolysis and permanganate oxidation). In the treatment of SWKP by *P. chrysosporium* without Mn(II) addition, the residual lignin was degraded and selective decrease of arylglycerol- $\beta$ -aryl ether unit was observed. On the other hand, the treatment of SWKP with partially purified MnP without Mn(II) addition revealed that MnP can not degrade the residual lignin because of lack of manganese in SWKP. These results suggested that enzyme(s) other than MnP may contribute to delignification of SWKP by *P. chrysosporium* under manganese-insufficient condition.

1996-208

白色腐朽菌のリグニン分解に関与する酵素系に関する研究 (X) ～*Phanerochaete sordida* YK-624 株の産生する NAD(P)H 依存性 Fe(III)還元酵素について～

平井浩文、近藤隆一郎、坂井克己

九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi. X. NAD(P)H-dependent ferrireductase produced by *Phanerochaete sordida* YK-624.

Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu university

Abstract: We have previously reported NAD(P)H-dependent reduction of manganese dioxide mediated by ferrous chelate in white-rot fungus *Phanerochaete sordida* YK-624. In the present study, we tried to isolate ferrireductase which would involve in the reduction of manganese dioxide by *P. sordida* YK-624. Ferrireductase activity was detected in cell-free extract, and most of the ferrireductase was precipitated by the addition of 30-65% ammonium sulfate saturation. The ferrireductase was purified to homogeneity by hydrophobic, gel filtration, and Mono Q chromatography. This enzyme was monomer protein, and pI and molecular weight were 5.1 and 35

kDa, respectively. Optimal pH for the reduction of ferric chelate by this enzyme was about 7.0. This reductase was dependent on NADPH although cellobiose could not act as electron donor. In the kinetic analysis, this enzyme showed higher substrate specificity for ferric chelate than Mn(III) and lignin model compounds.

1996-209

*Ganoderma* sp. YK505 株の産生するマンガンペルオキシターゼの諸特性とクラフトパルプ漂白性  
原園幸一、近藤隆一郎、坂井克己  
九州大学農学部

Bleaching of kraft pulp with manganese peroxidase secreted from *Ganoderma* sp. YK-505 and properties of the enzyme.

Koichi Harazono, Ryuichiro Rondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We performed *in vitro* bleaching of an unbleached hardwood kraft pulp (UKP) with manganese peroxidase (MnP) from the white rot fungus *Ganoderma* sp. YK-505 or *Phanerochaete sordida* YK-624. MnP from *Ganoderma* sp. YK-505 could brighten UKP at higher temperature and concentration of H<sub>2</sub>O<sub>2</sub> than with MnP from *P. sordida* YK-624. Two MnP isoenzymes were purified from shaken culture of *Ganoderma* sp. YK-505. The molecular masses of both isoenzymes were about 43 kDa. Maximum activities of both isoenzymes were exhibited at 55°C. Both isoenzymes had higher resistance to H<sub>2</sub>O<sub>2</sub> and different pH dependency from other MnPs, e.g. MnP from *Phanerochaete chrysosporium* and *P. sordida*, and maintained activities at high pH (6-8.5).

1996-210

アルカリ耐性担子菌 *Phellinus* sp. IS-847 株が産生するフェノールオキシダーゼについて  
国澤直子、近藤隆一郎、坂井克己  
九州大学農学部

Characterization of phenoloxidases from anti-alkaline basidiomycete *Phellinus* sp. IS-847.

Naoko Kunizawa, Ryuichiro Rondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: Anti-alkaline basidiomycete *Phellinus* sp. IS-847 isolated from nature grew in an alkaline wood mill + buffer medium (pH 8) very well, and secreted extracellular phenol oxidases, which contained two isoenzymes. The main isoenzyme (PhO I) was isolated and purified by using hydrophobic, gel filtration and anion exchange chromatography. This isoenzyme had molecular mass of about 60 kDa and isoelectric point of about 6.3. The optimal pH was 6.0 when guaiacol was used as a substrate. The substrate specificities and the effect of inhibitors were similar to the behavior of known laccases. The minor isoenzyme (PhO II) had molecular mass of about 63 kDa and pI 4.8, and showed high activity in an alkaline region than PhO I did.

1996-211

木材腐朽菌 IO-427 株による難分解性  $\beta$ -O-4 型リグニンモデル化合物のエーテル結合開裂について

瀧下 寛、平井浩文、近藤隆一郎、坂井克己

九州大学農学部

Cleavage of ether linkage in recalcitrant  $\beta$ -O-4 lignin model compound by wood-rot fungus IO-427.

Hiroshi Takishita, Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: The  $\beta$ -ether linkage is the most abundant in chemical structure of lignin, therefore, it

seems that the cleavage of this linkage is the most important process in the lignin biodegradation. From this viewpoint, we tried to isolate fungi which can release fluorescent 4-methylumbelliferone by the cleavage of the  $\beta$ -ether bond in Substrate I, which is recalcitrant  $\beta$ -O-4 type lignin model compound, 3-hydroxy-2-(4-methylumbelliferyl)-1-phenyl-1-propanone. By this screening method, we selected a wood-rotting fungus IO-427. In the present study, we tried to determine the metabolites from Substrate I in order to examine cleavage process of  $\beta$ -ether linkage. After 24 hour-incubation, Substrate I decreased by 23%, and 20% of 4-methylumbelliferone was produced. Two kinds of C6-C3 compounds were found, and they were identified as 2,3-dihydroxy-1-phenyl-1-propanone, and 3-hydroxy-1-phenyl-1-propanone. These compounds and 4-methylumbelliferone weren't detected in the culture of *Phanerochaete chrysosporium* although decrease of Substrate I was observed. It was expected that IO-427 might possess different function of the cleavage of  $\beta$ -O-4 linkage from other white-rot fungi.

1996-212

木材腐朽菌による LCC の分解について (VI) DSC 分析によるリグニン-糖マトリックスの変化の検出

辻山彰一

京都府立大学農学部

Degradation of lignin-carbohydrate complex by wood-rotting fungi. VI. Detection of changes of lignin-carbohydrate matrix by differential scanning calorimeter (DSC).

Sho-ichi Tsujiyama

Faculty of Agriculture, Kyoto Prefectural University

Abstract: Differential scanning calorimetric (DSC) analysis was applied to the akamatsu LCC (Lignin-Carbohydrate Complex) degraded by wood-rotting fungi, a brown-rot fungus *Tyromyces palustris* and a white-rot fungus *Coriolus versicolor*. Original LCC indicates two exothermal peaks at 440-470°C and one shoulder at 330°C. Comparing with the component materials prepared from akamatsu wood, the peak determined at 440-470°C is considered to be due to the lignin-carbohydrate matrix. DSC analysis of degraded LCC indicated that *T. palustris* degraded only the carbohydrate portion in lignin-carbohydrate matrix and that *C. versicolor* decomposed the lignin portion to form the fragments with less lignin amount.

1996-213

針葉樹の常圧プロピレングリコールパルプ化

佐野嘉拓、村田裕之、浦木康光

北海道大学農学部

Pulping of softwoods by propylene glycol system at atmospheric pressure.

Yoshihiro Sano, Hiroyuki Murata, Yasumitsu Uraki

Faculty of Agriculture, Hokkaido University

Abstract: Organosolv pulping of softwoods was investigated in polyhydric alcohols containing mineral acids at atmospheric pressure. The propylene glycol (PG) pulping with sulfuric acid gave satisfactory pulps with little rejects and the very low content of residual lignin, which were readily bleached. Mechanical properties of the pulps were comparable to those of KP. The bleached pulp has considerably high glucose and  $\alpha$ -cellulose contents, and high crystallinity that was further increased by simple chemical treatment. Therefore, the pulps are suggested to be utilized as not only paper but also dissolved pulp and highly crystalline cellulose. The pulping solvent is supplied from hydrolyzed hemicellulose, and the waste liquor including hemicellulose after removal of PG lignin can be re-used as the solvent. This suggests to reduce the cost of the pulping. Consequently,

the PG pulping is considered an alternative process to conventional chemical pulping.

1996-211

ササ稈の触媒添加蒸煮処理

津田真由美<sup>\*1</sup>、関 一人<sup>\*1</sup>、青山政和<sup>\*1</sup>、Nam-Seok CHO<sup>\*2</sup>

<sup>\*1</sup> 北海道立林産試験場、<sup>\*2</sup> 韓国忠北大学

Acid-catalyzed steaming treatment of bamboo grass, *Sasa senanensis* Rehd.

Mayumi Tsuda<sup>\*1</sup>, Kazuto Seki<sup>\*1</sup>, Masakazu Aoyama<sup>\*1</sup>, Nam-Seok Cho<sup>\*2</sup>

<sup>\*1</sup>Hokkaido Forest Products Reserch Institute, <sup>\*2</sup>Chungbuk National University, Republic of Korea

Abstract: The effect of acid catalysts in the steaming treatment on solubilization of bamboo grass xylan was investigated. Among catalysts used, FeCl<sub>3</sub> and CaCl<sub>2</sub> were efficient in solubilization of xylo-oligosaccharides at a level of 10 mmole/kg substrate and below. When the substrate was steamed in the presence of these catalysts at 191°C for 10 min, xylo-oligosaccharides were obtained in a yield of 8-9% based on the raw material. The enzymatic digestibility of residual fiber was also determined. The catalysts were found to be effective on enhancement of the susceptibility to cellulase. Water extract of steamed bamboo grass showed inhibitory activity to the angiotensin I-converting enzyme (ACE). The IC<sub>50</sub> value was 0.06 mg/ml.

1996-215

水蒸気圧縮処理による樹液抽出法の開発

鈴木悦子<sup>\*1\*2</sup>、棚橋光彦<sup>\*1</sup>、重松幹二<sup>\*1</sup>

<sup>\*1</sup> 岐阜大学農学部、<sup>\*2</sup> ウッディテックコーポレーション

Development of sap extraction method associated with the compressive molding process.

Etsuko Suzuki<sup>\*1\*2</sup>, Mitsuhiro Tanahashi<sup>\*1</sup>, Mikiji Shigematsu<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Gifu University, <sup>\*2</sup>Woody Tech Corporation, Japan

Abstract: For the utilization method of forest resources, there is a gathering of sap for the particular purpose excepting the use of wood itself for building materials, pulp and paper. The purpose of this study was a development of sap extraction method associated with the compressive molding process of *Cryptomeria japonica* D.Don. and *Camaecypariss obutusa* Endl. for effective utilization of wood. In analysis of wood sap squeezed from *Cryptomeria japonica* during compressive molding process of raw wood with steam treatment, four compounds were isolated from the chloroform extraction and identified by <sup>1</sup>H-NMR and MS. These compounds were coniferyl alcohol, D,L-pinoresinol, lariciresinol and dihydrodehydrodiconiferyl alcohol. On the other hand, judging from the fact that two compounds, D,L-pinoresinol and dihydrodehydrodiconiferyl alcohol, were isolated from the hydrolyzed water layer, high amount of lignan-glycosides was contained in original sap. From the *Camaecyparis obutusa* wood sap, hinokinin was isolated from the chloroform extraction and identified by NMR and MS.

1996-216

リグニンを原料とするポリウレタンの熱的及び粘弾性的特性

広瀬重雄<sup>\*1</sup>、伊豆田良信<sup>\*2</sup>、畠山兵衛<sup>\*2</sup>

<sup>\*1</sup> 物質研究所、<sup>\*2</sup> 福井工業大学工学部

Thermal and viscoelastic properties of polyurethanes from lignin.

Shigeo Hirose<sup>\*1</sup>, Yoshinobu Izuta<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>National Institute of Materials and Chemical Research, <sup>\*2</sup>Fukui Institute of Technology

Abstract: Polyurethane (PU) sheets were prepared from alcohol-solvolysis lignin (AL) and kraft lignin (KL) by the following procedures. Lignin and polyethylene glycol having a molecular weight of

400 (PEG 400) were dissolved in tetrahydrofuran (THF). Diphenylmethane diisocyanate (MDI) was added to the above solution and the reaction was continued at room temperature until a prepolymer solution was obtained. The prepolymer solution was cast on a glass plate which was placed in a desiccator. After the removal of THF, the obtained prepolymer sheet was cured at 120 °C for 24 hr. The thermal and viscoelastic properties of PU's were studied by thermogravimetry (TG), differential scanning calorimetry (DSC), and dynamic thermomechanometry (DMA). Thermal degradation temperatures ( $T_d$ 's) slightly decreased with increasing lignin contents in PU's. Glass transition temperatures increased with increasing lignin contents in PU's. A large peak was observed in a  $\tan\delta$  curve at the temperature region where  $E'$  showed a sudden decrease. It is considered that this peak can be attributed to the main chain motion of PU's.

1996-P01

熱分解ガスクロマトグラフィーによる南洋材リグニンの分析

大井 洋、安田有紀野、和泉明子、黒田健一

筑波大学農林工学系

Analysis of lignin in tropical hardwoods by pyrolysis-gas chromatography.

Hiroshi Ohi, Yukino Yasuta, Akiko Izumi, Ken-ichi Kuroda

Institute of Agricultural and Forest Engineering, the University of Tsukuba

Abstract: Ratios of syringyl units to guaiacyl units (S/G ratios) of lignin in tropical hardwoods were estimated by pyrolysis-gas chromatography (Py-GC). The wood meals were extracted with benzene and successively with 70% acetone/ water to remove tannins and other phenols. The observed S/G ratios were in good agreement with syringaldehyde/vanillin (S/V) ratios obtained by nitrobenzene oxidation. Furthermore, the extracted kapur wood meals were treated with hot 1 % NaOH solution to extract lignin-like substances in a tropical wood. Both syringyl and guaiacyl pyrolysis products were obtained from a chloroform soluble part of the 1 % NaOH extractives. In order to simplify a method for determination of acid-insoluble (Klason) lignin in tropical hardwoods, wood samples were hydrolyzed at 121°C, and the acid-insoluble residue was characterized by Py-GC.

1996-P02

シリングル基又はグアイアシル基を持った化合物の酸化によって生成するフリーラジカル

鬼木隆幸、高浜有明夫

九州歯科大学一般教育部

Free radicals produced by oxidations of compounds containing syringyl or guaiacyl groups.

Takayuki Oniki, Umeo Takahama

Kyushu Dental College

Abstract: Electron spin resonance spectra of free radicals produced by oxidations of compounds containing syringyl or guaiacyl group were measured at pH 13.0. Syringaldehyde or 2,6-dimethoxy-*p*-hydroquinone showed an ESR signal of 2,6-dimethoxy-*p*-benzo-semiquinone radical by the oxidation with H<sub>2</sub>O<sub>2</sub>. This radical was also produced by the oxidation of dioxane lignins with hexacyanoferrate (III) or H<sub>2</sub>O<sub>2</sub>. Vanillin or methoxy-*p*-hydroquinone showed an ESR signal due to methoxy-*p*-benzosemiquinone radical by the oxidation with H<sub>2</sub>O<sub>2</sub>. A radical produced by the oxidation of methoxy-*p*-hydroquinone with O<sub>2</sub> or hexacyanoferrate (III) was also observed when dioxane lignin was oxidized with O<sub>2</sub> or hexacyanoferrate (III). Two kinds of radicals which were observed in the oxidation of dioxane lignins were identified to be due to syringyl and guaiacyl groups in the lignins.

1996-P03

フェノキシラジカルと酸素との反応性

杉元倫子、森下智之、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Reactivity of phenoxyl radical with molecular oxygen.

Tomoko Sugimoto, Tomoyuki Morishita, Yuji Matsumoto and Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: The possibility of the reaction between phenoxyl radical and molecular oxygen was examined. Vanillyl alcohol (VA) or syringyl alcohol (SA) was treated with a one electron oxidizing reagent, manganese (III), and the effect of oxygen pressure on the yield of methanol from these phenols was determined. Methanol can be released when the radical produced at the carbon to which a methoxyl group is attached combines either with phenoxyl radical or with molecular oxygen. Although methanol was produced from a reaction under nitrogen pressure (oxygen 0 MPa), the increased yield of methanol under increased oxygen pressure was thought to indicate the reaction between phenoxyl radical and molecular oxygen.

1996-P04

酸素-アルカリ漂白過程における多糖類の分解機構(7)-リグニンの酸素酸化反応の速度論的特徴-

松本雄二、横山朝哉、飯塚堯介

東京大学大学院農学生命科学研究科

Degradation mechanism of carbohydrate during oxygen-alkali bleaching. (7). Kinetic behavior of lignin during oxygen oxidation in aqueous alkali solution.

Yuji Matsumoto, Tomoya Yokoyama, Gyosuke Meshitsuka

Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Isolated kraft lignin was treated with oxygen-alkali and the extent of oxygen oxidation was evaluated on the basis of the consumption of permanganate by the kraft lignin before and after the oxygen oxidation. One unit of kraft lignin (200 g) was found to be oxidized by 8.5 mole electron during oxygen-alkali treatment. Kinetic analysis showed that the process of oxygen oxidation can mainly be divided into two first order reactions. An acceleration of oxidation during the reaction, which was observed when model phenols were treated by oxygen-alkali, was not observed.

1996-P05

*Thuja* 属のリグナン生合成について

杉下千洋、河合真吾、大橋英雄

岐阜大学農学部

Lignan biosynthesis of *Thuja* species.

Kazuhiro Sugishita, Shingo Kawai, Hideo Ohashi

Faculty of Agriculture, Gifu University

Abstract: In addition to the previously found 2-(3,5-dimethoxy-4-hydroxybenzyl)-3-(3,4-methylenedioxy-benzyl)-butyrolactone (4-O-demethylatein), three lignans, secoisolariciresinol, matairesinol and dihydrodehydrodiconiferyl alcohol as minor components were confirmed in young shoots and leaves of *Thuja occidentalis*. Next, to investigate biosynthesis of lignans in *Thuja* species. [9,9-<sup>2</sup>H<sub>2</sub>,O<sup>2</sup>H<sub>3</sub>]coniferyl alcohol was fed to excised young shoots of *T. occidentalis* and *T. plicata*. Following metabolism for 24 hr, deuterated pinoresinol, lariciresinol and dihydrodehydrodiconiferyl alcohol were formed in *T. occidentalis* young shoots. Cell-free extracts from *T. occidentalis* leaves

catalyzed the formation of deuterated pinoresinol, when incubated with [9,9-<sup>2</sup>H<sub>2</sub>,O<sup>2</sup>H<sub>3</sub>]coniferyl alcohol in the presence of NADPH and H<sub>2</sub>O<sub>2</sub>.

1996-P06

植物培養細胞によるフェノール類のグルコシル化の試み

村中俊夫、伊藤和貴、沖 妙、橘 燦郎

愛媛大学農学部

Trial for glucosylation of phenols by plant cell cultures.

Toshio Muranaka, Kazutaka Itoh, Tae Oki, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Production of phenolic glucosides from three phenols, salicyl alcohol, coniferyl alcohol and coniferyl aldehyde by cell suspension cultures of *Coffea arabica* was tried. From the results of HPLC analysis of each reaction product, we found that salicin, phenolic glucoside of salicyl alcohol was produced in the maximum yield of 17.5% by the cultures of *C. arabica*. However, the glucosides from the two other phenols could not be produced by the cultures of *C. arabica*.

1996-P07

カワラタケラッカーゼ遺伝子の解析

三国順子<sup>\*1</sup>、中村雅哉<sup>\*2</sup>、西田篤実<sup>\*2</sup>、川合伸也<sup>\*1</sup>、片山義博<sup>\*3</sup>、諸星紀幸<sup>\*3</sup>

<sup>\*1</sup> 東京農工大学農学部、<sup>\*2</sup> 森林総合研究所、<sup>\*3</sup> 東京農工大学大学院 BASE

Analysis of laccase genes from *Coriolus versicolor*.

Junko Mikuni<sup>\*1</sup>, Masaya Nakamura<sup>\*2</sup>, Atsumi Nishida<sup>\*2</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*3</sup>, Noriyuki Morohoshi<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*3</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology.

Abstract: Eight chromosomal DNA bands of *Coriolus versicolor* have been resolved by pulsed-field gel electrophoretic analysis. The estimated sizes of the chromosomal DNAs ranged from 5.6 to 2.5 megabase pairs. Previously, we cloned and sequenced Laccase III gene (*CVL3*) and other laccase gene (*CVLG1*) of *C. versicolor*. The membrane, which was transferred the separated chromosomal DNAs of *C. versicolor*, was hybridized with gene specific probes of *CVL3* and *CVLG1*. It is cleared that *CVL3* and *CVLG1* were different chromosomal DNAs.

1996-P08

担子菌 *Coriolus versicolor*(カワラタケ) のフェノールオキシダーゼ遺伝子のクローニング

飯村洋介、辰巳憲司

資源環境技術総合研究所

Cloning and sequencing of a phenoloxidase gene from the basidiomycete *Coriolus versicolor*.

Yosuke Iimura, Kenji Tatsumi

National Institute for Resources and Environment

Abstract: The gene (*cvmnp*) encoding a manganese peroxidase from *Coriolus versicolor* IFO 30340, a lignin-degrading basidiomycete, was cloned and sequenced, and the corresponding *cvmnp* cDNA was also cloned and sequenced. The isolated gene consist of 1,397 bp, with the coding sequence being interrupted by 5 introns and flanked by an upstream region in which putative TATA and inverted CCAAT consensus sequences could be identified at positions -81 and -162, respectively. A potential metal response element (MRE), xenobiotic response element (XRE), and nitrogen regulatory consensus sequence (NIT) are recognized in the upstream region of the gene.

The mature translation product, preceded by a 26-residue signal peptide, should consist of 339 residues.

1996-P09

白色腐朽菌 *Pleurotus ostreatus* のフルトランニル耐性変異株におけるコハク酸デヒドロゲナーゼ Ip サブユニット遺伝子の解析

松山拓郎、入江俊一、本田与一、渡辺隆司、桑原正章

京都大学木質科学研究所

Analysis of the genes encoding succinate dehydrogenase Ip subunit from flutolanil-resistant mutant *Pleurotus ostreatus* strains.

Takuro Matsuyama, Toshikazu Irie, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: For development of an useful vector system in basidiomycetes, it is desired to develop a dominant genetic marker which requires no genetic background of the host strains. We have obtained several mutant *P. ostreatus* strains resistant to a carboxin-derived fungicide, flutolanil, from UV irradiated basidiospores of wild-type strains. We examined to clone a gene encoding succinate dehydrogenase iron-sulfur (Sdh Ip) subunit, *Sdi*, which is thought to be concerned with the flutolanil resistance, using PCR technologies. And we tried to determine the nucleotide sequence of the gene from wild-type and mutant strains. As a result, total sequence of wild-type *Sdi* has been determined, and those of mutant strains are currently being analyzed.

1996-P10

天然からのダイオキシン分解能を有する分解菌のスクリーニング

大川浩樹、平林達也、伊藤和貴、沖 妙、橘 燦郎

愛媛大学農学部

Screening of fungi having ability for degradation of dioxins.

Hiroki Ohkawa, Tatuya Hirabayasi, Kazutaka Itho, Tae Oki, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: The time-course of the activities of lignin peroxidase, manganase peroxidase and laccase from the six fungi having ability for degradation of 2,7-Dichlorodibenzo-*p*-dioxin (2,7-DCDD) isolated by the screening method was measured in connection with the degradation rate of 2,7-DCDD. Correlation between the activity of lignin peroxidase and the degradation rate of 2,7-DCDD was observed. However, the activities of manganese peroxidase and laccase were not correlated to the degradation rate of 2,7-DCDD. From the results obtained above, we tried to modify the screening method found previously.

1996-P11

白色腐朽菌 WD544 菌株による色素の分解について

高野麻理子、西田篤実、中村雅哉

森林総合研究所

Degradation of dyes by white-rot fungus WD544 strain.

Mariko Takano, Atsumi Nishida, Masaya Nakamura

Forestry and Forest Products Research Institute

Abstract: Four dyes decolorization plates tests using RBBR, PolyR, Poly S and Azure B were conducted with 26 wood-rotting fungi. WD544 was the only strain that decolorized all of 4 dyes on the test plates containing High-C, Low-N medium. WD544 decolorized RBBR and Poly R not only on the H-C, L-N plates while Poly S and Azure B were decolorized only under H-C, L-N condition.

RBBR was also decolorized in both shaken and stationary liquid cultures, but the other 3 dyes were decolorized only under static conditions. Laccase activity was assayed during stationary cultivation but lignin peroxidase activity was rarely observed in these cultures. Time course change in visible spectrum of each of 4 dyes suggested that RBBR was degraded in the liquid culture and the other 3 dyes were removed predominantly by fungal adsorption and further degraded on or in the mycelium.

1996-P12

ケナフ化学成分の総合利用 – 靱皮部と本部のパルプ化 –

教日格勒、佐野嘉拓、浦木康光

北海道大学農学部

Utilization of kenaf component. –Pulping of bast and wood–.

Aorigele, Yoshihiro Sano, Yasumitsu Uraki

Faculty of Agriculture, Hokkaido University

Abstract: Oxygen pulping of kenaf bast was carried out with 150% NaOH of o.d. bast at 110°C and 7 kg/cm<sup>2</sup> of O<sub>2</sub> for 90 min. After boiling with 70% AcOH, bast pulps with much great delignification and satisfactory physical properties were obtained in yields of 48%. The pulp was easily bleached at 85% brightness by ECF bleaching. For the total utilization of kenaf stalk kenaf wood (core) and stalk (core and bast) were pulped by solvent systems using aqueous AcOH with mineral acids at refluxing temperature and aqueous EtOH with AcOH at 170.

1996-P13

リグニン生分解に関する研究 (VIII) –マンガンペルオキシダーゼによる針葉樹クラフトパルプの濃色化–

江原克信、堤 祐司、西田友昭

静岡大学農学部

Studio a on lignin biodegradation (VIII). The darkening of softwood kraft pulp with manganese peroxidase.

Katunobu Ehara, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: The brightening performance of softwood kraft pulp (SWKP) during manganese peroxidase (MnP) treatment and the yields of alkaline nitrobenzene oxidation products from the treated pulp were compared to clarify the mechanism of darkening of SWKP by MnP treatment. The yields of oxidation products markedly decreased with the brightness started to decrease, and the yields kept same level after when the pulp brightness increase thereafter. On the other hand, the yields from untreated hardwood kraft pulp (HWKP) were much less than that from SWKP and kept the same level during the brightness increase by MnP treatment. These results suggest that non-condensed type lignin may be oxidatively condensed and lead to the darkening of SWKP during MnP treatment.

1996-P14

$\beta$ -O-4 型 LCC モデル化合物のリグニンペルオキシダーゼによる分解

宮田 聡、梅澤俊明、服部武文、島田幹夫

京都大学木質科学研究所

The degradation of  $\beta$ -O-4 type lignin carbohydrate complex model compounds by lignin peroxidase.

Satoshi Miyata, Toshiaki Umezawa, Takefumi Hattori, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Nonphenolic  $\beta$ -O-4 type lignin carbohydrate complex model compounds (LCCs) as

well as the corresponding  $\beta$ -O-4 dimers were degraded by lignin peroxidase (LiP), and time course of oxidation of the substrates and product formation was monitored. No significant differences in the LiP catalyzed oxidation were observed between the LCC model compounds and the  $\beta$ -O-4 dimers. The result indicated that the sugar moiety of the LCC model compounds did not prevent, at least qualitatively, oxidation of the LCC model compounds by LiP.

1996-P15

白色腐朽菌のリグニン分解に関与する酵素系に関する研究(XI)～クラフトパルプのバイオブリーチングにおけるパルプ中のマンガニオンの状態変化～

平井浩文<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>、坂井克己<sup>\*1</sup>、鬼木隆幸<sup>\*2</sup>

<sup>\*1</sup>九州大学農学部、<sup>\*2</sup>九州歯科大学一般教育部

Studies on ligninolytic enzymes of white-rot fungi (XI). Change of oxidation number of manganese in kraft pulp during biological bleaching.

Hirofumi Hirai<sup>\*1</sup>, Ryuichiro Kondo<sup>\*1</sup>, Kokki Sakai<sup>\*1</sup>, Takayuki Oniki<sup>\*2</sup>

<sup>\*1</sup>Department of Forest Products, Faculty of Agriculture, Kyushu university, <sup>\*2</sup>Kyushu Dental College

Abstract: The oxidation number of manganese in unbleached hardwood kraft pulp (UKP) was determined by the electron spin resonance (ESR) method. The spectrum of Mn(II), which revealed hyperfine splitting, was not observed, and the spectrum of dioxide could be observed. After fungal-treatment of UKP with *Phanerochaete sordida* YK-624, the spectrum of Mn(II) could be detected in the UKP. It is concluded that manganese dioxide is dominant in UKP, and that *P. sordida* YK-624 reduced manganese dioxide to Mn(II) which may stimulate production and function of manganese peroxidase.

1996-P16

イネワラのセルラーゼ及びアンモニアを用いたパルプ化とパルプの性状

朴 承栄<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup>東京大学大学院農学生命科学研究科、<sup>\*2</sup>東京大学アジア生物資源環境研究センター

Preparation and characterization of rice straw pulps by cellulase or ammonia treatments.

Park Seung Young<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>, Gyosuke Meshitsuka<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agriculture and Life Science, the University of Tokyo, <sup>\*2</sup>Asian Natural Environmental Science Center, the University of Tokyo

Abstract: It is expected to develop the effective utilizations of agricultural wastes, such as rice straws, with environmentally sustainable processes. In this paper, pulping of rice straw by treatments with polysaccharide hydrolases or alkaligenic chemicals, but not by conventional alkaline treatments, were examined. The pulps were characterized by chemical analyses of the components, and their behaviors during laboratory scale defibration of treated rice straws were observed by SEM-EDXA. There were no significant improvements for defibration of rice straws by any enzyme treatments, but ammonia treatment which improved defibration and caused considerable delignification probably due to the cleavage of ester-linkage between lignin and polysaccharides through ferulic acids, together with effective removal of silica from pulps. In addition we confirmed that all of *p*-hydroxybenzaldehydes in an alkaline nitrobenzene oxidation products of rice straw are produced from *p*-coumaric acids esterified or etherified to wall polymers, and lignin in rice straws is not characterized by the presence of *p*-hydroxyphenyl nuclei.

1996-P17

リグニン系土壌改良剤の開発(5)各種リグニンの添加と根の伸長生長

斉藤京子<sup>\*1</sup>、中西友子<sup>\*2</sup>、松林政仁<sup>\*3</sup>、飯塚堯介<sup>\*1</sup>

\*1 東京大学大学院農学生命科学研究科、\*2 日本原子力研究所

Development of new lignin derivatives as soil conditioning agent. (5). Growth of plants root under various soil condition containing lignin samples.

Kyoko Saito<sup>\*1</sup>, Tomoko Nakmishi<sup>\*2</sup>, Masahito Matsubayashi<sup>\*3</sup>, Gyosuke Meshitsuka<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo

<sup>\*2</sup>Faculty of Agriculture, the University of Tokyo, <sup>\*3</sup>Japan Atomic Energy Research Institute

Abstract: It is well known that aluminium ion gives seriously damages to plant growth in acid soil. We have developed a new lignin derivative (radically sulfonated: S-1) from kraft lignin, which strongly associates with soil and also traps Al ion. So, there is a possibility of utilization of kraft lignin as a soil conditioning agent. In this paper, the length of roots of radish (*Raphanus Sativus*.) were determined during the growth on various soils containing lignin samples, and these effects on the growth of root were examined. As a results, all lignin samples apparently removed the inhibitory effects of aluminium ion. And, S-1 may be more effective than LSA.

## 第 42 回 (1997.10.27-28) 北海道大学学術交流会館

1997-101

イネ培養細胞におけるヒドロキシケイ皮酸類の形成機構

福島和彦、山下耕司、加藤由佳、安田征市

名古屋大学農学部

Formation of hydroxycinnamic acids in the suspension culture of *Oriza sativa*.

Kazuhiko Fukushima, Koji Yamashita, Yuka Kato, Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: Formation of hydroxycinnamic acids in the suspension culture of *Oriza sativa* was investigated. This culture was the cluster of a number of cells which did not have the secondary cell wall. It was shown ferulic acid was deposited in the cell wall at the early stage prior to the deposition of *p*-coumaric acid. Feeding experiment showed that labeled ferulic acid was incorporated into cell wall as esterified ferulic acid selectively, while labeled *p*-coumaric acid was incorporated after the major conversion to ferulic acid. It was also suggested that considerable amount of ferulic acid fed to the culture was covalently linked at the 5 position of its aromatic ring during long term incubation.

1997-102

イネ節間柔組織形成異常 mutant を用いた細胞壁形成過程の解析

西窪伸之<sup>\*1</sup>、荒木智之<sup>\*1</sup>、藤川 裕<sup>\*1</sup>、平田 豊<sup>\*2</sup>、北野英己<sup>\*3</sup>、黒田健一<sup>\*4</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院BASE、<sup>\*2</sup>東京農工大学農学部、<sup>\*3</sup>名古屋大学農学部、<sup>\*4</sup>筑波大学農林工学系

Chemical and molecular biological analysis of cell wall formation in dwarf mutant of rice plant (Fukey-71).

Nobuyuki Nishikubo<sup>\*1</sup>, Tomoyuki Araki<sup>\*1</sup>, Yutaka Fujikawa<sup>\*1</sup>, Yutaka Hirata<sup>\*2</sup>, Hidemi Kitano<sup>\*3</sup>, Kenichi Kuroda<sup>\*4</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate school of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Tokyo University of Agriculture and Technology, <sup>\*3</sup>Faculty of Agriculture, Nagoya University, <sup>\*4</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Recessive mutations at single locus cause the collapse of parenchyma cells in internode of Rice plant "Fukey-71". This irregular parenchyma mutation was identified by gamma-ray irradiation of seed of "Fujiminori". The mutated Rice plant "Fukey-71" show dwarf form and

accumulates lignin-like material from *p*-coumaric acid and ferulic acid in parenchyma cell. The lignin-like material may be esterified cross-link between phenylpropanoids and polysaccharide. Furthermore existence of pathway related to ester cross-link separate from is suggested by strong expression of PAL and OMT of lignin biosynthesis pathway in parenchyma cell. This mutant is regarded as mutation participating in the factor that controls the cell wall formation with single regulation factor recessive at higher position than regulation of lignin and polysaccharide biosynthesis. The mutation should be useful in facilitating the identification of factors that control the synthesis and deposition of lignin and other cell wall components.

1997-103

イネ科植物リグニンにエーテル結合したヒドロキシ桂皮酸の結合位置

角谷和芽<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学アジア生物資源環境研究センター

Hydroxycinnamic acid bridges between wall polysaccharides and lignin in Gramineous plants.

Kazume Kadoya<sup>\*1</sup>, Gyousuke Meshitsuka<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, The University of Tokyo, <sup>\*2</sup>Environmental Science Center, the University of Tokyo,

Abstract: The hydroxycinnamic acids, *p*-coumaric (PCA) and ferulic acid (FA), are esterified and/or etherified to cell wall polymers in Gramineous plants, but of which position etherified to lignin side chain are not clear and argued for the  $\alpha$ - or  $\beta$ -positions. In this study, lignin-polysaccharide complexes (bridges between lignin and wall polysaccharide through FA) extracted from walls of oat (*Avena sativa* L.) internodes were examined by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation followed by alkaline hydrolysis. The quantities of hydroxycinnamic acids liberated by alkaline hydrolysis were compared between before and after DDQ oxidation. Relatively high quantities of liberated FA and PCA after DDQ oxidation than those before DDQ oxidation suggests that they could etherify lignin at  $\alpha$ -position of lignin side chain.

1997-104

*Eucalyptus camaldulensis* および *E. globulus* の樹幹内変異を用いたリグニン含有率、リグニンのモノマー組成比とヘミセルロース組成比の関係について

小名俊博、園田哲也、伊藤一弥、柴田 勝

王子製紙株式会社森林資源研究所

Relationship of lignin content, and lignin monomeric composition and hemicellulose composition in the same trunk sought by their within-tree variations in *Eucalyptus camaldulensis* and *E. globules*.

Toshihiro Ona, Tetsuya Sonoda, Kazuya Ito, Masaru Shibata

Kameyama Research Center, Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: The relationship of extractives-free (EF) lignin content, lignin monomeric composition as syringyl/guaiacyl (S/G) ratio by thioacidolysis, and neutral sugars constituting hemicellulose by hydrolysis with trifluoroacetic acid was examined. This was performed in the same trunk by their within-tree variations, which mean the investigation with the same genes, in *Eucalyptus camaldulensis* and *E. globulus*. As results, each species had a high negative correlation between EF-lignin content and lignin S/G ratio although the difference between species and/or individuals was observed in the trend of within-tree variations of the wood properties. The relationship between EF-lignin content and lignin S/G ratio is considered to be caused from the difference in the fiber morphology from the relationship between lignin and EF-basic density which may relate to the fiber morphology. Furthermore, the relationship between the lignin monomeric composition derived from  $\beta$ -O-4 bonds and the hemicellulose composition is concluded to exist since common trend was

observed between two species as higher lignin S/G ratio with the increase in xylan and or with decrease in arabinogalactan (galactan). We also discuss and suggest that the hemicellulose composition can influence on the lignin monomeric composition.

1997-105

*Eucalyptus globulus* Lignin の化学的性状 –改良ニトロベンゼン酸化–

片平 類、中坪文明

京都大学大学院農学研究科

The chemical characterization of *Eucalyptus globulus* lignin. –Analysis by a modified nitrobenzene oxidation.

Rui Katahira, Fumiaki Nakatubo

Graduate school of Agriculture, Kyoto University

Abstract: Recently, *Eucalyptus globulus* has been regarded as one of the most suitable trees for pulping, because it can grow largely in short time and gives a high yield of pulping. It is really important to find the reason for its high yield. Thus, we intended to investigate the chemical structure of *E.globulus* lignin. Here we propose a modified nitrobenzene oxidation method, which was applied to *E. globulus* lignin.

1997-106

超音波照射したリグニン溶液の ESR 法による研究 –スピントラッピング法の適用–

清野晃之、吉岡亜希、藤原政司、陳 克利、恵良田知樹、田畑昌祥、高井光男

北海道大学大学院工学研究科

An electron spin resonance study of radicals produced by ultrasonic irradiation of lignin solution. An application of spin-trapping method.

Teruyuki Seino, Aki Yoshioka, Masashi Fujiwara, Ke-Li Chen, Tomoki Erata, Masayoshi Tabata, Mituo Takai

Graduate School of Engineering, Hokkaido University

Abstract: A spin trapping technique combined with an electron spin resonance (ESR) method was successfully applied to the lignin solution which was subjected to ultrasonic irradiation in order to trap and identify the origin radical of the phenoxy radicals stabilized in the wood lignin. It was found, consequently, that nitroxide radicals called spin adducts produced by the reaction of secondary carbon radicals and 2,4,6-tri-*tert*-butylnitrosobenzenes as the spin trapping reagent were generated from the lignin dissolved in dimethylsulphoxide (DMSO) when the lignin solution was subjected to ultrasonic irradiation at 50 °C. The resulting secondary carbon radical was supposed to be created by the  $\beta$  bond scission in the HC <sup>$\beta$</sup> -O-4 phenol group called  $\beta$ -O-4 bond which combines the three dimensional network structure of the wood lignin. Further the secondary carbon radical was also considered as a counter radical of the phenoxy radical stabilized in the not only solution but also lignin solid.

1997-107

リグニン化学構造の不均一性(2)–エーテル結合の選択的開裂を用いたリグニンの性状の検討–

堀啓映子、飯塚堯介

東京大学大学院農学生命科学研究科

Structural heterogeneity of hardwood lignin (2) – Characterization of lignin by selective cleavage of ether linkages.

Keko Hori, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Trimethylsilyl iodide (TMSiI) was known to cleave  $\alpha$ - and  $\beta$ - ether bonds selectively under mild condition. We used TMSiI to degrade high molecular weight lignin, and analyzed the newly formed low molecular weight fractions. It was found that there are some endwise lignin fractions in methylated-periodate lignin of birch, however it was not the case for birch MWL. Every low molecular weight fraction from MWL by TMSiI treatment showed quite similar characteristics. An end-wise lignin fraction from periodate lignin was confirmed to be depolymerized mainly to monomeric units by excess amount of TMSiI.

1997-108

CAD 阻害によって形質転換させた樹木中に生成する異常リグニンの化学的構造について 一種々の化学分解反応に対するシンナミルアルデヒド構造の挙動—

伊藤 隆<sup>\*1</sup>、河合真吾<sup>\*1</sup>、大橋英雄<sup>\*1</sup>、樋口隆昌<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学大学院連合農学研究科、<sup>\*2</sup> 京都大学名誉教授

Chemical study on abnormal lignin of transgenic plants with antisense cinnamyl alcohol dehydrogenase gene. – The behavior of cinnamyl aldehyde groups for various chemical degradation reactions.

Takashi Ito<sup>\*1</sup>, Shingo Kawai<sup>\*1</sup>, Hideo Ohashi<sup>\*1</sup>, Takayoshi Higuchi<sup>\*2</sup>

<sup>\*1</sup>The United Graduate School of Agriculture Science, Gifu University, <sup>\*2</sup>Professor emeritus Kyoto University

Abstract: Novel thioacidolysis products derived from sinapaldehyde and coniferyl aldehyde were isolated and identified by GC-MS and <sup>1</sup>H-NMR analyses, It is clear that the cinnamyl aldehydes were converted to many degradation products by thioacidolysis. On the other hand, sinapaldehyde and coniferyl aldehyde were not altered by acidolysis. The acidolysis treatment of coniferyl aldehyde DHP gave vanillin, coniferyl aldehyde and an unknown product as degradation products. Coniferyl aldehyde and sinapaldehyde were effectively altered by mild alkali treatment to give vanillin and syringaldehyde, respectively.

1997-109

樹木細胞壁リグニン生合成及び糖代謝過程の免疫組織化学的研究

吉富圭織<sup>\*1</sup>、増野洋子<sup>\*1</sup>、西窪伸之<sup>\*1</sup>、真壁和彦<sup>\*1</sup>、川合伸也<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 東京農工大学農学部

Immunohistochemistry of lignin biosynthesis and carbohydrate metabolism in woody plant.

Kaori Yoshitomi<sup>\*1</sup>, Yoko Mashino<sup>\*1</sup>, Nobuyuki Nishikubo<sup>\*1</sup>, Kazuhiko Makabe<sup>\*1</sup>, Shinya Kawai<sup>\*2</sup>, Noriyuki Morohosi<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Tokyo University of Agriculture and Technology

Abstract: Lignin is a major component of plant cell wall. We have investigated enzymes involved in the phenylpropanoid biosynthesis by biochemical and immunochemical methods. We prepared antiserums raise against PAL, OMT, 4CL, CAD, POX, and investigate immunochemical localization of these enzymes. As a result, we suggested the tissue-specific expression and relevance of each enzyme in protoxylem. We will report localization of each enzyme in metaxylem tissue and propose functions of them. Carbohydrate chain biosynthesis closely related to lignin biosynthesis in cell wall fomlation in plant. Therefor, we prepared antiserums raise against enzymes involved in the carbohydrate chain biosynthesis and investigate immunochemical relationship between lignin and carbohydrate chain biosynthesis.

1997-110

土壤微生物 *Sphingomonas paucimobilis* SYK-6 株のリグニン分解に關与するテトラヒドロ葉酸依存性脱メチル化酵素遺伝子 (*lig H*) の構造と機能に關する研究

園木和典<sup>\*1</sup>、笠原健秀<sup>\*2\*3</sup>、西川誠司<sup>\*4</sup>、川合伸也<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>東京農工大学農学部、<sup>\*3</sup>日本製紙株式会社、<sup>\*4</sup>コスモ総合研究所  
Structure and function of tetrahydroforic acid dependent *Sphingomonas paucimobilis* SYK-6 gene essential to degradation of lignin.

Tomonori Sonoki<sup>\*1</sup>, Takehide Kasahara<sup>\*2\*3</sup>, Seiji Nishikawa<sup>\*4</sup>, Shinya Kawai<sup>\*2</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Yoshihiro Ktayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Tokyo University of Agriculture and Technology, <sup>\*3</sup>Cosmo research institute, <sup>\*4</sup>Nippon paper industries

Abstract: The soil bacterium, *Sphingomonas paucimobilis* SYK-6 is able to degrade various types of dimeric lignin compounds such as biphenyl,  $\beta$ -aryl ether, phenylcoumaran etc. In this study, we report here about the 1.8 kbp DNA fragment essential to *O*-demethylation of syringic acid (SA) and vanillic acid (VA). Sequencing analysis showed an open reading frame of 1671bp in this fragment, and this ORF has homolog to formyltetrahydrofolate synthetase. When this gene was expressed in mutant DC-49, which was deficient in demethylation of SA and VA, the enzymatic activity of VA and SA demethylation was observed. For enzymatic activity of *O*-demethylation of SA and VA, *lig H* and tetrahydroforic acid were essential.

1997-111

担子菌における菌体外へム酵素合成系の解析 -外因性 5-アミノレブリン酸の菌体外酵素分泌への影響-

松下啓太、割石博之、田中浩雄

九州大学農学部

Effect of exogenous 5-aminolevulinic acid on fungal production of extracellular heme peroxidases.

Keita Matsushita, Hiroyuki Wariishi, Hiroo Tanaka

Abstract: Extracellular activity of heme peroxidases (LiP, MnP) was closely related to 5-aminolevulinic acid biosynthetic activity in white-rot fungi. ALA biosynthetic activity was higher in the white-rot fungi, *Coriolus versicolor* and *Phanerochaete chrysosporium*, than that in the brown-rot fungus, *Tyromyces palustris*. The effects of exogenous ALA on extracellular heme peroxidases were investigated. Exogenous addition of ALA increased the relative amounts of free protoheme and of secreted MnP. ALA had no effect on MnP activity. These results suggested that the rate-determining step for extracellular heme peroxidase production may not be protein but heme biosynthesis.

1997-112

ペルオキシラジカル及びスーパーオキサイドアニオンの關与する遷移金属錯体 -電子移動系反応によるリグニンの解重合-

渡辺隆司<sup>\*1</sup>、Karin Koller<sup>\*2</sup>、Kurt Messner<sup>\*2</sup>、仲亀誠司<sup>\*1</sup>、榎 牧子<sup>\*1</sup>、本田与一<sup>\*1</sup>、桑原正章<sup>\*1</sup>

<sup>\*1</sup>京都大学木質科学研究所、<sup>\*2</sup>ウィーン工科大学生物化学工学微生物研究所

Depolymerization of lignin by transition metal complex-electron transfer reactions involving peroxy radical and superoxide anion.

Takashi Watanabe<sup>\*1</sup>, Karin Koller<sup>\*2</sup>, Kurt Messner<sup>\*2</sup>, Seiji Nakagame<sup>\*1</sup>, Makiko Enoki<sup>\*1</sup>, Yoichi Honda<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>

<sup>\*1</sup>Wood Rsearch Insdtute, Kyoto University, <sup>\*2</sup>Research Institute for Biochemical Technology and Microbiology, University of Technology, Vienna

Abstract: In aqueous solutions,  $^{14}\text{C}$ -labelled synthetic lignin was intensively depolymerized with Cu(II) and lipid hydroperoxide model compounds at room temperature in the presence of pyridine, which is known as a metabolite of lignin-degrading fungi. Reaction of Cu(II)/pyr with  $\text{H}_2\text{O}_2$  was less effective for the lignin depolymerization, but this system enhanced the brightness of UKP from 34.5 to 81 point. Spin trapping experiments demonstrated that peroxy radical is involved in the former reaction while the latter involves superoxide anion and active oxidants other than hydroxyl radical. A wide variety of practical application will be developed based on the copper/coordination compound/peroxide reactions.

1997-113

リグニンペルオキシダーゼによるベラトリルアルコールの酸化機構

桃原郁夫

森林総合研究所

Veratryl alcohol oxidation catalyzed by lignin peroxidase.

Ikuo Momohara

Forestry and Forest Products Research Institute

Abstract: Mechanism of veratryl alcohol oxidation catalyzed by lignin peroxidase was investigated. Relationship between LiP inactivation and amount of veratraldehyde formation suggests that the amount of hydrogen peroxide consumed for inactivating LiP is negligible. Reactions under single turn over conditions suggest reaction of LiP-I with veratryl alcohol is necessary for veratraldehyde formation in the absence of oxygen. Stopped-flow technique reveals that two veratryl alcohol molecules are involved in LiP catalytic cycle.

1997-114

Lignin Peroxidase によるリグニンの直接酸化 –DHP と LiP compound I, II の反応性の検討–  
城島 透、割石博之、田中浩雄

九州大学農学部

Direct oxidation of lignin by lignin peroxidase. – Reactivity of LiP compound I, II with DHP.

Toru Johjima, Hiroyuki Wariishi, Hiroo Tanaka.

Faculty of Agriculture, Kyushu University

Abstract: Reactivity of lignin peroxidase (LiP) from *Phanerochaete chrysosporium* against a synthetic lignin (DHP) were studied utilizing transient kinetic technique. A one-electron transfer from DHP to LiP compound I (LiPI) exhibited saturation kinetics, from which the dissociation equilibrium constant for LiPI-DHP interaction was calculated to be  $350\ \mu\text{M}$ . Kinetic characterization of LiPI reaction with DHP strongly suggested that LiP is capable of oxidizing DHP directly at the protein surface via a long-range electron transfer process.

1997-特別講演

地球環境とバイオマス

戸倉清一

北海道大学大学院地球環境科学研究科

Sustainability of earth environment through biotechnology.

Seiichi Tokura

Graduate School of Environmental Earth Science, Hokkaido University

Abstract: The higher quality of foods is requested due to rapid progress of human life, the more heavy environmental pollution is caused by a tremendous amount of food, agricultural and marine wastes. Several polysaccharides in these wastes have been studied as renewable resource due to

relatively easier extraction and purification from waste. Chitin, one of biofunctional mucopolysaccharides of natural occurrence, has been investigated to apply for biomedical materials following to the removal of calcium and protein. Although waste paper is recycled in paper industry, cellulosic resources are able to find out easily in agricultural or food wastes. These cellulosic wastes were studied to reconstruct into novel polysaccharides with new functions through bacterial cultivation. The direct filamentation of novel polysaccharide has been achieved successfully by the use of shallow culture pan which was designed to form a thinner gel on the surface of culture medium. The filamentation was proceeded continuously with the rate of 30mm/h. The functionalization of cellulosic products were also achieved successfully with change of carbon source in the culture medium.

1997-201

トチュウの粗酵素によるネオリグナン・リグナンのエナンチオ選択的生成

加登優樹、片山健至

香川大学農学部

Enantioselective formation of neolignans/lignans by cell-free extracts of *Eucommia ulmoides*.

Yuki Kado, Takeshi Katayama

Faculty of Agriculture, Kagawa University

Abstract: Formation of (+)-*erythro* and (-)-*threo* guaiacylglycerol- $\beta$ -coniferyl ethers was found, following incubation of coniferyl alcohol with cell-free extracts from stems of *Eucommia ulmoides* young shoots in the presence of H<sub>2</sub>O<sub>2</sub>. Enantiomeric excesses of the both diastereomers increased in a linear fashion for 1 hr. When the ( $\pm$ )-*erythro* isomer was incubated as a substrate under the same conditions, it was recovered as an almost racemate. The *erythro* isomer formed by the action of cell-free extracts from the leaves was an almost racemate. Incubation of sinapyl alcohol with insoluble residues from the stems in the absence of provided cofactors gave syringaresinol with (+)-enantiomer slightly preferred.

1997-202

*Linum flavum* のリグナン生合成酵素について

三亀啓吾、梅澤俊明、島田幹夫

京都大学木質科学研究所

Lignan synthesis by cell-free extracts from *Linum flavum*.

Keigo Mikame, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Three lignans, (+)-pinoresinol (65% e. e.), (+)-lariciresinol (70% e. e.) and (-)-secoisolariciresinol (>99% e. e.) were isolated from *Linum flavum*. When [9,9-<sup>2</sup>H<sub>2</sub>,OC<sup>2</sup>H<sub>3</sub>] coniferyl alcohol was administered to this plant, incorporation of deuterium atoms into pinoresinol, lariciresinol and secoisolariciresinol was observed. Cell-free extracts from *Linum flavum* catalyzed the formation of the three lignans, when incubated with coniferyl alcohol in the presence of NADPH and H<sub>2</sub>O<sub>2</sub>. These results suggested that the step to produce the optically pure lignan is the formation of secoisolariciresinol from lariciresinol in *L. flavum*.

1997-208

ベンジル化木材樹脂の発泡性を支配する諸因子

平岡俊治、上田昌見、高見泰博、越島哲夫

日本化学機械製造株式会社

Foaming-regulating factors of benzylation reaction on wood.

Toshiharu Hiraoka, Masami Ueda, Yasuhiro Takami, Tetsuo Koshijima  
Japan Chemical Engineering & Machinery Co. Ltd.

Abstract: Foaming is one of the most interesting practical use of wood plastics. In the case of benzylated wood resins, it becomes the biggest advantages for use of the resin that the foaming can be performed without use of any plasticizers. The present investigations were conducted to make clear the principal production conditions of well-foamable benzylated resin: Foaming temperature depended on the softening or flow temperatures, and the most adequate at about 5°C above the softening temperature. Ferric ion was found to catalyze the decomposition of benzylchloride and diminished extensively the foaming extent of the benzylated wood resins. The influences of mercerization temperature were one of the biggest factors, and the extensive foaming appeared at 20 to 46°C. Above 50°C, foaming decreased less than 40% owing to liberation of lignin moiety from the LCC contained.

1997-204

リグニン含有型吸水性ポリウレタンフォームの形態的及び物理的性質

畠山兵衛<sup>\*1</sup>、伊豆田良信<sup>\*1</sup>、兼松幹生<sup>\*1</sup>、廣瀬重雄<sup>\*2</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 物質工学工業技術研究所

Morphological and physical properties of water-sorption type polyurethane foams containing lignin. Hyoe Hatakeyama<sup>\*1</sup>, Yoshinobu Izuta<sup>\*1</sup>, Mikio Kanematsu<sup>\*1</sup>, Sigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui Institute of Technology, <sup>\*2</sup>National Institute of Materials and Chemical Research

Abstract: Polyurethane (PU) foams were prepared from molasses (MOL), kraft lignin (KL) and an organosolv lignin (Alcel lignin, AL). The prepared PU foams were analyzed by differential scanning calorimetry (DSC), thermogravimetry (TG) and mechanical measurements. Using the obtained results, water-sorption type PU foams were prepared. The prepared PU foams showed thermal degradation temperature ( $T_d$ ) at around 220 – 230 °C. Water absorptivity ( $W_s$ ) was calculated according to the following equation:  $W_s = (W_1 - W_0) / V$ , where  $W_0$  is weight of dry sample (g),  $W_1$  weight of sample after water-absorption (g),  $V$  volume of dry sample ( $\text{cm}^3$ ).  $W_s$  of the prepared PU foams depended on the density of sample and a maximum value was ca. 0.9. Stress/density value ( $\text{kPa}/\text{kg} \pm \text{m}^{-3}$ ) of dry sample was ca. 1.9 and ca 1.7 after water-absorption.

1997-205

リグニンベースポリカプロラクトン誘導体からのポリウレタンの調製と熱的性質

伊豆田良信<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、廣瀬重雄<sup>\*2</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 物質工学工業技術研究所

Preparation and thermal properties of polyurethanes derived from lignin-based PCL.

Yoshinobu Izuta<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>, Sigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui Institute of Technology, <sup>\*2</sup>National Institute of Materials and Chemical Research

Abstract: Polyurethane (PU) sheets were prepared from kraft (KL) and Alce1 (AL) lignin-based polycaprolactones (PCL). The obtained lignin-based PCL's were analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG). The glass transition temperature ( $T_g$ ) decreased from -10 to -60 °C with increasing CL/OH ratio from 2 to 25 mol/mol. The cold-crystallization and melting were observed when CL/OH ratio of the samples exceeds 15 mol/mol. DSC results suggest that CL molecules form crystalline structure by molecular rearrangement occurred at around 0 °C. Phase diagrams were established for both KL and AL lignin-based PCL's.

1997-206

タンニン-タンパク質沈澱機構

河本晴雄<sup>\*1</sup>、中坪文明<sup>\*2</sup>

<sup>\*1</sup> 京都大学大学院エネルギー科学研究科、<sup>\*2</sup> 京都大学大学院農学研究科

Tannin-protein co-precipitation mechanism.

Haruo Kawamoto<sup>\*1</sup>, Fumiaki Nakatsubo<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Energy Science, Kyoto University, <sup>\*2</sup>Graduate School of Agriculture, Kyoto University

abstract: Stoichiometric analysis of successive washing of galloylglucose (hydrolysable tannin) – protein precipitates by aqueous solution was carried out. The following results were obtained: 1) at least two bindings, strong and weak bindings, respectively, are included in the galloylglucose-protein bonds; 2) although maximum number of the binding site on a protein molecule increases linearly with an increase in protein molecular weight, content of the number of the strong binding sites (NSB) is quite different depending on the protein structure; this explains different relative affinities of proteins for tannin; 3) stability of the precipitates is explainable by the relationships between galloylglucose/protein molar ratio required for the precipitation and NSB.

1997-207

高分子量 procyanidin gallate の合成とその性質

米田 聡、中坪文明

京都大学大学院農学研究科

Synthesis of procyanidin gallates with high molecular weight and their function.

Satoshi Yoneda, Fumiaki Nakatsubo

Graduate School of Agriculture, Kyoto University

Abstract: The preparation methods of the high-molecular-weight procyanidin gallate was developed. These methods may be also applicable to the conversion of lignins into the functional polymer with protein-precipitating capacity like tannins.

1997-208

炭素化非木材繊維シートの物性

大谷慶人、中島綾子、鮫島一彦

高知大学農学部

Characterization of resin-impregnated and carbonized nonwood fiber sheets.

Yoshito Ohtani, Ayako Nakajima, Kazuhiko Sameshima

Faculty of Agriculture, Kochi University

Abstract: Ten nonwood bleached chemical pulps and one softwood bleached kraft pulp were used to make handsheets. All pulps were beaten by PFI mill and also subjected to handsheet making. Every handsheet was impregnated with phenol resin, polymerized by heating and carbonized at 800°C. Resulting carbonized pulp sheets were characterized and evaluated as an electromagnetic shielding material. The sheets from bagasse, kenaf and jute pocessed good electric wave shielding effects rather than the cupper sheet. But the magnetic shielding effects were inferior to that of cupper sheet. The electric wave shielding effect correlates to the sheet thickness and density.

1997-209

*Ganoderma* sp. YK-505 株の産生するマンガンペルオキシダーゼの安定性について

原園幸一、近藤隆一郎、坂井克己

九州大学農学部

Stability of manganese peroxidase secreted from *Ganoderma* sp. YK-505.

Koichi Harazono, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We evaluated stabilities of manganese peroxidases (MnPs) secreted from white rot fungi, *Phanerochaete chrysosporium*, *Phanerochaete sordida* YK-624 and *Ganoderma* sp. YK-505. Two MnP isoenzymes (G-1 and G-2) from *Ganoderma* sp. YK-505 exhibited stabilities against high temperature and pH. Change in the heme environment of MnPs from *Ganoderma* sp. YK-505 during incubation at high temperature and pH was investigated by electronic absorption spectroscopy. The absorption spectra of MnPs after incubation at high temperature or pH were similar to those of low-spin hexacoordinate ferric heme proteins, as described previously in the report that MnP from *P. chrysosporium* was very susceptible to thermal inactivation due to the loss of calcium from the enzyme. The results demonstrated that the same structural changes as MnP from *P. chrysosporium* occur during inactivation, resulting from the release of calcium from MnPs from *Ganoderma* sp. YK-505 although inactivation of MnPs from *Ganoderma* sp. YK-505 occur in severer condition than that of MnP from *P. chrysosporium*,

1997-210

担子菌 *Bjerkandera adusta*(ヤケイロタケ)の生産するマンガンペルオキシダーゼの有機溶媒中における反応

茶谷明伸<sup>\*1</sup>、吉田晋一<sup>\*2</sup>、本田与一<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>、桑原正章<sup>\*1</sup>

<sup>\*1</sup> 京都大学木質科学研究所、<sup>\*2</sup> 鳥取県工業試験所

Reaction of manganese-dependent peroxidase from *Bjerkandera adusta* in organic solvents.

Akinobu Chatani<sup>\*1</sup>, Shinichi Yoshida<sup>\*2</sup>, Yoichi Honda<sup>\*1</sup>, Takashi Watanabe<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Industrial Research Institute of Tottori Prefecture

Abstract: To characterize activities of manganese-dependent peroxidase (MnP) in organic media, aromatic compounds and DHPs were oxidized with MnP from *Bjerkandera adusta* in water-miscible organic solvents. In 70% aqueous organic solvents, MnP exhibited high activities toward several phenolics and aromatic amines such as guaiacol, 2,6-dimethoxyphenol, 3,3-dimethoxybenzidine, *o*-phenylenediamine and *m*-aminophenol. Oxidation of DHPs by MnP was also observed in aqueous organic solvents. In 70% acetone, guaiacyl DHP was polymerized by MnP while syringyl DHP was depolymerized with concomitant formation of a small amount of polymerized compounds.

1997-211

白色腐朽菌のリグニン分解に関与する酵素系に関する研究(XIII)－白色腐朽菌の産生する siderophore 様物質について－

平井浩文、近藤隆一郎、坂井克己

九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi (XIII) – Siderophore-like compounds produced by white-rot fungi.

Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We primarily tried to detect and isolate siderophore-like compounds from white-rot fungus *Phanerochaete sordida* YK-624. Fe(II) binding ability was detected in 70% acetone-insoluble fraction from the liquid culture without Fe. The siderophore-like compounds were also secreted under Fe-sufficient culture. Two compounds (compound I and II) were purified from the fraction with gel permeation chromatographies. The molecular weight of these compounds were estimated about 3000-5000. IR spectra of these compounds showed the presence of both peptide bonds and alcoholic hydroxyl groups. It is suggested that these compounds selectively bound iron or cobalt.

The addition of these compounds to the reaction mixture of ferrereductases accelerated consumption of NADPH.

1997-212

白色腐朽菌 *Phanerochaete sordida* YK-624 株より得られた突然変異体によるクラフトパルプのバイオブリーチング

石村大児、近藤隆一郎、坂井克己、平井浩文

九州大学農学部

Biobleaching of kraft pulp with mutants from white-rot fungus *Phanerochaete sordida* YK-624.

Daiji Ishimura, Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: We isolated mutant 1 and mutant 2 which have weak and strong tetrazolium salts reductive activity, respectively from *Phanerochaete sordida* YK-624 by UV irradiation. When unbleached hardwood and oxygen-bleached softwood kraft pulps were treated with wild type and these mutants, mutant 1 made highly pulp brightness increasing and secreted more manganese peroxidase (MnP) in the early incubation period compared with wild type, although mutant 2 showed the same tendency as wild type. Mutant 1 secreted MnP under lower Mn(II) concentration, and uptook Mn(II) faster than wild type.

1997-213

The Study on the <sup>13</sup>C-NMR Spectra of Dissolved Lignin from Na<sub>2</sub>S Pretreatment Kraft Cooking.

金永燦<sup>\*1</sup>、李忠正<sup>\*1</sup>、Diesheng Tai<sup>\*1</sup>、佐渡篤<sup>\*2</sup>

<sup>\*1</sup>南京林業大学、<sup>\*2</sup>東京農工大学農学部

The study on the <sup>13</sup>C-NMR spectra of dissolved lignin from Na<sub>2</sub>S pretreatment kraft cooking.

Yongcan Jin<sup>\*1</sup>, Zhongzheng Lee<sup>\*1</sup>, Diesheng Tai<sup>\*1</sup>, Atsushi Sawatari<sup>\*2</sup>

<sup>\*1</sup>Nanjing Forestry University, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: Kraftban lignins from Na<sub>2</sub>S pretreatment liquor and cooking black liquor were isolated and analyzed by <sup>13</sup>C-NMR spectroscopy. The results were compared with those from conventional kraft cooking with similar degree of delignification. Kraft lignin from Na<sub>2</sub>S pretreatment liquor contains less etherified structures than that from conventional cooking. This indicates that the lignin removal during the Na<sub>2</sub>S pretreatment is different from that in normal kraft cooking. The structure of lignin from pretreatment liquor differs appreciably from that of lignin obtained from conventional pulping. Because of the relatively mild condition, a large amount of terminal groups in the lignin molecule are removed one by one as peeling reaction in the Na<sub>2</sub>S pretreatment. In contrast, the fragmentation of lignin is more random in the conventional kraft cooking.

1997-214

リグニンのオゾン酸化に伴う過酸化水素の生成

真柄謙吾<sup>\*1</sup>、富村洋一<sup>\*1</sup>、細谷修二<sup>\*1</sup>、池田努<sup>\*2</sup>

<sup>\*1</sup>森林総合研究所、<sup>\*2</sup>筑波大学農林工学系

Generation of hydrogen peroxide during the ozonation of lignin.

Kengo Magara<sup>\*1</sup>, Yoichi Tomimura<sup>\*1</sup>, Shuji Hosoya<sup>\*1</sup>, Tsutomu Ikeda<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Product Research Institute, <sup>\*2</sup>Tsukuba University

Abstract: Ozone reacts with lignin through two pathways. One is ionic cyclo-addition to cleave a C3-C4 double bond. This reaction generates hydrogen peroxide as a reaction product. Another way is one-electron transfer from a dissociated phenolic hydroxyl group. This reaction reads to the

formation of hydroxyl radicals which cause the non-selectivity of ozone reaction. In the case of the radical reaction pathway, hydrogen peroxide will not be produced. To investigate the contribution of these two pathways, we determined the generated hydrogen peroxide. When 2 mmol of veratryl alcohol was reacted with excess amount of ozone, 4.7mmol of hydrogen peroxide was detected. On the other hand, vanillyl alcohol gave only 0.7mmol of hydrogen peroxide under the same reaction conditions. In the case of veratryl alcohol, because of the lack of phenolic hydroxyl group, the ionic reaction pathway dominated. Although the dissociation of phenolic hydroxyl groups is very little under neutral conditions, the radical reaction pathway dominated in the case of ozonation of vanillyl alcohol. This is probably because the radical reaction is much faster than the ionic reaction.

1997-215

酸素脱リグニンに影響を与える要因 -溶解性有機物とリグニン量のばらつき-

種田英孝, 飯嶋純フェルナンド

日本製紙株式会社

Effect of several factors on oxygen delignification.-Carryover and lignin contents variation in fibers.

Hidetaka Taneda, Jun Fernando Iijima

Nippon Paper Industries Co., Ltd.

Abstract: The process factors which affect the delignification in a medium consistency oxygen delignification process were investigated. The effect of carryover to oxygen process consisted of the negative one by the organic compounds like lignin and the positive one by residual alkali in it. After the initial reaction with oxygen, COD and TOC values of the effluent did not change greatly. Therefore the further oxidation with oxygen did not observed. The variation of the lignin contents in each fiber showed the positive effect on the delignification in the case of oxygen delignification. The reason for this phenomena is under investigation.

1997-216

酸素系の漂白過程における活性酸素種の反応経路と反応選択性

横山朝哉、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Reaction route and reaction selectivity of active oxygen species in oxygen containing bleaching processes.

Tomoya Yokoyama, Yuji Matsumoto, Gvosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: A cellulose model compound, methyl  $\beta$ -D-glucopyranoside (MGP), and/or lignin model compounds were subjected to a reaction in an alkaline hydrogen peroxide solution. The initial concentration of MGP and the presence of a lignin model compound did not affect the recoveries of MGP. Recoveries of MGP were smaller when hydrogen peroxide was stepwisely added than when hydrogen peroxide was added at once initially. These results confirmed a competition between model compounds and hydrogen peroxide in reacting with active oxygen species which were produced from the degradation of hydrogen peroxide itself, and suggested that active oxygen species attacked hydrogen peroxide preferentially rather than model compounds. The competition was observed most clearly when ferric ion was added.

1997-217

フェノキシラジカルと酸素との反応性について(2)

杉元倫子、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Reactivity of phenoxy radical with molecular oxygen. (2).

Tomoko Sugimoto, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: In order to examine the possibility of the reaction between phenoxy radical and molecular oxygen, syringyl alcohol (SA) was treated with a one electron oxidizing reagent, manganese (III), and the effect of oxygen pressure on the yield of methanol from this phenol was determined. The increased formation of methanol under increased oxygen pressure was thought to indicate the reaction between phenoxy radical and molecular oxygen. The yields of the starting material SA and one of the reaction products, syringaldehyde, were constant regardless of the oxygen pressure. Post-treatment with alkali was essential for the complete formation of methanol. The reduction by NaBH<sub>4</sub> after the sufficient alkali-treatment resulted in increased formation of methanol. This is due to the reduction of formaldehyde formed by the coupling reactions of C1 radical.

1997-218

塩素漂白で生成した高分子有機塩素化合物の環境中での挙動(1)-熱分解ガスクロマトグラフによる分析法の確立-

幸田圭一、新谷博幸、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Environmental fate of high molecular weight chloroorganics produced by chlorine bleaching (1):

Development of a new analytical method by the use of pyrolysis gas chromatography.

Keiichi Koda, Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: High molecular weight chloroorganics were extracted from chlorinated pulps by the use of aqueous dioxane and were used as authentic samples of chloroorganics in the effluent. The extracted chloroorganics were subjected to pyrolysis GC. The pyrogram of chloroorganics is quite different from that of milled wood lignin (MWL), which is assumed to be representative of the native lignin in wood. Over five hundred of pyrolysis products were detected in the GC and their mass fragmentation patterns were stored in the mass library. Interestingly, the majority of the pyrolysis products were not aromatics. By the use of the mass library thus constructed, samples obtained from the discharged bleaching effluents were successfully analyzed.

1997-219

塩素漂白過程で環開裂した芳香核に由来する低分子化合物の検出

新谷博幸、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Liberation of low molecular weight compounds from oxidatively cleaved aromatic ring of chlorolignin.

Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Unbleached softwood kraft pulp, unbleached hardwood kraft pulp and oxygen prebleached hardwood kraft pulp were chlorinated, and residual chlorolignin in pulps were extracted by aqueous dioxane. When extracted chlorolignins were treated with alkali, formic acid, glycolic acid, acetic acid and carbon dioxide were produced. These low molecular weight compounds should be liberated from the muconic acid type structure or its derivatives which were produced by the oxidative cleavage of aromatic ring during chlorine bleaching.

1997-P01

#### 脱成分処理によるコルク細胞壁微細構造の変化

白井伸侍、吉永 新、藤田 稔

京都大学大学院農学研究科

Ultrastructure and histochemistry of phellem cell wall after solvent extraction and depolymerizations.

Shinji Shirai, Arata Yoshinaga, Minoru Fujita

Faculty of Agriculture, Kyoto University

Abstract: Phellem, or cork tissue, of tree bark is well known to have suberized cell walls. It is accepted that suberin layers have polymeric suberin and soluble waxes, and that they appear as a fine lamellar structure in transmission electron microscopy. In this study, to clarify the relationship between chemical components and fine lamellar structure, removing process of cell wall components were observed in detail. Wax extracting with chloroform-methanol mixture at room temperature did not affect the lamellar structure, Whereas electron translucent lamellae are not observed after the extraction at 60°C. KOH saponification for a brief time disrupted partially the lamellar structure. Possible explanations for these observations are discussed.

1997-P02

#### ニトロベンゼン酸化後のヒノキ材細胞壁の構造

大野清三、吉永 新、藤田 稔

京都大学大学院農学研究科

Structure of cell walls after nitrobenzene oxidation in *Camacyparis obtusa* Endl.

Seizo Ohno, Arata Yoshinaga, Minoru Fujita

Graduate School of Agriculture, Kyoto University

Abstract: In alkaline nitrobenzene oxidation, degree of condensation in lignin has been evaluated from total yields of the oxidation products. The condensed units in lignin is expected to be resistant to the nitrobenzene oxidation. To clarify delignification process, wood sections after nitrobenzene oxidation with various reaction time were observed under an UV microscope, a SEM, and a TEM. As a result, the major part of lignin was removed from cell walls by the oxidation. This result suggested that condensed lignins were removed from cell walls by the cleavage of non-condensed units.

1997-P03

#### ニトロベンゼン酸化後の数種の広葉樹材細胞壁の構造

吉永 新、藤田 稔

京都大学大学院農学研究科

Structure of cell walls after nitrobenzene oxidation in several hardwoods.

Arata Yoshinaga, Minoru Fujita

Graduate School of Agriculture, Kyoto University

Abstract: Alkaline nitrobenzene oxidation has been used as a useful means of characterizing monomeric composition and also degree of condensation of lignin. However, syringaldehyde / vanillin molar ratio (S/V ratio) obtained from the nitrobenzene oxidation provides information on only a part of lignin. To clarify behavior of the whole lignin during nitrobenzene oxidation, lignin distribution in cell walls were examined on several hardwoods after the nitrobenzene oxidation using UV microscopy and transmission electron microscopy. As a result, in both vessel elements and wood fibers, the major part of lignin was removed from cell walls by the oxidation.

1997-P04

#### ラジオトレーサー法によるリグニン試料調製中のペクチンおよびキシランの挙動の解明

今井貴規、中井陽子、安田征市  
名古屋大学農学部

Behaviors of pectin and xylan during lignin preparations studied by radiotracer technique  
Takanori Imai, Youko Nakai, Seiichi Yasuda  
Faculty of Agriculture, Nagoya University

Abstract: Pectin and xylan were labeled with  $^{14}\text{C}$  and  $^3\text{H}$  respectively by administration of D-glucuronic acid- $[6-^{14}\text{C}]$  and *myo*-inositol- $[2-^3\text{H}]$  to a growing stem of magnolia. The doubly radio-labeled wood meal was subjected to preparations of Klason lignin and milled wood lignin (MWL), and the radioactivities of the various fractions were determined to compare the behaviors of pectin and xylan during the preparations. Value of  $^3\text{H}/^{14}\text{C}$  of the Klason lignin was smaller than that of original wood meal, and the value of the soluble part was larger than that of the original. While, the  $^3\text{H}/^{14}\text{C}$  value of the MWL fraction was smaller than that of the original, and the value of the lignin-carbohydrate-complex (LCC) fraction was near to the original value. These results indicate that pectin and xylan behaved differently during the lignin preparations, and pectin were ready to remain in Klason lignin and MWL compared with xylan.

1997-P05

リグニン前駆体とペルオキシダーゼの親和性と反応性  
土橋英紀、伊藤岐仁、重松幹二、棚橋光彦  
岐阜大学農学部

Affinities and reactivities between monolignols and peroxidase.  
Hidenori Tsuchihashi, Michihito Itoh, Mikiji Shigematsu, Mitsuhiro Tanahashi  
Faculty of Agriculture, Gifu University

Abstract: To clarify biosynthetic process of lignin, we studied affinities and reactivities between monolignols (*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol and horseradish peroxidase (HRP). Affinities and reactivities were defined as  $k_{+1}/k_{-1}$  and  $k_{+2}$  of enzyme reaction, respectively. Affinities and reactivities between monolignols and HRP were reduced by increases number of methoxyl groups. However, the reduction of reactivity was extremely larger compared with the reduction of affinity.

1997-P06

フェノール性  $\beta$ -O-4 型ジリグノール合成法の改良  
置田恭子、飛鳥井雅倫、田中 愛、杉下千洋、河合真吾、大橋英雄  
岐阜大学農学部

The convenient synthetic method of  $\beta$ -O-4 dilignols.  
Kyoko Okita, Masanori Asukai, Ai Tanaka, Kazuhiro Sugishita, Shingo Kawai, Hideo Ohashi  
Faculty of Agriculture, Gifu University

Abstract: Lignin substructure model compounds, especially  $\beta$ -O-4 dilignols, play important role for biodegradation and structural studies of lignin. Many synthetic routes were reported, but these methods need chloric solvents which have been forbidden for environment problems, different protecting groups for the reactivity between guaiacyl and syringyl nuclei and/or strict anhydrous condition. To make up for such disadvantages, we tried a few modification based on method of Adler and Eriksson. This convenient method has relatively short reaction time and high yields without strict anhydrous conditions, chloric solvents and drastic reagents.

1997-P07

近赤外フーリエ変換ラマン分光法によるリグニン中の  $\alpha$  および  $\gamma$  位のカルボニル基の定性および定

量

高山 幸、割石博之、田中浩雄  
九州大学農学部

FT Raman spectroscopic characterization of carbonyl groups in lignin.

Miyuki Takayama, Hiroyuki Wariishi, Hiroo Tanaka

Faculty of Agriculture, Kyushu University

Abstract: A near infrared fourier transform Raman (NIR-FTR) spectroscopic technique was utilized to characterize lignin. The  $\nu$  (C=O) band, which could be a good monitoring probe to follow wood deterioration, can be seen as an isolated sharp band with medium intensity on NIR-FTR spectra of wood. On the other hand, it has been known to give a broad absorption with strong intensity on FTIR spectra. DHP prepared from coniferaldehyde exhibited a band at  $1620\text{ cm}^{-1}$ , while DHP prepared from coniferyl alcohol did not show this band. In NIR-FTR spectra of MWL and wood meals  $1620\text{ cm}^{-1}$  disappeared as reduction with  $\text{NaBH}_4$ . From these results, this band was assigned to  $\gamma$ -carbonyl band.

1997-P08

Cloning of novel cytochrome P450 monooxygenase in quaking aspen (*Populus tremuloides*).

Keishi Osakabe, Vincent L. Chiang

Plant Biotechnology Research Center, School of Forestry, Michigan Technological University

Abstract: Using a modified mRNA differential display technique to analyze differentially expressed P450 genes in the 6th to 10th internodes that were absent in the 1st to 4th internodes of young aspen shoots, we cloned a full-length cDNA (*asc6*), which encodes a typical P450 of 508 amino acids. The deduced *asc6* protein sequence shows a less than 40% sequence identity with all other known plant P450s in DNA databases. Thus, *asc6* can be considered to represent a novel class of P450.

1997-P09

カワラタケ (*Coriolus versicolor*) 菌体外粗酵素によるカテキン類の変換とその Gtase 阻害活性

西田容子、光永 徹、船岡正光

三重大大学生物資源学部

Conversion of catechins by the extracellular enzymes of *Coriolus versicolor* and inhibitory action of converted compounds on GTase.

Yoko Nishida, Tohru Mitsunaga, Masamitsu Funaoka

Faculty of Bioresources, Mie University,

Abstract: The chemical structures of bioconverted compounds from catechins by *Coriolus versicolor* and their inhibitory activities on glucosyltransferase (GTase), relating to the generation of dental caries are examined. Dimeric compounds Y-2, Y-3 from (+)-catechin and trimer Y-4, dimer Y-5 from (-)-epicatechin were produced. According to the NMR data, oxidative coupling occurred between A ring and B ring of catechins to generate a conjugated carbonyl group in the molecules. In spite of the dimeric classes the converted compounds showed high inhibitory activities on GTase, especially Y-3 and Y-5 were remarkable. The MM2 energy calculation of these compounds showed a good correlation between stretch-bend energy and GTase inhibitory activity. Therefore, it was presumed that the planar and strained structure is one of the important factor on GTase inhibitory action.

1997-P10

CAD 遺伝子を導入したタバコでの CAD の分布

伊藤真記<sup>\*1</sup>、高部圭司<sup>\*1</sup>、藤田 稔<sup>\*1</sup>、佐藤 茂<sup>\*2</sup>、柴田大輔<sup>\*2</sup>、日尾野隆<sup>\*3</sup>

<sup>\*1</sup> 京都大学大学院農学研究科、<sup>\*2</sup> 三井植物バイオ研究所、<sup>\*3</sup> 王子製紙株式会社森林資源研究所

Localization of CAD in CAD gene induced tobacco cell.

Masaki Ito<sup>\*1</sup>, Keiji Takabe<sup>\*1</sup>, Minoru Fujita<sup>\*1</sup>, Shigeru Sato<sup>\*2</sup>, Daisuke Shibata<sup>\*2</sup>, Takashi Hibino<sup>\*3</sup>

<sup>\*1</sup> Graduate School of Agriculture, Kyoto University, <sup>\*2</sup> Mitsui Plant Biotechnology Research Institute,

<sup>\*3</sup> Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: Considerable works has revealed the presence of enzymes involved in lignin biosynthesis, and the biosynthetic pathway of lignin is, now, generally accepted. However, the localization of each enzyme in the cell, the regulation of the synthesis of each enzyme and the transporting mechanism of lignin precursors are unresolved. Cinnamyl alcohol dehydrogenase (CAD) is the final enzyme for the synthesis of monolignols. This enzyme catalyzes the reduction of cinnamaldehydes to their corresponding cinnamyl alcohols. Immunocytochemistry revealed the difference of CAD distribution between the normal tobacco cell and the CAD gene induced tobacco cell. The latter showed the remarkable increase of labelling in cyto-sol. The labelling was also observed on the cell wall in both cells. From above results, localization and role of CAD were discussed.

1997-P11

植物培養細胞を用いたバイオトランスフォーメーションによる有用物質の生産

坪田弘志、伊藤和貴、橘 燦郎

愛媛大学農学部

Production of useful substances by biotransformation with plant cell cultures.

Hiroshi Tsubota, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Production of pinoresinol diglucoside from pinoresinol by cell suspension cultures of *Coffea arabica* was tried. From the results of HPLC analyses of the reaction products, we found that pinoresinol diglucoside was produced from pinoresinol in the maximum yield of 33.6% by the cultures of *C. arabica*. We also found that the concentrations of the substrate added to the cultures was lower, the yields of the glucoside was higher. However, the yields of the glucoside was higher. However, the yields of the yields of the glucoside decreased with the incubation time.

1997-P12

数種の植物懸濁培養細胞を用いたフェノール性化合物のバイオトランスフォーメーション

好川 恵、光度知代、伊藤和貴、橘 燦郎

愛媛大学農学部

Biotransformation of phenol compounds by some plant cell suspension cultures.

Megumi Yoshikawa, Tiyo Mitsuvara, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Production of phenol glucosides from two phenols, 4-methoxy phenol and scopoletin by cell suspension cultures of *Coffea arabica*, *Nicotiana tabacum* and *Vinca rosea* were tried. From the results of HPLC analysis of each reaction product, we found that methylarbutin, phenolic glucoside of 4-methoxy phenol was produced from 4-methoxy phenol in the maximum yield of 22.7 % and 15.6 % by the cell suspension cultures of *C. arabica* and *N. tabacum*, respectively. Scopolin, glucoside of scopoletin could be produced from scopoletin by the cell suspension cultures of *V. rosea*, however, the maximum yield of scopolin was 2.6 % of the added substrate.

1997-P13

原子間力顕微鏡を用いたクラフトパルプ表面の観察 –脱リグニンが表面性状に及ぼす影響–  
岡本哲明、飯塚堯介

東京大学大学院農学生命科学研究科

Observation of the surface of kraft pulp fibers by atomic force microscopy. – Influence of delignification on the character of the surface of kraft pulp fibers.

Tetsuaki Okamoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: The surfaces of unbleached kraft pulp and some treated kraft pulp fibers were observed by contact mode AFM in the air. Clear and high-resolution images of AFM of fine fibrils were obtained. The size of fine fibrils was estimated to be 2–5nm according to the artifact by tip-sample convolution. Apparent swelling of fine fibrils was observed in the case of Cl<sub>2</sub>-alkali treated sample probably due to the removal of lignin and hemicellulose during the treatment.

1997-P14

酸素漂白過程における共酸化現象の評価

童 国林、横山朝哉、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Oxygen oxidation of non-phenolic lignin units by a co-oxidation mechanism.

Guolin Tong, Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Kraft lignin and isolated residual lignin from unbleached softwood kraft pulp were subjected to oxygen-alkali oxidation, and the extent of the oxidation were evaluated by permanganate consumption of oxidized lignin. The residual lignin was much more easily oxidized by oxygen-alkali than kraft lignin. Three phases are observed during the oxidation of the isolated residual lignin. The first phase was the fastest and most of electrons (about 5) were lost in this phase. The lost electrons during total three phases were 9 per lignin unit. Model experiments by the use of phenolic and non-phenolic lignin model compounds confirmed that even a non-phenolic unit can be oxidized during oxygen-alkali treatment by the co-oxidation mechanism. However, the extent of oxidation of the model system which contains equimolar amount of phenolic model and non-phenolic model compound was much smaller than the extent of oxidation of the isolated residual lignin.

1997-P15

生ゴミ処理スギチップのリグニン、ノルリグナンの変化とパルプ化に及ぼす影響

島田謹爾<sup>\*1</sup>、加藤 厚<sup>\*1</sup>、富村洋一<sup>\*1</sup>、真柄謙吾<sup>\*1</sup>、大原誠資<sup>\*1</sup>、石原光朗<sup>\*1</sup>、福田清春<sup>\*2</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 東京農工大学農学部

Changes of lignin and norlignans of Sugi (*Cryptomeria japonica*) chips during the garbage treatment and their effects on kraft pulping.

Kinji Shimada<sup>\*1</sup>, Atsushi Kato<sup>\*1</sup>, Yoichi Tomimura<sup>\*1</sup>, Kengo Magara<sup>\*1</sup>, Seiji Ohara<sup>\*1</sup>, Mitsuro Ishihara<sup>\*1</sup>, Kiyoharu Fukuda<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: To investigate the changes of lignin and norlignans of Sugi (*Cryptomeria japonica*) chips during the treatment of garbage, the alkaline-nitrobenzene oxidation products were analyzed by means of GLC, <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopy. In addition, the effects of the changes of them on kraft pulping was also examined. Following results were obtained. 1) The yield of total aldehydes on nitrobenzene oxidation decreased in the treated chips. 2) The yields of the oxidation products of

treated chip were higher for *p*-hydroxybenzaldehyde and lower for methoxyl group than those of non-treated chip. This result implies that the polymerized norlignans have remained in the chip and decomposed on nitrobenzene oxidation to yield *p*-hydroxybenzaldehyde. 3) In the initial stage of kraft pulping, the treated chip was well cooked and the delignification proceeded faster than the non-treated chip. In the last stage, however, the large amounts of lignin remained in the pulp. 4) Both the changed lignin and norlignans could not be easily removed during the pulping process.

1997-P16

担子菌による含硫黄ヘテロ環化合物の変換 —基質認識および代謝応答—  
—瀬博文、中溝真啓、割石博之、田中浩雄  
九州大学農学部

Biotransformation of sulfur containing heterocyclic compounds by basidiomycetes. – Substrate recognition and metabolic response.

Hirofumi Ichinose, Masahiro Nakamizo, Hiroyuki Wariishi, Hiroo Tanaka  
Faculty of Agriculture, Kyushu University

Abstract: Lignin degrading basidiomycete *Coriolus versicolor* was utilized to degrade sulfur containing heterocyclic compounds which are recalcitrant compounds found in fossil resources. The transformation of these compounds by *C. versicolor* were occurred in different manner under different metabolic conditions. Nonaromatic compounds such as 2-hydroxymethylthiophene were metabolized in primary metabolic conditions and utilized as a sulfur source for growth. While aromatic compounds such as 2-hydroxymethylbenzothiophene and 4-methyldibenzothiophene were metabolized as xenobiotic detoxification. It was suggested that substrate recognition controls the metabolic response.

1997-P17

担子菌原形質膜機能解析モデルへのプロトプラストの適用  
小林芳徳、割石博之、田中浩雄  
九州大学農学部

Utilization of fungal protoplasts as a plasma membrane model for functional analysis.

Yoshinori Kobayashi, Hiroyuki Wariishi, Hiroo Tanaka  
Faculty of Agriculture, Kyushu University

Abstract; White-rot basidiomycetes are capable of degrading lignin. The extracellular lignin degrading enzymes catalyze the depolymerization of lignin. But a little is known about mechanism of uptake of lignin degradation fragments. As an active plasma membrane model, we attempted to utilize protoplasts. In this study, we analyze the reduction of quinones and uptake of lignin degradation fragment using protoplasts prepared from a brown-rot basidiomycete. 2,6-Dimethoxy-1,4-benzoquinone and 2,5-dihydroxy-1,4-benzoquinone were effectively reduced by protoplasts and formed 1,4-dihydroxy-2,6-dimethoxybenzene and 1,2,4,5,-tetrahydroxybenzene, respectively. Syringaldehyde, syringic acid and protocatechuic acid was not converted into other compounds. However, only protocatechuic acid was detected intracellularly, showing the selective permeability of fungal plasma membrane.

1997-P18

絶対嫌気性ルーメン細菌による非フェノール性ベンジルエーテルの解裂  
渡辺隆司\*<sup>1</sup>、梶川 博\*<sup>2</sup>、工藤 博\*<sup>2</sup>、近藤恒夫\*<sup>3</sup>、城代 進\*<sup>4</sup>、中島由美\*<sup>1</sup>、本田与一\*<sup>1</sup>、桑原正章\*<sup>1</sup>  
\*<sup>1</sup> 京都大学木質科学研究所, \*<sup>2</sup> 農林水産省畜産試験所, \*<sup>3</sup> 農林水産省東北農業試験所、\*<sup>4</sup> 近畿大  
学農学部

Cleavage of non-phenolic benzyl ether bonds by strictly anaerobic rumen bacteria.

Takashi Watanabe<sup>\*1</sup>, Hiroshi Kajikawa<sup>\*2</sup>, Hiroshi Kudo<sup>\*2</sup>, Tsuneo Kondo<sup>\*3</sup>, Susumu Johdai<sup>\*4</sup>, Yumi Nakajima<sup>\*1</sup>, Yoichi Honda<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>National Institute of Animal Industry, <sup>\*3</sup>Tohoku National Agricultural Experiment Station, <sup>\*4</sup>Faculty of Agriculture, Kinki University

Abstract: Fluorescent benzyl ether model compounds with non-phenolic unit were chemically synthesized. The models were incubated with rumen microorganisms under anaerobic conditions in the presence and absence of bactericidal and fungicidal antibiotics. Fluorescent spectrometry of the culture fluid showed that the non-phenolic benzyl ethers were rapidly cleaved by strictly anaerobic rumen bacterial fraction.

1997-P19

白色腐朽菌によるポリエチレンの分解(III)

飯吉由佳、堤 祐司、西田友昭

静岡大学農学部

Polyethylene degradation by white rot fungi.

Yuka Iiyoshi, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract; We previously reported that polyethylene degradation by manganese peroxidase (MnP) required Tween 80 or 20 and Mn(III) generated from Mn(II) in the MnP catalytic cycle but not H<sub>2</sub>O<sub>2</sub> which is recognised to be indispensable for the generation of Mn(III) by MnP. In this study, therefore, Mn(III) formation by MnP without exogenous H<sub>2</sub>O<sub>2</sub>-supply was investigated. Neither Tween 80 nor Tween 20 affected on the Mn(III) formation by MnP very much. The Mn(III) formation was slightly accelerated under oxygen atmosphere, but was strongly restrained under nitrogen atmosphere. Addition of catalase into MnP reaction mixture to decompose endogenous H<sub>2</sub>O<sub>2</sub> did not inhibit the Mn(III) formation. These results indicate that Mn(III) formation by MnP in polyethylene degradation is dependent on oxygen under the condition without exogenous H<sub>2</sub>O<sub>2</sub>.

1997-P20

Differential Display 法による、カワラタケの有害化学物質分解関連遺伝子の検索

飯村洋介、辰巳憲司

工業技術院資源環境技術総合研究所

Isolation of mRNAs induced by a hazardous chemical in white-rot fungus, *Coriolus versicolor*, by differential display.

Yosuke Iimura, Kenji Tatsumi

Department of Hydrospheric Environmental Protection, National Institute for Resources and Environment

Abstract; White-rot fungus *Coriolus versicolor*, a ligninolytic basidiomycete, has been studied because of its ability to degrade hazardous chemicals. In this study, we searched for genes that are induced by a hazardous chemical using the mRNA differential-display technique and *C. versicolor* IFO30340 that has been exposed to pentachlorophenol (PCP). Five cDNA fragments were cloned and the DNA sequences of two fragments were analyzed in further detail. The clones corresponded to novel genes that have not previously been identified in *C. versicolor*. One of the cDNAs exhibited homology to a heat shock protein. The expression of the gene was up-regulated in PCP-treated *C.versicolor*.

1997-P21

リグニン系土壌改良剤の開発(6)–改質リグニンの金属イオンとの相互作用–

齊藤京子、飯塚堯介

東京大学大学院農学生命科学研究科

Development of lignin derivatives as soil conditioning agents (6). – Interaction between modified lignins and metal ions.

Kyoko Saito, Giosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Soil conditioning agents to remove toxic metal ions released in acid soil were prepared by radical-sulfonation and alkaline-oxygen treatment of kraft lignin. Interaction between modified lignins and metal ion ( $Al^{3+}$ ) was investigated using potentiometric titration. It is well known that proton is released by coordination of acidic functional groups in organic compounds to metal ion. The coordination bond between lignin and Al was estimated by the change of shape of titration curves. It was suggested that carboxyl and phenolic groups in modified lignins behave as a ligand, because formation of coordinate bond was clearly observed in the complex of Al and modified lignin by only alkaline-oxygen treatment.

1997-P22

*Daphne odora* におけるリグナン生合成について

奥西智哉、梅澤俊明、島田幹夫

京都大学木質科学研究所

Lignan biosynthesis in *Daphne odora*.

Tomoya Okunishi, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: (–)-Pinoresinol and (+)-matairesinol were isolated from *Daphne odora*. These lignans were (almost) optically pure. In addition, lariciresinol, secoisolariciresinol and isolariciresinol were detected by GC-MS.  $[9,9-^2H_2, OC^2H_3]$ Coniferyl alcohol was administered to this plant, and incorporation of deuterium atoms into several lignans were observed. The results suggested that the step to produce optically pure lignan is the formation of pinoresinol from coniferyl alcohol in *D. odora*.

1997-P23

8-O-4' 型ネオリグナンの *Fusarium solani* M-13-1 による変換(第2報)

岡本茂樹、片山健至

香川大学農学部

Transformation of 8-O-4' neolignans by *Fusarium solani* M-13-1. II.

Shigeki Okamoto, Takeshi Katayama

Faculty of Agriculture, Kagawa University

Abstract:  $\Delta^8$ -4,7-Dihydroxy-3,3'-dimethoxy-8-O-4'-neolignan was prepared by incubation of intact *Fusarium solani* M-13-1 cells with ( $\pm$ )- $\Delta^8$ -4-hydroxy-3,3'-dimethoxy-7-oxo-8-O-4'-neolignan in the presence of  $\alpha$ -oxo-guaiacylglycerol- $\beta$ -vanilfin ether. The neolignan obtained was a mixture of (–)-*erythro* and (+)-*threo* isomers, which were enantiomerically pure. Their absolute configuration were determined with the modified Mosher's method as (7*S*, 8*R*)-(–)-*erythro* and (7*S*, 8*S*)-(+)–*threo*, which would be derived from both enantiomers of the racemic substrate. This fungal reduction seems to be highly enantioselective but of low substrate specificity, indicating that this reduction could be applied to preparation of other 8-O-4' neolignans.

## 第 43 回 (1998.10.26-27) 府中グリーンプラザ

1998-101

ゲニンの水酸基の新しい定量法

片平 類<sup>\*1</sup>、中坪文明<sup>\*1</sup>、Hou-min Chang<sup>\*2</sup>

<sup>\*1</sup> 京都大学大学院農学研究科、<sup>\*2</sup> North Carolina State University

The new method for the quantitative determination of the hydroxyl groups in lignins.

Rui Katahira<sup>\*1</sup>, Fumiaki Nakatsubo<sup>\*1</sup>, Hou-min Chang<sup>\*2</sup>

<sup>\*1</sup> Graduate school of Agriculture, Kyoto University, <sup>\*2</sup> North Carolina State University

Abstract: Lignins have aliphatic hydroxy groups at C- $\gamma$  and C- $\alpha$  positions on the side chain in addition to phenolic hydroxy group at C-4 position of aromatic ring. The chemical and physical properties of lignin are almost determined by these hydroxy groups. Therefore, it is very important to determine these hydroxy group contents in lignins. Several methods for quantitative determination of three hydroxy groups in lignins have been reported. Here, we propose a new method for the quantitative analysis of these three hydroxyl groups.

1998-102

酢酸リゲニンの性質及び利用

藩 学軍、佐野嘉拓

北海道大学農学部

Xue-Jun Pan, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Acetic acid lignins from rice straw (R-AcL), birch (B-AcL) and fir (F-AcL) were methylolated by three routes: direct methylolation with formaldehyde, condensation with phenol formaldehyde resins and methylolation after phenolization. By the third route, as many as 6-8% methylol groups could be introduced into the lignins. Thermo-setting adhesive with acceptable bonding strength was made from F-AcL in a ratio of 2: 1 (lignin to phenol). Cold-setting adhesives were also prepared with satisfactory bonding quality from both F-AcL and B-AcL in a proportion of 2 : 1 : 1.2 (lignin/phenol/resorcinol).

1998-103

ケナフ靱皮繊維からの高粘度溶解用パルプの調製法

ビブチ・B・マズンダル、程 舟、大谷慶人、鮫島一彦

高知大学農学部

Pulping method of kenaf bast fiber for high viscosity pulp.

Bibhuti B. Mazumder, Chen Zhou, Yoshito Ohtani, Kazuhiko Sameshima

Faculty of Agriculture, Kochi University,

Abstract: In order to obtain high viscosity pulp from kenaf bast, a combination of Amox pretreatment, soda pulping under normal pressure and chlorite bleaching is found the most suitable method. The pulp viscosity did not directly correlate to the fiber length or the carbohydrate composition of kenaf bast pulp, but it rather depends on the treatment history of the pulping.

1998-104

酸素漂白過程における酸化反応の解析

童 国林、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Quantitative analysis of oxidation reaction during oxygen-alkali bleaching.

GuolinTong, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, The University of Tokyo

Abstract: Residual lignin and residual hemicellulose were isolated from unbleached softwood kraft pulp. They were separately or as a mixture, subjected to alkali treatment with or without oxygen, and the change in the permanganate consumption during the treatment was analyzed. The permanganate consumption by the isolated residual lignin decreased to about one third of the initial value by prolonged oxygen alkali treatment whereas it changed only to a minor extent when oxygen was absent. Contrary to this, permanganate consumption by the isolated residual hemicellulose increased significantly during the alkali treatment without regard to the presence of oxygen. This result indicates that new structures, which consume permanganate, are produced from hemicellulose even during a weak alkali treatment such as oxygen bleaching and these can not be oxidized by oxygen. By taking those into account, the progress and the extent of the lignin oxidation during oxygen-alkali bleaching of kraft pulp was reevaluated.

1998-105

リグニンのオゾン酸化過程で生じるラジカル反応の抑制

真柄謙吾<sup>\*1</sup>、富村洋一<sup>\*1</sup>、細谷修二<sup>\*1</sup>、池田 努<sup>\*2</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 筑波大学農林工学系

Suppression of radical reaction caused during ozonation of lignin.

Kengo Magara<sup>\*1</sup>, Yoichi Tomimura<sup>\*1</sup>, Shuji Hosoya<sup>\*1</sup>, Tsutomu Ikeda<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Tsukuba University

Abstract: Ozone reacts with lignin through two pathways. One is an ionic reaction which generates muconic acid derivatives and hydrogen peroxide. The other one is a radical reaction. The first step of which is the one electron oxidation of dissociated phenolic OH and thus the radical chain reactions are initiated. To control the initiation of radical reactions which brings about the non-selectivity of ozone reactions, ozonation was performed at quite low pH for the purpose of suppressing the dissociation of phenolic OH. The result showed that even at pH 0.7, the amount of hydrogen peroxide formed by the ionic reactions was 1 mmol more for veratryl alcohol (non-phenolic) than that for vanillyl alcohol (phenolic). To explain the difference in the yield of hydrogen peroxide, we have investigated the H<sub>2</sub>O<sub>2</sub>-stabilizing effect of MeOH since a doublet amount of MeOH was formed from veratryl alcohol and MeOH is known as a radical scavenger. Furthermore, hydrogen peroxide is also formed by the reaction of MeOH with ozone. But, both possibilities were neglected.

1998-106

リグニン立体構造の解析を目的としたオゾン分解法の定量性の検討

秋山拓也、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Investigation of lignin stereo structure by ozonation.

Takuya Akiyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Ozonation method as an analytical tool of stereo-structure of lignin was reexamined by the use of a lignin model compound veratrylglycerol- $\beta$ -guaiacyl ether (VG). The yield of erythronic and threonic acids from VG was found to be 58%, which was higher than that formerly reported. Prolonged ozonation (20 min to 120 min) did not result in a significant yield loss of these products. Contrary to this, when erythronic and threonic acid in their free acid form were subjected to ozone treatment, their recovery decreased with prolonged reaction time. However, if the reaction

mixture were reduced by sodium thiosulfate, their recovery was improved. *Erythro* and *threo* ratio of VG determined based on the yield of ephronic acid and threonic acid was slightly higher than the ratio determined by <sup>1</sup>H-NMR. Reproducibility of the GC determination of the products was quite satisfactory when ozonation products were trimethylsilylated from their ammonium salts by a mixture of HMDS and TMSCl in DMSO.

#### 1998-特別講演 I.

The challenges and opportunities of lignin.

Wolfgang G. Glasser

Virginia Polytechnic Institute and State University

Abstract: Lignin comprises approximately 1/4 of the earth's biomass production of estimated 10<sup>10</sup> tops per year. In the process of pulp and paper production, approximately one ton of lignin is separated from biomass for each two tons of paper produced. This means that approximately 100 million tons of lignin are commercially separated from biomass annually worldwide. Only about one percent of that amount is actually recovered from spent pulping liquors for commercial, non-fuel uses. Virtually all of the approximately one million tons of lignin co-generated from pulp and paper operations in the world annually are marketed as water-soluble lignin sulfonate derivatives (Table I). The worldwide value of this market is estimated to be \$600 million per year (1). Lignosulfonates have captured the majority of the industrial ionic surfactant markets owing to their favorable price/performance relationship. Prominent uses are in concrete admixtures, animal feed, oil well drilling muds, and dust control agents. Having satisfied major commodity markets, lignosulfonate producers are now focusing on markets for specialty water-soluble polymers. Since the majority of lignin is separated from biomass in non-sulfonated form, as water-insoluble polymer, the potential exists for lignin to become a competitor in the market for structural polymers, adhesives, and composites. The use of lignin in thermosets and thermoplastics requires a significant level of understanding regarding the structure-property relationships of the polymeric resource. This understanding concerns in particular (a) the chemistry of the basic repeat unit structure(s); (b) the nature of the intermonomer bonds; (c) the size and weight distributions of the molecular mixture; and (d) aspects of the inter/intramolecular interactions. This paper deals with a review of the current state-of-art of the quantitative analysis of lignin's chemical and molecular structure, and on techniques qualified to characterize the performance of lignin in thermosetting resins and in melt-processed thermoplastics.

#### 1998 特別講演 II.

リグニン利用の現状と将来展望

町原 晃

日本製紙株式会社

The current usage of lignin and its prospects.

Akira Machihara

Nippon Paper Industries Co. Ltd.

Abstract: Currently, industry utilizes lignosulfonate (obtained from sulfite liquor) and kraft lignin (extracted from kraft black liquor). Demand for lignin products are increasing in the field such as concrete admixtures and dye dispersants. In order to enhance the usefulness of lignin, it is essential that the features of lignin should be characterized and the original properties must be improved to be the value added products and the mass consumption. Also, it is necessary in future to solve technical problems, explore new applications and continually develop the values of lignin.

1998-201

Kapok 繊維の油吸着特性と繊維の化学的・組織学的性状

堀 啓映子<sup>\*1</sup>、Maxima E. Flavier<sup>\*2</sup>、空閑重則<sup>\*1</sup>、飯山賢治<sup>\*3</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> フィリピン大学化学研研究所、<sup>\*3</sup> 東大アジア生物資源環境研究センター

An excellent oil absorbent, Kapok (*Ceiba pentandra* (L.) Gaertn.) fibre: its fibre structural and chemical characteristics.

Keko Hori<sup>\*1</sup>, Maxima E. Flavier<sup>\*2</sup>, shigenori Kuga<sup>\*1</sup>, OKenji Iiyama<sup>\*3</sup>

<sup>\*1</sup> Graduate School of Agriculture and Life Sciences, the University of Tokyo, <sup>\*2</sup> Institute of Chemistry, the University of Philippines, <sup>\*3</sup> ANESC, the University of Tokyo

1998-202

リグニンと古紙を原料とする成形活性炭の吸着性能

久保智史<sup>\*1</sup>、浦木康光<sup>\*1</sup>、佐野嘉拓<sup>\*1</sup>、陳 克利<sup>\*2</sup>

<sup>\*1</sup> 北海道大学農学部、<sup>\*2</sup> 秋田県立農業短期大学

Adsorption property of molded activated carbon prepared from lignin and waste paper.

Satoshi Kubo<sup>\*1</sup>, Yasumitsu Uraki<sup>\*1</sup>, Yoshihiro Sano<sup>\*1</sup>, Ke-Li Chen<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Hokkaido University, <sup>\*2</sup> Akita Prefectural College of Agriculture

Abstract: The activated carbon (AC) with sheet shape (ACS) which was a new type of molded AC was prepared from the mixture of isolated lignins and waste news paper. The adsorption capacities of ACSs were higher than those of commercial powdery and granulated ACs. Particularly, ACSs prepared from acetic acid lignin (AL) showed the excellent adsorption capacity: iodine 1,350 mg/g; metylene blue 225 mg/g and *p*-chlorophenol 1,250 mg/g, respectively. Furthermore, *p*-chlorophenol adsorption rate of AL-ACSs was faster than that of the commercially granulated activated carbon. These results revealed that AL was an effective material for molded activated carbon. The ratio of internal surface to external surface area of AL-ACSs from nitrogen sorption was much higher than that of commercial powdery AC, suggesting that the excellent adsorption capacity of AL ACS was based on development of meso- and micro-pores which acts as adsorption sites.

1998-203

ヒドロキシプロピル化リグノセルロースの性質

半崎亜希子、浦木康光、佐野嘉拓

北海道大学農学部

Characteristics of hydroxypropylated lignocellulose.

Akiko Hanzaki, Yasumitsu Uraki, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Hydrophobically associating water-soluble polymers (HAWSP) have been focused on their unique theological properties and the functions as inclusion compounds for drugs and proteins. HAWSP was prepared from acetic acid pulp (AWP) by hydroxypropylation. The association of hydroxypropylated AWP (HP-AWP) was found to occur in water, and even in chloroform by TEM observation and viscometric measurement. The interactions between HP-AWP molecules in water and in organic solvent seemed to be due to the hydrophobic interaction of residual lignin and to hydrogen bonding of polysaccharides, respectively. HP-AWP was suggested to have an excellent complexation ability to low molecular-mass compounds. With respect to the interaction with biopolymer, HP-AWP was also indicated to play a role as a stabilizer that prevented protease (papain) from its autolysis.

1998-204

リグニン及びリグニン関連型フェノールを原料とするエポキシ樹脂の調製と熱的性質

畠山兵衛<sup>\*1</sup>、吉田考範<sup>\*1</sup>、谷口 誠<sup>\*1</sup>、永田 茂<sup>\*1</sup>、広瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>物質工学研究所、<sup>\*3</sup>大妻女子大学家政学部

Preparation and thermal properties of epoxy resins derived from lignin and lignin-related phenol.

Hyoe Hatakeyama<sup>\*1</sup>, Takanori Yoshida<sup>\*1</sup>, Makoto Taniguchi<sup>\*1</sup>, Shigeru Nagata<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Fukui University of Technology, <sup>\*2</sup>National Institute of Materials and Chemical Research,

<sup>\*3</sup>Otsu Women's University

Abstract: Epoxy prepolymers were synthesized from alcoholysis lignin (AL), and lignin-related phenols such as *p*-hydroquinone and methoxy-*p*-hydroquinone by reaction with epichlorohydrin. Epoxy resins were synthesized from the above prepolymers by reaction with poly(azelaic anhydride). The molar ratios of acid anhydride groups to epoxy groups ([AA]/[EPOXY] ratios) were varied at 10/10 and 12/10. The thermal properties of the obtained prepolymers and epoxy resins were studied by differential scanning calorimetry (DSC), thermogravimetry (TG) and TG-Fourier transform infrared spectroscopy (FTIR). Glass transition temperatures ( $T_g$ 's) increased with increasing [AA]/[EPOXY] ratios. Thermal degradation temperatures ( $T_d$ 's) of epoxy resins were almost constant regardless of [AA]/[EPOXY] ratios, suggesting that the curing of prepolymers with poly(azelaic anhydride) does not affect  $T_d$  values. The intensities of absorption peaks at 2900  $\text{cm}^{-1}$  (CH) and 1730  $\text{cm}^{-1}$  (C=O) in IR spectra of the evolved gases during thermal degradation increases with increasing [AA]/[EPOXY] ratios.

1998-205

分子状酸素によるアルデイトール類の直接酸化

前川 巖、横山朝哉、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Direct oxidation of alditols by molecular oxygen.

Iwao Maekawa, Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Alditols can be easily oxidized by oxygen-alkali treatment without any active oxygen generator such as a phenolic compound. When alditol (xylitol, D-arabinitol or ribitol) was treated at 95°C, the oxidation was quite rapid and no induction period seemed to be present until the oxidation started. However, when the reaction was carried out at 55°C or 70°C, the presence of induction period was clearly observed. The induction period at these temperatures increased when a small amount of a known stabilizer of peroxides (diethylenetriaminepentamethylene-phosphonic acid, DTMPA) was added to the reaction system. These observations suggest that the oxidation of alditols during oxygen-alkali treatment proceeds by an auto-oxidation type reaction, which consists of an initiation reaction (direct reaction of alditols and molecular oxygen) and the following chain oxidation type reaction. The fact that the addition of DTMPA did not result in a visualization of induction period at 95°C seems to indicate that the direct reaction with molecular oxygen is much more important in the oxidation of alditols at this temperature than at lower temperature, but no direct proof for this was obtained.

1998-206

リグニンの熱分解: グァイアシルグリセロールおよびコニフェリルアルコール末端基由来の熱分解生成物

黒田健一

筑波大学農林工学系

Analytical pyrolysis of lignin: pyrolysis products derived from guaiacylglycerol moieties and coniferyl alcohol-end groups.

Ken-ichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Pyrolysis products of acetylated lignin model compounds and reference lignins were analyzed to determine guaiacylglycerol moieties and coniferyl alcohol-end groups.

Guaiacylglycerol- $\beta$ -coniferyl ether tetraacetate produced 3-(4-hydroxy-3-methoxy-phenyl)-propyl acetate **1**, 3-(4-acetyloxy-3-methoxyphenyl)-propyl acetate **2**, and 3-(4-acetyloxy-3-methoxyphenyl)-prop-2-enyl acetate **3**. Guaiacylglycerol- $\beta$ -guaiacyl ether triacetate produced **2** and **3**. These findings suggested that **1** is indicative for coniferyl alcohol-end groups, and **2** and **3** for guaiacylglycerol moieties. Acetates of reference lignins, synthetic lignins, Japanese cedar wood, its dioxane lignin, and Japanese Douglas fir wood, also produced **1-3**. Large differences in yields of **1-3** were observed among the acetylated lignins. Pyrolysis using acetylated samples is effective for analyzing guaiacylglycerol moieties and coniferyl alcohol-end groups in lignins.

1998-207

熱分解ガスクロマトグラフィーによるユーカリ中のリグニンの樹幹内変異の解析

横井裕明<sup>\*1</sup>、石田康行<sup>\*1</sup>、大谷 肇<sup>\*1</sup>、柘植 新<sup>\*1</sup>、園田哲也<sup>\*2</sup>、小名俊博<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院工学研究科、<sup>\*2</sup>王子製紙株式会社森林資源研究所

Characterization of within-tree variation of lignin in *Eucalyptus camaldulensis* by pyrolysis-gas chromatography.

Hiroaki Yokoi<sup>\*1</sup>, Yasuyuki Ishida<sup>\*1</sup>, Hajime Ohtani<sup>\*1</sup>, Shin Tsuge<sup>\*1</sup>, Tetsuya Sonoda<sup>\*2</sup>, Toshihiro Ona<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Engineering, Nagoya University, <sup>\*2</sup>Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: Pyrolysis-gas chromatography (Py-GC) using a vertical micro furnace pyrolyzer was applied to the detailed estimation of "the within-tree variation" of the ratio of syringyl and guaiacyl units (S/G ratio) for lignin in *Eucalyptus camaldulensis*. On the pyrogram of the *Eucalyptus* obtained at 450°C, many characteristic peaks derived from syringyl and guaiacyl units of lignin were reproducibly observed together with those from cellulose and hemicellulose. On the basis of the intensities of these characteristic peaks, "the within-tree variation" of the S/G ratio for lignin were estimated rapidly using  $\mu\text{g}$  order of the powdered tree sample, and the obtained results were also discussed comparing with those obtained by the thioacidolysis method.

1998-208

コーヒー酸の酸化的二分子縮合における反応機構の考察

田崎弘之、田口大祐、鍋田憲助

帯広畜産大学生物資源学部

Reaction mechanism of oxidative bimolecular condensation of caffeic acid.

Hiroyuki Tazaki, Daisuke Taguchi, Kensuke Nabeta

Department of Bioresource Science, Obihiro University of Agriculture and Veterinary Medicine

Abstract: We examined a formation of furofuran-type lignan 2,6-*exo*-bis(3,4-dihydroxyphenyl)-3,7-dioxabicyclo[3.3.0]octane-4,8-dione (**4**) from 3,4-dihydroxycinnamic acid (caffeic acid, **1**) with  $\text{NaIO}_4$ , as a model of bimolecular condensation. The first step of bimolecular condensation was thought as the oxidation of **1** to highly reactive  $\sigma$ -quinone (**3**). It was confirmed by NMR analysis and the reaction of **3** in MeOH with 1,2-phenylenediamine to produce phenazine derivative. Further

labeling studies by using [8-<sup>13</sup>C] **1** revealed that the condensation occurred between **1** and **3**.

1998-209

クロマツあて材リグニンの形成と構造

斉藤香織、福島和彦、安田征市

名古屋大学農学部

Formation and structure of lignin in the compression wood of *Pinus thunbergii*.

Kaori Saito, Kazuhiko Fukushima, Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: Lignin is considered to be different in coupling type of its component according to a kind of cell or a position of cell wall. In this study, we analyzed lignin by thioacidolysis at the level of monomer or dimer. We prepared 50 mm-thick tangential sections (cambial zone to mature xylem) from compression or normal wood of *Pinus thunbergii*, and analyzed how lignin deposit in the process of cell wall differentiation in secondary xylem. By the dimer analysis, heterogeneity of the inter units linkage in lignin was suggested.

1998-210

The behaviors of deuterium labeled monolignols and monolignol glucoside in lignin biosynthesis.

陳 方、福島和彦、安田征市

名古屋大学農学部

Fang Chen, Kazuhiko Fukushima, Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: To examine the different behavior of monolignol and monolignol glucoside in lignin biosynthesis, pentadeutero[ $\gamma$ ,  $\gamma$ , -D<sub>2</sub>, OMe-D<sub>3</sub>]-coniferyl alcohol and pentadeutero[ $\gamma$ ,  $\gamma$ -D<sub>2</sub>, OMe-D<sub>3</sub>]-coniferin were synthesized and fed to growing trees. The difference in patterns of incorporation of labeled precursors was studied by GC-MS. The results indicate that both precursors can be incorporated into lignin effectively, but the labeled coniferyl alcohol can be incorporated into lignin more directly, resulting high proportion of 5D-labeled guaiacyl and syringyl units in newly formed xylem. On the other hand, labeled coniferin tends to be incorporated into 4D-labeled guaiacyl and syringyl units, releasing one  $\gamma$ -deuterium atom due to oxidation.

1998-211

*In situ* hybridization 法によるリグニン生合成関連遺伝子の発現解析

島田武明\*<sup>1</sup>、川合伸也\*<sup>2</sup>、諸星紀幸\*<sup>1</sup>

\*<sup>1</sup>東京農工大学大学院生物システム応用科学、\*<sup>2</sup>東京農工大学農学部

Expression analysis of lignin-biosynthesis related genes with *in situ* hybridization.

Takeaki Shimada\*<sup>1</sup>, Shinya Kawai\*<sup>2</sup>, Noriyuki Morohoshi\*<sup>1</sup>

\*<sup>1</sup>Graduate School of Bio-application and Systems Engineering, Tokyo University

of Agriculture and Technology, \*<sup>2</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: We have attempted to construct the experimental system of *in situ* hybridization to detect the expression of lignin-biosynthesis related genes in, *Populus kitakamiensis*, hybrid aspen. *In situ* hybridization is widely employed to analyze tissue-specific gene expressions in both plants and animals. With this method, the analysis of tissue-specific gene expression can be achieved in very short term, comparing to other methods such as promoter-GUS assay and so on. In this report, we used one year old stems of *P. kitakamiensis* and detected the *pal* expression in several phloem cells locating cambial zone nearby. This result partially coincided with that of promoter-GUS assay

which was conducted formerly. Although *pa*/expression was detected, now ye are thinking the signal was not intact, therefore further study is necessary to decide the strict localization of *pa*/mRNA and also the identification of isozymes.

1998-212

ダイオキシン分解菌 V2 からのリグニンペルオキシダーゼによるダイベンゾフランの分解

大川浩樹、伊藤和貴、橘 燦郎

愛媛大学農学部

Degradation of 2,4,8-trichlorodibenzofuran by lignin peroxidase produced by fungus V2 having ability for degradation of dioxins.

Hiroki Ohkawa, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: The time-course of the activities of lignin peroxidase (Lip) and dioxygenase from fungus V2 separated by a screening from natural world and a wood-rotting fungus *Phanerochaete chrysosporium* having ability for degradation of dioxins (2,7-Dichlorodibenzo-*p*-dioxin) was measured in connection with the degradation rate of 2,4,8-Trichlorodibenzofuran (2,4,8-TCDF) with two fungi. We tried to isolate Lip by fungus V2 separated by the screening method. Three Lip fractions were purified by DEAE-BioGel A. Three Lip fractions ( I , II. III) degraded 10.5% to 49.7% of 2,4,8-TCDF. The maximum degradation rate of 2,4,8-TCDF was obtained by Lip fraction II-9 when the incubation was conducted for 3 hours after addition of 0.25 mmol of 2,4,8-TCDF to the fraction. The activity of Lip from fungus V2 was higher in the initial stage of the culture. the degradation rate of 2,4,8-TCDF was larger. The activity of Lip from fungus V2 was decreased with the incubation time. the activity kept a constant level after the incubation for 15 days. However, the degradation rate of 2,4,8-TCDF was increased after the incubation for 15 days. The degradation rate of 2,4,8-TCDF was increased with the increase in the activity of dioxygenase from fungus V2. The activity of dioxygenase from fungus V2 was higher, the degradation rate of 2,4,8-TCDF was larger. These results suggested the participation of both Lip and dioxygenase in degradation of 2,4,8-TCDF.

1998-213

白色腐朽菌のリグニン分解に関与する脂質過酸化に関する研究

榎 牧子<sup>\*1</sup>、片山志歩子<sup>\*1</sup>、仲亀誠司<sup>\*1</sup>、本田与一<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>、桑原正章<sup>\*1</sup>、Karin Koller<sup>\*2</sup>、Kurt Messner<sup>\*2</sup>

<sup>\*1</sup> 京都大学木質科学研究所、<sup>\*2</sup> ウィーン工科大学生物化学工学・微生物研究所

Studies on lipid peroxidation during lignin degradation by white-rot fungi

Makiko Enoki<sup>\*1</sup>, Shihoko Katayama<sup>\*1</sup>, Seiji Nakagame<sup>\*1</sup>, Karin Koller<sup>\*2</sup>, Kurt Messner<sup>\*2</sup>, Yoichi ttonda<sup>\*1</sup>, Takashi Watanabe<sup>\*1</sup>, Masaaki Kuwahara<sup>\*1</sup>

<sup>\*1</sup>Wood Research Institute, Kyoto University, <sup>\*2</sup>Research Institute for Biochemical Technology and Microbiology, University of Technology, Vienna

Abstract: White-rot fungus *Coriariopsis subvermispora* is known to decompose cell wall lignin without morphological changes of wood cell walls. Since enzymes cannot penetrate inside of the wood cell walls during this stage, this reaction must be catalyzed by low molecular mass compounds. To elucidate the selective ligninolytic system, we focused on extracellular peroxidizable compounds such as lipid since the peroxidizable compounds can generate active radicals inside of wood cell walls even at the site far from enzymes. Analysis of peroxidizable compounds produced by *C. subvermispora* is reported.

1998-214

## 化学修飾法を用いたリグニンペルオキシダーゼ基質酸化機構の解析

城島 透、割石博之、田中浩雄

九州大学農学部

Spectroscopic and kinetic characterization of chemically modified lignin peroxidase.

Toru Johjima, Hiroyuki Wariishi, Hiroo Tanaka

Faculty of Agriculture, Kyushu University

Abstract: To investigate a reaction mechanism, chemically modified lignin peroxidases were prepared using N-bromosuccinimide (LiP-NBS) and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide with and without 2-aminoethanesulfonic acid (S- and EDC-LiP). Reactivity of LiP against veratryl alcohol (VA), 2,6-dimethoxyphenol, and ferrocyanide was remarkably reduced by the chemical modification. On the other hand, reactivity against 2,2'-azinobis-(3-ethylbenzthiazoline-6-sulfonate), KI, and ferrocyanide was almost unchanged upon the modification. This observation strongly suggests that LiP may have two or more substrate oxidation sites. To further characterize the mechanism, steady state kinetic parameters of modified LiPs on VA oxidation were determined, indicating that the NBS modification reduces all electron transfer efficiency rather than a substrate binding. The effects of the chemical modification on the role of VA in LiP oxidation of ferricytochrome *c* were determined. The extents of the inhibition by the chemical modification using NBS and EDC against VA oxidation and VA-supported oxidation of ferricytochrome *c* were very similar, suggesting that VA binding sites may be the same when acting as a reducing substrate and as a cofactor during ferricytochrome *c* oxidation.

1998-215

## デンドリティックポルフィリンの触媒するペルオキシダーゼ型反応

山中 猛、堤晋一郎、割石博之、田中浩雄

九州大学農学部

Dendritic porphyrin designed for catalyzing peroxidative reaction.

Takeshi Yamanaka, Shinichiro Tsutsumi, Hiroyuki Wariishi, Hiroo Tanaka

Faculty of Agriculture, Kyushu University

Abstract: Lignin peroxidase (LiP) oxidizes a variety of nonphenolic aromatic compounds including chlorinated dibenzo-*p*-dioxins and biphenyls to their aryl cation radicals. To maximize LiP-catalyzing oxidation of those pollutants, a stable one electron oxidation activity in organic media has been expected. Using an iron-*meso*-tetra(4-carboxyphenyl)porphine as a core, which has higher redox potential than the iron-protoporphyrin IX, the dendritic porphyrin was synthesized to mimic LiP catalysis. The relationships between the size of dendron (generation 1 (G1) to G4) and LiP activity, peroxide-derived inactivation, and kinetic characteristics were examined. G4-dendritic porphyrin shows a stable one-electron oxidation activity in organic media via a typical peroxidase catalytic cycle. The addition of imidazole derivatives improved either LiP or peroxidase activity of G4-dendritic porphyrin.

1998-216

## 白色腐朽菌によるポリエチレンの分解(IV)―過酸化水素非存在下での MnP による Mn(III)の生成機構―

飯吉由佳、堤 祐司、西田友昭

静岡大学農学部

Polyethylene degradation by white-rot fungi (IV). -Formation of Mn(III) by MnP in the absence of hydrogen peroxide.

Yuka Iiyoshi, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University,

Abstract: We have investigated the degradation of high-molecular-weight polyethylene membrane by (MnP). The previous study clearly indicated that Mn(III) formed by MnP function closely relates to the polyethylene degradation in the absence of hydrogen peroxide. We, therefore, studied the mechanism for formation of Mn(III) by MnP without hydrogen peroxide supply during polyethylene degradation. The Mn(III) formation was completely inhibited under nitrogen atmosphere and was accelerated by addition of Mn(III) or Mn(IV) in the reaction system. The effect of the Mn(III)-addition was also restrained under nitrogen atmosphere. These results indicate that the reaction of oxygen, Mn(III), and MnP initiates the MnP catalytic cycle. The peroxidation of unsaturated lipid did not participate in the formation of Mn(III) by MnP nor polyethylene degradation in the our system.

1998-217

*Phanerochaete sordida* YK-624 株のマンガンペルオキシダーゼ遺伝子について  
廣末慎嗣<sup>\*1</sup>、平井浩文<sup>\*1</sup>、渡辺吉雄<sup>\*2</sup>、深津武馬<sup>\*1</sup>、倉根隆一郎<sup>\*1</sup>

<sup>\*1</sup>NEDO 複合・工業技術院生命研究所、<sup>\*2</sup>NEDO 複合・メルシヤン中央研究所

Manganese peroxidase genes from the white-rot fungus *Phanerochaete sordida* YK-624.

Shinji Hirotsue<sup>\*1</sup>, Hirofumi Hirai<sup>\*1</sup>, Yoshio Watanabe<sup>\*2</sup>, Takema Fukatsu<sup>\*1</sup>, Ryuichiro Kurane<sup>\*1</sup>

<sup>\*1</sup>NEDO Bioconsortia Program, National Institute of Bioscience and Human Technology, Agency of Industrial Science and Technology, <sup>\*2</sup>Central Research Laboratory, Mercian Corp.

Abstract: We have cloned and sequenced the *mnp* genes encoding isoenzymes of manganese peroxidase (MnP) from the white-rot fungus *Phanerochaete sordida* YK-624 under nitrogen-limiting condition. At least four *mnp* cDNAs were cloned. The predicted amino-acid sequence of these isozymes showed a high degree of identity each other and also highly conserved to MnP families of other white-rot fungi.

1998-218

1-HBT 存在下における非フェノール性  $\beta$ -O-4 型ジリグノールのカワラタケラッカーゼによる芳香環開裂

河合真吾、中川 誠、飛鳥井雅倫、大橋英雄  
岐阜大学農学部

Aromatic ring cleavage of nonphenolic  $\beta$ -O-4 dilignol by laccase of *Coriolus versicolor* in the presence of 1-HBT.

Shingo Kawai, Makoto Nakagawa, Masanori Asukai, Hideo Ohashi

Faculty of Agriculture, Gifu University

Abstract: Aromatic ring cleavage products, 1-(4-ethoxy-3-methoxyphenyl)glycerol- $\gamma$ -formyl ester and 1-(4-ethoxy-3-methoxyphenyl)glycerol- $\beta$ ,  $\gamma$ -cyclic carbonate, were identified as degradation products of nonphenolic  $\beta$ -O-4 lignin substructure model compound, 1,3-dihydroxy-2-(2,6-dimethoxyphenoxy)-1-(4-ethoxy-3-methoxyphenyl)propane, by a *Coriolus versicolor* laccase in the presence of 1-hydroxybenzotriazole.

1998-219

非水媒体中で機能する界面活性剤-ラッカーゼ複合体-

岡崎信也<sup>\*1</sup>、後藤雅宏<sup>\*1</sup>、古崎新太郎<sup>\*1</sup>、割石博之<sup>\*2</sup>、田中浩雄<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院工学研究科、<sup>\*2</sup>九州大学農学部

Surfactant-laccase complex catalytically active in anhydrous media.

Shin-ya Okazaki<sup>\*1</sup>, Masahiro Goto<sup>\*1</sup>, Shintaro Furusaki<sup>\*1</sup>, Hiroyuki Wariishi<sup>\*2</sup>, Hiroo Tanaka<sup>\*2</sup>

\*<sup>1</sup>Graduate School of Engineering, Kyushu University, \*<sup>2</sup>Faculty of Agriculture, Kyushu University

Abstract: A surfactant-laccase complex was prepared with a nonionic surfactant utilizing water-in-oil emulsions. The complex was easily soluble in anhydrous toluene and effectively catalyzed the oxidation of *o*-PDA in such bitterly harsh environment. In contrast, lyophilized laccase hardly catalyzed the reaction process. The preparation and reaction conditions of the complex have been optimized through studies of the effect of aqueous pH in the W/O emulsions, surfactant concentration, enzyme concentration at preparation stage, and the nature of the organic solvents.

1998-P01

カワラタケの Hsp30 の遺伝子解析

飯村洋介、辰巳憲司

工業技術院資源環境技術総合研究所

Yosuke Imura, Kenji Tatsumi

Department of Hydrospheric and Environmental Protection, National Institute for Resources and Environment

Abstract: White-rot fungus *Coriolus versicolor*, a ligninolytic basidiomycete, has been studied because of its ability to degrade hazardous chemicals. In this study, two genomic DNAs coding for the Hsp30 were isolated from *C. versicolor*. The nucleotide sequences of the two genes differ by 37 base changes within the open reading frames resulting in 3 amino acid substitutions. Three small introns interrupt genomic DNAs. Putative eukaryotic regulatory sequences, CAAT-box and TATA-box, are exist in the promoter regions. The regions contain the consensus heat shock element, xenobiotics response element and metal response element sequences. Northern blot hybridization indicate that the expression of the Hsp30 gene is constitutive at a normal temperature and is accelerated at elevated temperature. That expression level is higher in *C. versicolor* cells that has been exposed to pentachlorophenol.

1998-P02

MnP バイオブリーチングにおける Tween 80 の役割

江原克信、堤 祐司、西田友昭

静岡大学農学部

The role of Tween 80 in biobleaching with manganese peroxidase.

Katsunobu Ehara, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: The role of Tween 80 in biobleaching of hardwood kraft pulp (HWKP) with manganese peroxidase (MnP) was investigated. The most increase of pulp brightness was obtained with Tween 80 among the surfactants, Tween 80, Tween 20, and CHAPSO. The MnP activity assayed in the presence of each surfactant was similarly increased by approximately 1.5 times that of control (no surfactants). Tween 80 had less stabilizing effect on MnP than other surfactants during MnP-biobleaching. Lipid peroxidation of Tween80 during MnP-biobleaching by TBA methods was not noticeable. Neither these characteristics of Tween 80 nor delignification by the radical derived from the lipid peroxidation did not explain the most appreciable effect on the brightness increase by Tween 80.

1998-P03

マンガンを除去した各種クラフトパルプのバイオブリーチング

石村大児、近藤隆一郎、坂井克己

九州大学農学部

Bio-bleaching of various kraft pulps removed manganese by EDTA.

Daiji Ishimura, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: When EDTA-extracted oxygen-bleached hardwood kraft pulp (EDTA-extracted LOKP) was bleached with *Phanerochaete sordida* YK-624, brightness was increased without secretion of manganese peroxidase. In order to clarify this phenomenon, various kraft pulps delignified with chlorine compounds and xylanase were treated with the fungus. When EDTA-extracted oxygen-bleached softwood kraft pulp delignified with chlorine dioxide was treated, the brightness was not increased. When EDTA-extracted unbleached hardwood kraft pulp delignified with chlorine and chlorine dioxide was treated, both pulps were not bleached. Effect of xylanase on biological bleaching of EDTA-extracted LOKP was not observed. Consequently, only EDTA-extracted LOKP was bleached.

1998-P04

シロアリによるリグニンの分解(II)ーイエシロアリによる高分子リグニンの分解ー

平井浩文<sup>\*1</sup>、中川明子<sup>\*1</sup>、渡辺吉雄<sup>\*2</sup>、深津武馬<sup>\*1</sup>、倉根隆一郎<sup>\*1</sup>

<sup>\*1</sup>NEDO 複合・工業技術院生命研究所、<sup>\*2</sup>NEDO 複合・メルシヤン中央研究所

Degradation of lignin by termites. (II). – Degradation of synthetic lignin by *Coptotermes formosanus*. Hirofumi Hirai<sup>\*1</sup>, Akiko Nakagawa<sup>\*1</sup>, Yoshio Watanabe<sup>\*2</sup>, Takema Fukatu<sup>\*1</sup>, Ryuichiro Kurane<sup>\*1</sup>

<sup>\*1</sup>NEDO Bioconsortia Program, National Institute of Bioscience and Human Technology, Agency of Industrial Science and Technology,

Abstract: We examined the degradation of lignin (DHPs) by termite *Coptotermes formosanus*. For 1 week treatment by *C. formosanus*, DHP combined with 4-methylumbelliferone was hardly degraded, and the low-molecular-weight fraction of the DHP was polymerized. <sup>13</sup>C-NMR spectrum of  $\beta$ -<sup>13</sup>C-DHP treated by *C. formosanus* for 12 days suggests that *C. formosanus* unselectively degraded DHP.

1998-P05

広葉樹培養細胞のリグニン生合成における前駆体投与の影響

浜田勝義、堤 祐司、西田友昭

静岡大学農学部

The effect of lignin precursors feeding on lignin biosynthesis in *Populus* calluses.

Katsuyoshi Hamada, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture Shizuoka University

Abstract: Precursors of lignin, ferulic acid (FA) and sinapic acid (SA), were administered to poplar (*Populus alba* L.) callus cultures. FA and SA addition induces increased levels of lignin in poplar calluses. Alkaline treatment of cell wall followed by determination of FA and SA from cell walls and alkaline nitrobenzene oxidation suggest that administered FA is incorporated into both guaiacyl and syringyl lignins, while SA into only syringyl lignin. A marked increase in 4-Coumarate:CoA ligase (4CL) activity against FA was not observed in the calluses cultured with FA-addition. The increased 4CL activity against SA was correlated with the increase in syringyl lignin composition in FA or SA administered calluses. The other class of 4CL which utilizes SA may be induced in poplar calluses by an extraordinarily high level of FA or SA in calluses.

1998-P06

*Anthriscus sylvestris* のリグニンの生合成について

鈴木史朗、梅澤俊明、島田幹夫

京都大学木質科学研究所

Lignan biosynthesis in *Anthriscus sylvestris* Hoffm.

Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: L-[Ring-<sup>13</sup>C<sub>6</sub>]phenylalanine and [9,9-<sup>2</sup>H<sub>2</sub>, OC<sup>2</sup>H<sub>3</sub>]coniferyl alcohol were incorporated into secoisolariciresinol and yatein in *Anthriscus sylvestris* Hoffm. (Umbelliferae). Furthermore, cell-free extracts from the leaves of *A. sylvestris* catalyzed the enantioselective formation of (+)-lariciresinol and (+)secoisolariciresinol from (±)-pinoresinols in the presence of NADPH. The enantiomeric compositions of the lignans formed by the cell-free extracts show the similarity to that in case of *Forsythia* enzyme preparations.

1998-P07

*Linum flavum* var. *compactum* から単離された新規ジベンジルブチロラクトンリグナンについて

三亀啓吾、梅澤俊明、島田幹夫

京都大学木質科学研究所

A new dibenzylbutyrolactone lignan from *L. linum* var. *compactum*.

Keigo Mikame, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: A new dibenzylbutyrolactone lignan 7, 6'-dihydroxyburshehernin was isolated from the methanol extracts of *L. linum* var. *compactum* which is known to contain an antitumor lignan methoxypodophyllotoxin. 7, 6'-Dihydroxyburshehernin was a unique dibenzylbutyrolactone lignan having 3', 4'-methylenedioxy-6'-hydroxy phenyl group.

1998-P08

ネジキにおけるシリングルリグナン生合成の初期反応について

中川貴志、片山健至

香川大学農学部

Initial reactions in syringyl lignan biosynthesis in *Lyonia ovalifolia* var. *elliptica*.

Takashi Nakagawa, Takeshi Katayama

Faculty of Agriculture, Kagawa University

Abstract: *Lyonia ovalifolia* var. *elliptica* contains (+)-lyoniresinol (LYR) which is a syringyl and aryltetrahydronaphthalene lignan. To investigate biosynthesis of (+)-LYR and the related syringyl lignans, feeding experiments of radio-isotopically labeled precursors to excised shoots of the plant were performed. It was found that [8-<sup>14</sup>C]sinapyl alcohol was incorporated into (+)-[<sup>14</sup>C]5,5'-dimethoxyariciresinol (DMLAR) and its glycosides, and (+)-[<sup>14</sup>C]LYR glycosides, but not into [<sup>14</sup>C]5,5'-dimethoxysecoisolariciresinol. The result suggested that an enantiospecific reduction of syringaresinol gave (+)-DMLAR which was then converted to (+)-LYR.

1998-P09

熱分解-質量分析(Py-MS)および多変量解析による草本類リグニンの分析

樺澤直樹、黒田健一

筑波大学農林工学系

Analysis of herbaceous lignins by pyrolysis-mass spectrometry (Py-MS) and multivariate analysis.

Naoki Kabasawa, Ken-ichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba,

Abstract: Several kinds of herbaceous materials were characterized using pyrolysis-mass spectrometry (Py-MS), The mass spectral data were further analyzed by principal component

analysis (PCA) and factor analysis (FA) in order to investigate the relationships between pyrolysis products and samples. PCA clearly showed the differences in fractions and growth stages of the samples, quantitative analysis of lignin by Py-MS and FA was examined. The results showed the correlation between acetyl bromide lignin content and factor score of FA.

1998-P10

塩素漂白で生成した高分子有機塩素化合物の環境中での挙動(3)酸化リグニンの熱分解生成物中に見出されるアルカンタイプ構造の起源について

幸田圭一、新谷博幸、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Environmental fate of high molecular weight chloroorganics produced by chlorine bleaching. (3).

Origin of alkane type structures detected in pyrolysis products from oxidized lignins.

Keiichi Koda, Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Pyrolysis gas chromatographic analysis showed that alkane type structures were produced as major pyrolysis products of oxidized lignins. Therefore, the authors assumed these structures might originate directly from oxidized aromatic structures of lignin when they underwent pyrolytic decomposition. By the further study, however, we have come to the conclusion that some unknown structures (i.e. extracts from wood) extracted together with lignin from unbleached kraft pulp are the main source of these alkane type structures. We'll also report the structural modification of extract components during bleaching, the knowledge of which is very limited.

1998-P11

FT-Raman 分光法を用いたリグニン S/G 比の非破壊的な定量

小名俊博、園田哲也、伊藤一弥、柴田 勝

王子製紙株式会社森林資源研究所

Non-destructive determination of lignin syringyl/guaiacyl monomeric composition in native wood by Fourier transform Raman spectroscopy.

Toshihiro Ona, Tetsuya Sonoda, Kazuya Ito, Masaru Shibata

Kameyama Research Center. Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: The feasibility of using FT-Raman spectroscopy for rapid non-destructive determination of lignin syringyl/guaiacyl (S/G) monomeric composition was examined using *Eucalyptus camaldulensis* and *E. globules*, including samples of various ages and colors, which are of importance as a plantation source. The application of 2nd derivatives transformation of Raman spectroscopic data revealed highly significant correlations between wet chemical and Raman predicted values with correlation coefficient ( $r$ ) = 0.998 and standard error of prediction (SEP) <0.07 points in the calibration (for known samples), and  $r=0.935$  and  $SEP<0.32$  points in the prediction (for unknown samples) respectively. Consequently, this non-destructive method has proved its validity for analyzing *Eucalyptus* native wood meal samples, regardless of their age and color to determine lignin S/G monomeric composition. Using FT-Raman spectroscopy, elite tree selection based on quality aspects for pulp and paper production can be performed.

1998-P12

マングローブ樹皮タンニンの性状

荻 陽子\*<sup>1</sup>、大井 洋\*<sup>1</sup>、大原誠資\*<sup>2</sup>

\*<sup>1</sup> 筑波大学農林工学系、\*<sup>2</sup> 森林総合研究所

Characteristics of tannins from the bark of *Sonneratia caseoralis*.

Yoko Ogi<sup>\*1</sup>, Hiroshi Ohi<sup>\*1</sup>, Seiji Ohara<sup>\*2</sup>

<sup>\*1</sup>Institute of Agricultural and Forest Engineering, The University of Tsukuba, <sup>\*2</sup>Forestry and Forest Products Research Institute

**Abstract:** Chemical characteristics of tannin components from the bark of *Sonneratia caseoralis* were investigated. The bark contained 15.9% polyphenols, 4.2% flavanols and 4.9% tannins. From the ethyl acetate extracts of 70% acetone aqueous extracts, gallic acid was isolated. The acetone aqueous extracts from the bark were submitted to both pyrolysis gas chromatography and on-line methylation pyrolysis gas chromatography. Consequently, it has been made clear that pyrogallol and 3,4,5-trimethoxybenzoic acid methyl ester were the main products of pyrolysis gas chromatography and on-line methylation pyrolysis gas chromatography, respectively. These results indicate that the bark of *S. caseoralis* contains condensed tannins with more amounts of pyrogallol-type B-rings in more amounts than with catechol-type B-rings, and that hydrolysable tannins are the main tannin components of *S. caseoralis*.

1998-P13

南洋材含有アントラキノン類の迅速な定量およびチーク材抽出物の蒸解助剤効果

大井 洋

筑波大学農林工学系

Rapid analysis of quinones in tropical hardwoods and catalytic effects of teak extract on pulping.  
Hiroshi Ohi

Institute of Agricultural and Forest Engineering, The University of Tsukuba

**Abstract:** Teak (*Tectona grandis*) wood contains 2-methyl anthraquinone (MAQ), which is an effective catalyst for alkaline pulping woods and other lignocellulosics. Pyrolysis-gas chromatography (Py-GC) was found to be a useful method for the rapid determination of MAQ and anthraquinone (AQ) in a very small amount of wood, bark and other samples. Teak heartwood of wood samples from Myanmar was shown to contain 0.47–1.10% MAQ, but not AQ. The sapwood, the bark, and other tropical hardwoods (approximately 20 species) did not contain MAQ at all. The teak wood samples were extracted with some organic solvents. The extract contents were 7.0–9.9%, and the results from GC showed that MAQ was approximately 5% of the extract. Compared with the GC method accompanied by extraction, the Py-GC method is very useful in searching for a plant which contains anthraquinones. Genetic modification of trees to produce MAQ that catalyzes their own pulping is an attractive topic. The alkaline pulping of eucalyptus (*Eucalyptus camaldulensis*) wood was carried out in the presence of 0.6% teak extract (0.06% as MAQ) and of 0.06% synthesized MAQ. The teak extract had better effects on delignification.

1998-P14

酸素-アルカリ漂白過程における多糖類の分解機構(10)

横山朝哉、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Degradation mechanisms of carbohydrate during oxygen-alkali bleaching process. (10).

Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

**Abstract:** A cellulose model compound, methyl  $\beta$ -D-glucopyranoside (MGP) and a non-phenolic lignin model compound, 3,4-dimethoxybenzyl alcohol (veratryl alcohol, VA) or 1-(3,4-dimethoxy-phenyl)-1,2-ethanediol (veratryl glycol, VG), were subjected to oxygen-alkali treatments with 2,4,6-trimethylphenol which was an active oxygen generator in this system. The degradation of VG was much larger than the degradation of VA under high pH. This indicates that the

side chain part of lignin model compounds participates in the reaction with active oxygen species more than the aromatic part does under high pH. Reaction selectivity was higher when VG was used as a non-phenolic lignin model compound than when VA was used as that under high pH, but the reverse was the case under low pH.

1998-P15

免疫法によるクラフト蒸解中のグルコマンナンおよびキシランの挙動の可視化

今井貴規、左合章太郎、安田征市

名古屋大学農学部

Visualization of the behaviors of glucomannan and xylan during kraft pulping by immunomicroscopical technique.

Takanori Imai, Shotaro Sago, Seiichi Yasuda

School of Agricultural Sciences, Nagoya University

The distribution of glucomannan and xylan in pine wood was visualized by immunomicroscopy at various stages of kraft pulping to investigate their behaviors during the pulping. Using anti-glucomannan antibody, secondary wall was entirely immuno-labeled in non-kraft treated wood, whereas in kraft treated wood lumen side of secondary wall was labeled preferentially. Using anti-xylan antibody, the lumen side was preferentially immuno-labeled in both non-kraft treated wood and kraft treated wood. These results indicate that during kraft pulping glucomannan and xylan were dissolved in pulping liquor in cell wall, and the hemicelluloses moved to lumen side of cell wall with diffusion of pulping liquor and were concentrated in this side, then eluted from wood.

1998-P16

未利用プランテーションバイオマスの有効利用開発:ココナッツ・コアイアダストからの土壌改良材の調製とその性状

市川朋子<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学アジア生物環境資源研究センター

Effective utilization of plantation waste biomass. -Soil conditioner from coconut coir dust.

Tomoko Ichikawa<sup>\*1</sup>, Gyosuke Mesitsuka<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

Graduate School of Agricultural and Life Sciences, the University of Tokyo, Asian Natural Environmental Science Center, the University of Tokyo

Abstract: There are many plantations producing latex, palm oil, coconut oil, sugar, cacao coffee beans, and so on, in tropical region. Huge quantities of waste and residue are produced during harvesting commercial products and replanting. The most of these waste and residues are not effectively utilized yet. It is significant important for conservation of global environmental and sustainable production of biomass to utilize these wastes and residue. In this paper, we focused coconut coir fiber (CCF) and coir dust (CCD) to develop their effective utilization. Chemical composition of these materials were analyzed and its structural feature were characterized. Both CCF and CCD were carboxymethylated to be utilized as soil conditioner. The Cm-CCF and CM-CCD were fractionated into water-soluble and insoluble fractions and characterized their chemical feature. Then their water absorbitivity was examined.

1998-P17

酸リグニンより可溶性アリールリグノスルホン酸および陽イオン交換樹脂の調製

浅野敦子、安田征市

名古屋大学農学部

Preparations of soluble aryllignosulfonic acid and cation exchange resin from acid lignin.

Kyoko Asano, Seiichi Yasuda

School of Agricultural Sciences, Nagoya University

Abstract: Preparations of soluble aryllignosulfonic acid and cation exchange resin from gymnosperm sulfuric acid lignin (Klason lignin) (SAL) were tried. Soluble aryllignosulfonic acid was prepared from SAL by sulfuric acid-catalyzed phenolation, chlorosulfonation and final alkali hydrolysis. Reaction mechanism was confirmed in a separate experiment with a model compound. Furthermore, cation exchange resin was prepared by a series of reactions of SAL, that is, resinification with formalin, chlorosulfonation and alkali hydrolysis. Ion exchange capacity of it was 3.2 meq/g.

## 第 44 回 (1999.10.7-8) 岐阜大学農学部

1999-101

スギ胚へのパーティクルガン法による遺伝子導入

田仲徹称、七澤雅治、諸星紀幸

東京農工大学大学院生物システム応用科学研究所

Gene introduction into Sugi embryo with particle bombardment.

Tetsuya Tanaka, Masaharu Nanasawa, Noriyuki Morohoshi

Graduate School of Bio-application and Systems Engineering, Tokyo University of Agriculture and Technology

Abstract: Lignin is one of the major components in woody plant cell wall. The quantity and quality of lignin have an influence on the pulping and the biomass utilization. In the future, their improvement will be required for utilization of the biomass more effectively. In this study, we tried to regenerate Sugi (*Cryptomeria japonica* D. Don), which is a useful conifer in Japan, and to establish a transformation system of Sugi. We succeeded to introduce foreign genes into Sugi embryo with particle bombardment.

1999-102

細胞壁の木質化に関与する酵素の局在

高部圭司<sup>\*1</sup>、伊藤真記<sup>\*2</sup>、竹内美由紀<sup>\*1</sup>、藤田 稔<sup>\*1</sup>、片山義博<sup>\*3</sup>

<sup>\*1</sup> 京都大学大学院農学研究科、<sup>\*2</sup> 日本製紙株式会社、<sup>\*3</sup> 東京農工大学大学院 BASE

Distribution of enzymes involved in lignification of cell wall.

Keiji Takabe<sup>\*1</sup>, Masaki Ito<sup>\*2</sup>, Miyuki Takeuchi<sup>\*1</sup>, Minoru Fujita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*3</sup>

<sup>\*1</sup> Graduate School of Agriculture, Kyoto University, <sup>\*2</sup> Nippon Paper Industries Co. Ltd., <sup>\*3</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology

Abstract: One of the most characteristic phenomena in woody plants is lignification of cell walls. Almost all of the enzymes involved in lignification are now well known. However, much more works are needed to elucidate the localization of these enzymes in the cell, relation of enzymes to cell differentiation, and regulatory mechanism of synthesis of these enzymes. We applied the immunocytochemistry by using the antibodies against the enzymes involved in lignification, and showed the enzymes involved in biosynthesis of monolignols are synthesized at polysomes and then are dispersed into the cytosol of the lignifying cells. Therefore, monolignols are synthesized in the cytosol and transported to the cell wall by passing through the plasma membrane. On the contrary, the enzyme involved in dehydrogenative polymerization of monolignols is synthesized in rough endoplasmic reticulum and transported to lignifying cell walls via the Golgi apparatus. Finally

lignification occurs in the cell walls.

1999-103

ケナフ (*Hibiscus cannabinus*) 靱皮、コア及び根の細胞壁成分の生長にともなう変化と光合成能  
Thi Bach Tuyet Lam<sup>\*1</sup>、角園敏郎<sup>\*2</sup>、飯山賢治<sup>\*3</sup>

<sup>\*1</sup>School of Biochemistry, La Trobe University, <sup>\*2</sup> 森林総合研究所、<sup>\*3</sup> 東京大学アジア生物資源環境  
研究センター

Core and root of maturing kenaf (*Hibiscus cannabinus*).

Thi Bach Tuyet Lam<sup>\*1</sup>, Toshio Sumizono<sup>\*2</sup>, Kenji Iiyama<sup>\*3</sup>

<sup>\*1</sup>School of Biochemistry, La Trobe University, <sup>\*2</sup>Forestry and Forest Products Research Institute,  
<sup>\*3</sup>Asian Natural Environmental Science Centre, the University of Tokyo

1999-104

リグニン化学構造の不均一性(3)–TMSiI を用いたエンドワイズリグニンの評価–  
掘啓映子、飯塚堯介

東京大学大学院農学生命科学研究科

Structural heterogeneity of hardwood lignin. (3). – Estimation of endwise lignin fraction by TMSiI  
treatment.

Keko Hori, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Endwise lignin fraction, was composed mostly of syringyl units and  $\beta$ -O-4  
intermonomer linkages, was found in birch periodate lignin. The endwise lignin fraction should be  
cleaved to monomer by TMSiI (trimethylsilyl iodide) under a very mild condition. Sinapyl alcohol was  
the main peak of GC chromatogram after TMSiI treatment for 3hr, but the yield was not very high.  
Syringylpropane monoiodide was detected by GC analysis after 72hr TMSiI treatment, but the peak  
was not detected after Zn treatment. The molecular weight distribution after Zn treatment is now  
under investigation.

1999-105

リグニンの三次元構造の推定方法に関する考察

寺島典二

名古屋大学

Possible approaches for estimating three dimensional structure of lignin.

Noritsugu Terashima

Nagoya University

Abstract: Lignin structural models proposed in the past provide information insufficient to  
predict chemical behavior of lignin in the cell wall. An advanced 3D structural model should contain  
information on structural heterogeneities and macromolecular properties as follows; (1) distribution  
and frequencies of different kinds of units, functional groups, inter-unit bonds, lignin-polysaccharide  
bonds in lignin macromolecule and in the cell walls, (2) higher order structure and size of lignin  
macromolecule, and (3) 3D assembly of lignin and polysaccharides in different morphological regions  
of cell walls and in different kinds of cells. Based on the information obtained by non-destructive  
analyses employing improved radio- and stable isotope tracer methods combined with the  
information by electron microscopy and other various destructive analyses, a 3D model can be  
proposed tentatively. For further revision of the model, improvements of the approaches to get more  
reliable information especially on (3) are required.

1999-106

TOF-SIMS イメージによるリグニン構造解析の試み

福島和彦<sup>\*1</sup>、陳 方<sup>\*1</sup>、山内一慶<sup>\*1</sup>、安田征市<sup>\*1</sup>、高橋元幾<sup>\*2</sup>、星 孝弘<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>アルバック・ファイ株式会社

Analysis of lignin structure by TOF-SIMS

Kazuhiko Fukushima<sup>\*1</sup>, Fang Chen<sup>\*1</sup>, Kazuchika Yamauch<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Motoki akahash<sup>\*2</sup>, Takahiro Hoshi<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>ULVAC-PHI. Inc.

Abstract: The structure of lignin of tree xylem was investigated by TOF-SIMS. Pine and beech MWLs gave some secondary ions which had guaiacyl or syringyl nuclei on TOF-SIMS analysis. Deuterium labeled magnolia xylem fed with phenylalanine-d<sub>7</sub> gave the image which represent the localization of deuterium on the surface of xylem on TOF-SIMS analysis.

1999-107

リグニンの熱分解:  $\beta$ -5 型構造由来の熱分解生成物

黒田健一

筑波大学農林工学系

Analytical pyrolysis of lignin: pyrolysis products derived from the  $\beta$ -5 building blocks.

Ken-ichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Dehydrodiconiferyl alcohol and its related compounds **II-V** were pyrolyzed at 500°C for 4s. The predominance of 4-methylguaiacol (a 27 % (mol/mol) yield from **I**) was observed in the monomeric products, suggesting that in pyrolysis of lignins parts of 4-methylguaiacol are derived from the  $\beta$ -5 building blocks. Pyrolysis product profile of **I** methylated by diazomethane showed that the products derived from the  $\beta$ -5 building blocks are extensively derived from the A ring-moiety in the  $\beta$ -5 building blocks. Comparison of the product yields from **I** with those from a Japanese cedar wood and its lignins suggested that the contributions of the  $\beta$ -5 building blocks are large to the formation of 4-methylguaiacol in pyrolysis of lignins.

1999-108

過マンガン酸カリウム酸化分解の新たな触媒を用いた改良法の開発

辻 幸子<sup>\*1</sup>、諸星紀幸<sup>\*1</sup>、大森茂俊<sup>\*2</sup>

<sup>\*1</sup>東京農工大学大学院生物システム応用科学研究所、<sup>\*2</sup>ニューヨーク州立大学

A potassium permanganate oxidation method modified with new catalysis.

Yukiko Tsuji<sup>\*1</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Shigetoshi Omori<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bio-application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Department of Paper Science and Engineering / ESPRI SUNY, Collage of Environmental Science and Forestry

Abstract: Potassium permanganate oxidation of lignin is a very important method to be able to obtain information about lignin chemical structures, and the higher the yield of degradation products is, the more useful the method will become. Then we tried to modify the method by addition of catalysis, cetyltrimethylammonium bromide, in order to increase the yield of degradation products. In conclusion, we got the result that the yield of degradation products of the modified method increased 10%-30% in comparison with control method.

1999-109

TIZ 分解法における  $\alpha$  エーテル構造の反応性

片平 類、中坪文明

京都大学大学院農学研究科

The chemical reactivity of  $\alpha$  ether structure in lignin in the TIZ degradation method.

Rui Katahira, Fumiaki Nakatsubo

Graduate school of Agriculture, Kyoto University

Abstract: Many degradation methods for  $\beta$ -O-4 structure reported so far are usually conducted under acidic or alkaline conditions, resulting in that unexpected secondary condensation reactions are caused. Therefore we have previously developed the quite novel degradation method of the  $\beta$ -O-4 structure in lignins without any secondary side reactions named TIZ method. But the stability of  $\alpha$  ether structure in the degradation reactions by TIZ method has not been recognized. In this study, we showed by  $\beta$ -O-4 lignin model experiments that  $\alpha$  ether structures were not cleaved by TIZ method.

1999-110

過ヨウ素酸化によるリグニン・多糖エーテル結合の定性的及び定量的検討

藤本文<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、Thi Bach Tuyet Lam<sup>\*2</sup>、飯山賢治<sup>\*3</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> La Trobe 大学生化学科、<sup>\*3</sup> 東京大学アジア生物資源環境研究センター

Qualitative and quantitative investigation of ether linkage between lignin and polysaccharide in plant cell walls by periodate oxidation.

Aya Fujimoto<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>, Thi Bach Tuyet Lam<sup>\*2</sup>, Kenji Iiyama<sup>\*3</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup> School of Biochemistry, La Trobe University, <sup>\*3</sup> Asian Natural Environmental Science Center, the University of Tokyo,

Abstract: It is exciting to make clear the structural feature of covalent associations between lignin and wall polysaccharides, so called LCC, because of their important roles for plant physiology and effective utilization of biomass. We are focusing to elucidate linkage positions of direct ether linkages between phenylpropane unit of lignin and glycosidic residue, which would be most important linkages for periodate oxidation followed by ozonolysis to remove sugar residues and phenylpropane units free from the associations, respectively. In this paper, we applied these procedures to cell walls of yezo spruce (*Picea jezoensis* Carr.) and investigated the optimum conditions for periodate oxidation, reduction of the residue of periodate oxidation, mild acid hydrolysis and so on.

Tetra-O-acetyl-erithritol was detected and quantified as a major product by an alditol acetate analysis of residue of the periodate oxidation followed by reduction and mild acid hydrolysis, together with tetra-O-acetyl-threitol. The result suggests that the presence of linkages between lignin and the C6-position of glucosyl residue, probably cellulose, and between lignin and the C6-position of galactosyl residue. We have applied the procedures to cell walls of beech (*Fagus crenata* Blume).

1999-111

脱リグニンに伴う  $\beta$ -O-4 型構造のエリスロ・スレオ比の変化について

杉本倫子、秋山拓也、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Tomoko Sugimoto, Takuya Akiyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: By the ozonation method, erythro and threo (E/T) ratio of arylglycerol- $\beta$ -aryl ether ( $\beta$ -O-4) structure can be obtained as a ratio between two ozonation products, erythronic and threonic acids. It was confirmed that the ozonation method can be successfully applied to a lignin

remaining in partially delignified samples if degraded lignin is well washed out from the sample. This method was applied to an analysis of the change in E/T ratio in the residual lignin after wood meal was stepwisely delignified. When delignified by alkali cooking, not only the total yield of erythronic acid and threonic acid per lignin but also the E/T ratio decreased significantly with the progress of delignification. In contrast to this, when delignified by NaClO<sub>2</sub> treatment, no significant change was observed in E/T ratio. It is likely that a part of lignin with higher content of β-O-4 structure was rich in erythro type and was preferentially removed by alkali cooking, and, the part of lignin with low content of β-O-4 structure was relatively poor in erythro type and resistant to alkali cooking. These results coincide well not only with the generally accepted delignification mechanism during alkaline pulping but also with our previous hypothetical proposal that the E/T ratio of secondary wall lignin is higher than that of compound middle lamella lignin. On the other hand, when delignified by NaClO<sub>2</sub>, the delignification seems to proceed almost homogeneously regardless of the content of β-O-4 structure and its E/T ratio. It is well understood from its reaction mechanism to oxidize lignin.

1999-112

バンガラデシュ産アカシア・カテチュ心材抽出物の化学組成

アブル・カラム・アザド、荻山紘一

山形大学農学部

The chemical constituents of Bengal catechu (*Acacia catechu*)-heartwood extractives.

Abul Kalam Azad, Koichi Ogiyama

Faculty of Agriculture, Yamagata University

Keywords: (+)-catechin, NMR spectrometry, PTLC. GC-MS

Abstract: *Acacia catechu* に属するベンガル・カテチュの水抽出物は、ベテルの葉(地方名パン)のスパイスとしてチューインガムに昔から用いられている。この樹木の赤色心材の主化学成分は、バンガラデシュではカテチュと呼ばれている。心材のメタノール抽出物(収量 8.64%)の TLC 分析は、この部分に 9 個のフェノール性化合物が存在することを示した。この抽出物の主ポリフェノール化合物は、(+)-カテキンで、メタノール抽出物の約 3.33%を占めていた。その母液から新規な化合物が単離された。それは(+)-カテキンと同じ A 環と B 環を持ち、七員ヘテロ環状の C 環を有していた。その収量は、メタノール抽出物の約 0.053%であった。

1999-113

ゴボウ (*Arctium lappa*)におけるセコイソラリシレジノール生成の立体化学的選択性について

鈴木史朗、梅澤俊明、島田幹夫

京都大学木質科学研究所

Stereochemical selectivity of secoisolariciresinol formation in *Arctium lappa* L.

Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: The difference in stereochemistry of secoisolariciresinol formation between petioles and ripening seeds of *Arctium lappa* L. was further investigated using the cell-free extracts. Both cell-free extracts from ripening seeds and petioles catalyzed the formation of (-)-secoisolariciresinol from (±)pinosresinols and (±)lariciresinols, but with different enantiomeric compositions of the product. However, we previously reported the enantioselective formation of (+)secoisolariciresinol from coniferyl alcohol using cell-free extracts from the petioles. These results indicate that stereochemistry of lignan biosynthesis in *A. lappa* is very complicated and diverse.

1999-特別講演、I.

## 植物の外部環境検知能力と形づくりについて

野方文雄

岐阜大学工学部

Cell-based sensing system for external stimuli and an adaptive modeling process in plant.

Fumio Nogata

Department of Mechanical and Systems Engineering, Gifu University

Abstract: Examining some biological load carriers such as plant and tree stems, animal bones and other biological hard tissues, we see that their geometry changes under loading to match mainly stress- or strain-dependent requirements. For example, the interior structure of a bone exhibits all optimized shape with respect to the principal stress directions and the shear stress magnitude in the body. This indicates that the bone is managed by a self-optimizing system with sensing mechanisms (e.g., piezoelectric and/or streaming potential effect of bone) that detect external mechanical stimuli to control the modeling/remodeling of the skeletal system. Thus, it can be inferred that the shape and ingenious construction of biological hard tissues are the result of a continuous process of intelligent optimization. The goals of this work are to gain an understanding of the principles of design and processes found in biological tissues and to apply these findings toward developing new, intelligent, superior material concepts by using and/or modifying those models which are found in living organisms. We begin by presenting bamboo as a typical example of the ingenious construction, depending on mechanical stresses/strains conditions, and a cell based sensing system for external stimuli as well as an adaptive modeling process in plant.

## 1999-特別講演、II.

リグニン生分解研究から派生したシュウ酸合成酵素研究への新局面。-木質資源の育成と保護に関わる菌類の役割-

島田幹夫

京都大学木質科学研究所

A new aspect of oxalic acid producing enzyme research derived from lignin biodegradation research. -Roles of fungi in production and preservation of woods.

Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Retrospective viewpoints of lignin biodegradation research are described focusing on development of the first biomimetic example of heme enzyme (LiP and MnP) model catalysts for the one electron oxidation of lignin and bleaching of unbleached kraft pulps. A new aspect of oxalic acid involved in ligninolytic systems in white-rot fungi is discussed in relation to a possible role of the glyoxylate cycle which may commonly occur in a wide variety of saprophytic, symbiotic, and edible mushrooms.

## 1999-201

耐塩性白色腐朽菌に関する研究(I) 高塩濃度条件下で生育する菌株の探索

李 シン、近藤隆一郎、坂井克己

九州大学大学院生物資源環境科学研究科

Study on hypersaline-tolerant white-rot-fungi. (I). Screening of lignin-degrading fungi at hypersaline.

Li Xin, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: In order to characterize marine fungi, which have high lignin-degrading ability at saline conditions, several marine fungi were screened from 28 fungus strains isolated from mushrooms and driftwood samples from the mangrove stands in Okinawa, Japan. The decolorization ability,

delignification activity of wood meals and biobleaching property were evaluated and then a strain MG-60, was selected as a prosperous marine fungus that had tolerance to hypersaline.

1999-202

白色腐朽菌 *Ceriporiopsis subvermispota* の生産する新規ジカルボン酸

榎 牧子、本田与一、渡辺隆司、桑原正章

京都大学木質科学研究所

A novel dicarboxylic acid produced by white-rot fungus *Ceriporiopsis subvermispota*.

Makiko Enoki, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: Novel fluorescent dicarboxylic acids, 1-heptadecene-2,3-dicarboxylic, 1,7-nonadecadiene 2,3-dicarboxylic and 1-nonadecene-2,3-dicarboxylic acids were isolated from wood meal cultures of white-rot fungus *Ceriporiopsis subvermispota*. These three compounds are itaconic acid derivatives having different aliphatic chain. The amount of these amphiphilic dicarboxylic acids increased with incubation time, suggesting that production of these dicarboxylic acids is related to lignin biodegradation.

1999-203

マンガンペルオキシダーゼによる非フェノール性リグニンモデル化合物の分解

鬼束愛子、近藤隆一郎、坂井克己

九州大学大学院生物資源環境科学研究科

Degradation of non-phenolic lignin model compounds by manganese peroxidase.

Aiko Onitsuka, Ryuitiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University,

Abstract: We previously reported that isolated manganese peroxidase (MnP) from white rot fungus *Phanerochaete sordida* YK-624 cleaved  $\beta$ -ether bond of 3-hydroxy-2-(4-methyl-umbelliferone)-1-phenylpropanone. The system required MnP, malonate, Tween 20 and MnSO<sub>4</sub> but not hydrogen peroxide. In this study, we tried to degrade nonphenolic lignin model compounds having  $\alpha$ -carbonyl or  $\alpha$ -hydroxyl group by MnP from *P. sordida* YK-624. Model compounds having  $\alpha$ -carbonyl group were degraded by MnP system (MnP, malonate, Tween 20. and MnSO<sub>4</sub>), however. model compounds having  $\alpha$ -hydroxyl group were not degraded at all. The reaction mechanism will be discussed.

1999-204

白色腐朽菌 *Pleurotus ostreatus* により生産される MnP アイソザイムの生産調節について

上辻久敏、河 考哲、本田与一、渡辺隆司、桑原正章

京都大学木質科学研究所

The effect of culture condition on the production of manganese peroxidase by white-rot fungi *Pleurotus ostreatus*.

Hisatoshi Kamitsuji, Ha Hyo-cheol, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: Manganese peroxidase (MnP) was secreted by *Pleurotus ostreatus* in liquid stationary culture. Two different MnP isozymes were produced in glucose/yeast-extract medium (GY) and peptone/glucose/yeast-extract medium (PGY). The isoelectric points of MnP produced in GY medium (MnP-GY) and PGY medium (MnP-PGY) were found to be 3.70 and 3.95, respectively. The molecular masses of both isozymes were 42 kDa. N-terminal amino acid sequences of MnP-PGY was found to be identical to that of MnP 3. It was also similar to that of MnP which was produced in

the sawdust culture.

1999-205

白色腐朽菌ヒラタケにおける組換えマンガンペルオキシダーゼ発現系の開発

入江俊一、本田与一、渡辺隆司、桑原正章

京都大学木質科学研究所

Homologous expression of recombinant manganese peroxidase gene in *Pleurotus ostreatus*.

Toshikazu Irie, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: The genomic and cDNA fragments encoding *Pleurotus ostreatus* MnP3 were cloned and analyzed. From sequencing analysis, it was demonstrated that *P. ostreatus* MnP3 has a property specific for both of manganese peroxidase and lignin peroxidase from *Phanerochaete chrysosporium*. The coding sequence was fused with promoter and terminator sequence of *P. ostreatus sdi1* encoding succinate dehydrogenase iron-sulfur protein subunit. The recombinant constructs were introduced into wild-type *P. ostreatus* strain via DNA-mediated transformation. Transformants which express higher MnP activity than wild type were isolated. One of the recombinants obtained by mating between two monokaryotic transformants, TMG9-C1 has shown several times higher MnP activity than the wild-type control in the early stage of liquid culture of the mycelium. Predominant transcription of the recombinant *mnp3* at the 6th day was demonstrated by a competitive RT-PCR experiment.

1999-206

シロアリ腸内から単離した放線菌の産生するペルオキシダーゼについて

原園幸一<sup>\*1</sup>、渡辺吉雄<sup>\*2</sup>、深津武馬<sup>\*1</sup>、倉根隆一郎<sup>\*1</sup>

<sup>\*1</sup> 工業技術院生命工学工業技術研究所、<sup>\*2</sup> メルシャン中央研究所

Peroxidase produced by *Streptomyces eurythermus* isolated from guts of lower termites, *Coptotermes formosanus*.

Koichi Harazono<sup>\*1</sup>, Yoshio Watanabe<sup>\*2</sup>, Takema Fukatsu<sup>\*1</sup>, Ryuichiro Kurane<sup>\*1</sup>

<sup>\*1</sup>Bioconsortia Program, National Institute of Bioscience and Human Technology, Agency of Industrial Science and Technology, <sup>\*2</sup>Central Research Laboratory, Mercian Corp.

Abstract: The production of peroxidase by actinomycete, *Streptomyces eurythermus* CA2 isolated from guts of lower termites, *Coptotermes formosanus* was studied in shaken liquid culture. The addition of 5-aminolevulinic acid increased peroxidase activity in culture of *S. eurythermus* CA2. Peroxidase activity in culture of *S. eurythermus* CA2 was dependent on H<sub>2</sub>O<sub>2</sub> and was inhibited with potassium cyanide and ethylene glycol bis(-aminoethyl ether) N,N,N',N'-tetraacetic acid (EGTA). Four peroxidase isozymes from concentrated culture filtrate were detected by nondenaturing polyacrylamide gel electrophoresis (PAGE) and activity staining with L-3,4-dihydroxyphenylalanine as the substrate. The molecular mass of main peroxidase isozyme P2 was about 53 kDa.

1999-207

白色腐朽菌の液体培養系による飛灰中ダイオキシン類の分解

好光正豪<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>、坂井克己<sup>\*1</sup>、水海吉太郎<sup>\*2</sup>

<sup>\*1</sup> 九州大学農学部、<sup>\*2</sup> 有限会社微創研

Degradation of dioxins in fly ash treated in the liquid culture of white rot fungi.

Masahide Yoshimitsu, Ryuichiro Kondo, Kokki Sakail, Yoshitaro Suimi

Faculty of Agriculture, Kyusyu University

Abstract: Seventy two strains of fungi were screened for the growth in the liquid medium mixed

with fly ash. White rot fungus MZ-340 was selected, because it grew well in the medium mixed with fly ash, and degraded 2,7-dichlorodibenzo-*p*-dioxin extensively. In this study, we demonstrated the degradation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/DFs) in fly ash by the liquid culture of the fungus. PCDDs/DFs content, 52.0 ng-TEQ/g, in the fry ash were reduced to 18.6 ng-TEQ/g by treatment with the fungus MZ-340 for 2 weeks.

1999-208

ラッカーゼおよびマンガンペルオキシダーゼによる内分泌攪乱物質の除去

羽田 崇<sup>\*1</sup>、堤 祐司<sup>\*1</sup>、西田友昭<sup>\*1</sup>、和田敏明<sup>\*2</sup>

<sup>\*1</sup> 静岡大学農学部、<sup>\*2</sup> 東京都林産試験場

Removal of endocrine disrupters by laccase and manganese peroxidase.

Thkashi Haneda<sup>\*1</sup>, Yuji Tsutsumi<sup>\*1</sup>, Tomoaki Nishida<sup>\*1</sup>, Toshiaki Wada<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Shizuoka University, <sup>\*2</sup>Tokyo Metropolitan Forestry Experiment Station

Abstract: Endocrine disrupters, such as bisphenol A (BPA) and nonylphenol (NP), may modify natural endocrine function and so affect human health and wildlife. In this study, therefore, we tried to remove the estrogenic activity of BPA and NP with partially purified laccase and manganese peroxidase (MnP). BPA and NP were removed by both enzyme treatments in 60 min, which was mainly due to polymerization. We also measured the estrogenic activity of BPA or NP before and after enzyme treatments by using yeast two-hybrid system. More than 95% of estrogenic activity of BPA and NP disappeared after 12h-treatment with both enzymes. These findings indicate that the treatment of BFA and NP with laccae and MnP is effective in removal and disappearance of estrogenic activity of them.

1999-209

リグニン分解酵素系によるパルプ繊維の改質 -MnP 処理が DIP パルプ繊維に及ぼす影響-  
土川圭一<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>、坂井克己<sup>\*2</sup>

<sup>\*1</sup> 特殊製紙株式会社、<sup>\*2</sup> 九州大学農学部

Application of ligninolytic enzymes to modification of pulp fibers. -Effects of MnP treatment on DIP.

Keiichi Tsuchikawa<sup>\*1</sup>, Ryuichiro Rondo<sup>\*2</sup>, Kokki Sakai<sup>\*2</sup>

<sup>\*1</sup>Tokushu Paper MFG Co. Ltd, <sup>\*2</sup>Faculty of Agriculture, Kyushu University

Abstract: The application of MnP treatment to DIP was examined. The ISO brightness of the DIP decreased slightly by MnP treatment, however, it was recovered with the combination of H<sub>2</sub>O<sub>2</sub> bleaching. The residual fluorescence intensity in DIP was decreased by MnP treatment. Physical properties of DIP was improved by Map treatment, and also Map treatment enhanced the effect of PAM addition on physical strength of the pulp.

1999-210

溶媒循環プロセスによる HBS パルプ化(1)-針葉樹材の脱リグニン

梶本純子、衣笠わか子、佐野嘉拓

北海道大学大学院農学研究科

HBS pulping with solvent-recycling process. (I). -Delignification of softwood.

Junko Kagimoto, Wakako Kinugasa, Yoshihiro Sano

Graduate school of Agriculture, Hokkaido University

Abstract: In order to develop a new pulping process with non-pollution and saving energy, softwood was subjected to delignification with high boiling-pint solvents (HBS) with and without acetic add. Todomatsu, ezomatsu, karamatsu and sugi were easily delignified under conditions with 60-80% HBS such as butanediol-1,4 at 220°C for 1-3 h with and without acetic acid. However, acetic

add promoted the delignification reaction. Pulp was washed with the same solvent or acetone, and then water. The water washing was poured into a mixture of the reaction liquor and solvent washing to precipitate water insolubles such as lignin and sugar modified products. A mixture of solvent and sugars recovered by evaporation of the water from water solubles could be reused more than 5 times as a pulping solvent for the new pulping procedure without hitch.

1999-211

硝酸と亜硝酸塩を添加した有機溶媒水媒体における広葉樹リグニンの分解挙動

大井 洋

筑波大学農林工学系

Behavior of hardwood lignin decomposition in organic solvent-water media with nitrite and nitric acid.

Hiroshi Ohi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Ethanol-water pulping has been proposed as one of organosolve pulping methods. Acid catalysts were investigated for improving the pulping conditions, but nitric acid is not studied yet. Nitric acid pulping is conducted at much lower temperatures than the ethanol-water pulping. The effects of nitrite and nitric acid on the pulping using ethanol-water media are not clear. It has been shown that at the dosage of 40% nitric acid and 90°C, the lignin decomposition was facilitated when a very small amount of catalytic nitrite was added. In addition, the pH of the media was increased by the consumption of nitric acid. In this study, behavior of lignin decomposition in such media is further discussed using an isolated lignin and wood chips.

1999-212

塩素漂白過程で生成するクロロホルムの可能生成量について

幸田圭一、新谷博幸、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Formation potential of chloroform during chlorine bleaching of kraft pulp.

Keiichi Koda, Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, The University of Tokyo

Abstract: Chloroform produced during chlorine bleaching of kraft pulp was quantitatively analyzed by GC-MS (SIM mode). The amount of chloroform that can potentially be formed was also estimated. Chlorination and alkali treatment of pulp and/or effluent was performed in a gas tight reaction vessel in order to determine chloroform as accurately as possible. The result suggested that by subjecting both chlorinated pulp and chlorination effluent to alkali treatment, chloroform precursors were quantitatively estimated. Even though hypochlorite addition is the major source of chloroform formation, chloroform formation during both C- and E-stages should properly be evaluated.

1999-213

マルチング中の剪定枝チップ細胞壁成分の変化

小野 芳<sup>\*1</sup>、市川朋子<sup>\*1</sup>、渡辺達三<sup>\*2</sup>、飯山賢治<sup>\*3</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学大学院新領域、<sup>\*3</sup> 東京大学アジア生物資源環境研究センター

Compositional changes of wood chips during mulching.

Kaori Ono<sup>\*1</sup>, Tomoko Ichikawa<sup>\*1</sup>, Satomi Watanabe<sup>\*2</sup>, Kenji Iiyama<sup>\*3</sup>

\*<sup>1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, \*<sup>2</sup>Graduate School of Frontier Science, the University of Tokyo, \*<sup>3</sup>Asian Natural Environmental Science Center, the University of Tokyo

Abstract: Huge quantities of pruned branches are produced from planted trees at urban area. Recently, they are utilized in the shape of wood chips as compost and mulch. In this paper, sequential changes in wood chip mulch were examined by using *sugi* (*Cryptomeria japonica*) and *keyaki* (*Zelcova serrata*). Changes in chemical composition were also investigated for wood chips buried at the bottom and the surface of mulch system. It was shown that *Z. serrata*, an Angiosperm wood, was modified biologically faster than *C. japonica*, a Gymnosperm wood, and compositional changes in mulch buried in the bottom was more significant than that at surface. The relative content of lignin increased significantly in *Z. serrata* mulch, and condensation of lignin made progress during mulching.

1999-214

リグニン系土壌改良剤による植物の AL 生育障害の改善

斎藤京子、飯塚堯介

東京大学大学院農学生命科学研究科

Improvement of growth inhibition of plant by AL using soil conditioning agent from lignin.

Kyoko Saito, Gyosuke Meshitsuka

Graduate School of Agriculture and Life Sciences, The University of Tokyo

Abstract: Aluminum ion (AL) is one of the main reasons of toxicity to plant growth in acid soil. AL is eluted from soil matrix below pH 4.5 and inhibits elongation of plant root. We modified kraft lignin by alkaline-oxygen treatment and obtained humin-like materials rich in acidic groups, especially carboxylic acid group. Modified kraft lignins were expected to form complex with AL, which has been confirmed by pH titration. In this study, the effect of pH and the formation of AL-lignin complex on grow of radish root were examined. It was found that toxicity of AL dissolved in the culture solution was effectively removed by the presence of enough amount of a modified lignin.

1999-215

両親媒性リグニン誘導体と蛋白質の相互作用

西田光邦、浦木康光、佐野嘉拓

北海道大学大学院農学研究科

Interaction of amphiphilic lignin derivative with protein.

Mitsukuni Nishida, Yasumitsu Uraki, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: Acetic acid lignin (AL) prepared by the atmospheric acetic acid pulping of birch was reacted with polyethylene glycol diglycidyl ether (PE) under alkaline conditions to yield an amphiphilic AL derivative (PE-AL). PE-AL was suggested to have a similar structure to the rigid Binstein's sphere in aqueous solution, and to shrink as increasing in the concentration probably due to the hydrophobic interaction of AL domains by viscometric study. PE-AL was found to form the complex with bovine serum albumin as model protein for about one week at 4°C by the measurements of size-exclusion chromatography and circular dichroism. Furthermore, the decrease in lipase activity in aqueous 20% ethanol was repressed by PE-AL. Thus, PE-AL seems to contribute to preserve the activity of enzyme.

1999-216

リグニンベースポリカプロラクトン誘導体の TG・FTIR

畠山兵衛<sup>\*1</sup>、吉田孝範<sup>\*1</sup>、伊豆田良信<sup>\*1</sup>、廣瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 工業技術院物質研究所、<sup>\*3</sup> 大妻女子大学家政学部

TG-FTIR of lignin-based polycaprolactone derivatives.

Hyoë Hatakeyama<sup>\*1</sup>, Takanori Yoshida<sup>\*1</sup>, Yoshinobu Izuta<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Fukui Institute of Technology, <sup>\*2</sup>National Institute of Materials and Chemical Research, <sup>\*3</sup>Otsu Women's University

Abstract: Lignin-based polycaprolactone derivatives (LigPCL) were prepared from kraft lignin (KL) and an organosolv lignin (Alcel lignin, AL). The gases evolved by thermal degradation of LigPCL were analyzed by simultaneous thermogravimetry (TG) and Fourier-transformed infrared spectrometry (TG-FTIR). The amounts of thermal degradation products having characteristic functional groups changed according to the length of PCL chains in the LigPCLs.

1999-P01

広葉樹シリングルリグニンの生成機構

山内一慶、福島和彦、斉藤香織、安田征市

名古屋大学大学院生命農学研究科

Biosynthesis of syringyl lignin in angiosperm.

Kazuchika Yamauchi, Kazuhiko Fukushima, Kaori Saito, Seiichi Yasuda

Faculty of Agriculture, Nagoya University

Abstract: 4-Coumarate:CoA ligase (4CL) activity for sinapic acid has not been detected in many dicotyledonous plants. In order to investigate the existence of the pathway (sinapic acid to sinapoyl-CoA), we perform the tracer experiment. Sinapic acid, both two methoxyl groups were labeled by deuteriums, was synthesized and fed to various angiospermous wood. If the pathway (sinapic acid to sinapoyl-CoA) exists, two labeled methoxyl groups should be introduced to lignin.

1999-P02

広葉樹分化中木部細胞における O-メチルトランスフェラーゼの局在

竹内美由紀<sup>\*1</sup>、高雄圭司<sup>\*1</sup>、藤田 稔<sup>\*1</sup>、片山義博<sup>\*2</sup>

<sup>\*1</sup> 京都大学大学院農学研究科、<sup>\*2</sup> 東京農工大学大学院 BASE

Localization of OMT in differentiating xylem cells of hard wood.

Miyuki Takeuchi<sup>\*1</sup>, Keiji Takabe<sup>\*1</sup>, Minoru Fujita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agriculture, Kyoto University, <sup>\*2</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology

Abstract: Considerable works has revealed the presence of enzymes involved in lignin biosynthesis, and the biosynthetic pathway of lignin is, now, generally accepted. However, the localization of each enzyme in cell is still open to discussion. O-Methyl transferase (OMT) catalyzes reactions from caffeic acid to ferulic acid or from 5-hydroxyferulic acid to sinapic acid. We produced rabbit anti-OMT antibody by using a fusion protein of a part of OMT and histidine as an antigen. Immunocytochemistry revealed localization of OMT at differentiating xylem cells of *populus* and *eucalyptus*. Labelings of OMT was not observed on any organelles but on cytosol.

1999-P03

シナピルアルコールの酵素的脱水素重合に対するコニフェリルアルコール混合の影響

小林孝行<sup>\*1</sup>、鈴木正史<sup>\*1</sup>、重松幹二<sup>\*1</sup>、棚橋光彦<sup>\*1</sup>、小名俊博<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学農学部、<sup>\*2</sup> 王子製紙株式会社森林資源研究所

Effect of the mixing of coniferyl alcohol on the enzymatic dehydrogenative polymerization of sinapyl alcohol.

Takayuki Kobayashi\*<sup>1</sup>, Masashi Suzuki\*<sup>1</sup>, Mikiji Shigematsu\*<sup>1</sup>, Mitsuhiko Tanahashi\*<sup>1</sup>, Toshihiro Ona\*<sup>2</sup>  
\*<sup>1</sup>Faculty of Agriculture, Gifu University, \*<sup>2</sup>Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: Sinapyl alcohol reacts very slowly by horseradish peroxidase (HRP) comparing with other monolignols, but it reacts so fast by addition of guaiacyl or *p*-hydroxyphenyl compound. Some phenolic materials were used to investigate the influence of their functional groups on the HRP reaction. Further, the possibility of the radical transportation was investigated by two-layer system in which sinapyl alcohol was separated from HRP by ultra filter. From the results, we proved that some phenolic materials play a roll as a radical mediator.

1999-P04

分子軌道法による種々の溶媒中でのリグニン前駆体のコンフォメーション解析

重松幹二、小林孝行、棚橋光彦

岐阜大学農学部

Molecular orbital analysis on the conformations of monolignols dissolved in various solvents.

Mikiji Shigematsu, Takayuki Kobayashi, Mitsuhiko Tanahashi

Faculty of Agriculture, Gifu University

Abstract: Solvent effect on the optimum conformations of monolignols was computer-simulated by MOPAC97 program including PM3 and COSMO methods. In the cases of guaiacol and coniferyl alcohol, the Boltzman's probability of hydrogen bond between phenolic hydroxyl and methoxyl groups was decreased by increase of the dielectric constant of solvent, for example, 96% in gas phase, 86% in benzene, 48% in pyridine and 36% in water. In the cases of 2,6-dimethoxyphenol and sinapyl alcohol, the 60% of phenol hydrogen oriented to either of two methoxyl oxygens in gas phase, but less than 30% in water.

1999-P05

リグニンの NMR におけるシフト試薬の効果

関口俊司、新谷博幸、飯塚堯介

東京大学大学院農学生命科学研究科

The effect of shift reagents on NMR spectra of lignin.

Syunji Sekiguchi, Hiroyuki Shintani, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: The shift reagents have been applied for the separation of overlapped peaks in NMR spectra. In this paper, the effect of Eu-FOD and Pr-FOD, which are common shift reagents, on NMR spectra of lignin was investigated. Signals in <sup>1</sup>H-NMR spectra of acetylated MWL (milled wood lignin) were broadened by the addition of those shift reagents, and the resolution of spectra became even worse. The main reason for this result must be the difficult complex formation caused by the bulkiness of lignin molecule. Further modifications of conditions (ex. solvent, temperature, kind of derivatization) are needed for the effective application of shift reagents on NMR spectrometry of lignin.

1999-P06

セプターパヤ細胞壁の成分とタンニンの特徴

鶴田暁史\*<sup>1</sup>、大井 洋\*<sup>1</sup>、大原誠資\*<sup>2</sup>

\*<sup>1</sup>筑波大学農林工学系、\*<sup>2</sup>森林総合研究所

Characteristics of cell wall components and tannins from the wood of *Pseudosindora palustris*.

Akifumi Tsuruta\*<sup>1</sup>, Hiroshi Ohi\*<sup>1</sup>, Seiji Ohara\*<sup>1</sup>

\*<sup>1</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba, \*<sup>2</sup> Forestry and Forest

Products Research Institute

Abstract: *Pseudosindora palustris* wood contained 18.9% of polyphenols and 23.6% of acid insoluble lignin. From acetone-water (7:3) extracts of the wood fisetinidol and fisetinidol-(4 $\alpha$ →8)-catechin were isolated after separation by column chromatography. <sup>13</sup>C-NMR spectra indicated that polymers from the acetone-water extracts were proanthocyanidin polymers which mainly consisted of profisetinidin. On-line methylation pyrolysis-gas chromatography gave 3, 4-dimethoxytoluene from the B ring, 1, 3-dimethoxybenzene from the A ring, and a pyrolysis product which was assumed to be 1-(2-methoxyethyl)-2, 4, 6-trimethoxybenzene. It has been made clear that the proanthocyanidin polymers consist of profisetinidin units including a small number of procyanidin units.

1999-P07

チヤボヒバ (*Chamaecyparis obtusa* cv. *Breviramea*) から単離された新規リグナンについて  
高久尚裕、奥西智哉、三亀啓吾、鈴木史朗、梅澤俊明、島田幹夫  
京都大学木質科学研究所

A new lignan from *Chamaecyparis obtusa* cv. *Breviramea*.

Naohiro Takaku, Tomoya Okunishi, Keigo Mikame, Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada  
Wood Research Institute, Kyoto University

Abstract: A new lignan, which is an isomer of actifolin named isoactifolin, and three known lignans, dihydrosesamin, piperitol, and sesamin, were isolated from the methanol extracts of leaves of *Chamaecyparis obtusa* cv. *Breviramea*.

1999-P08

ニオイヒバリグナンの検索とそれらリグナン類の生合成について  
榎本慎一、河合真吾、大橋英雄  
岐阜大学農学部

Isolation and identification of *Thuja occidentalis* lignans and their biosyntheses.

Shin-ichi Enomoto, Shingo Kawai, Hideo Ohashi

Faculty of Agriculture, Gifu University

Abstract: Five lignans, (8*R*, 8'*R*)-(–)-yatein, dihydroxythujaplicatin methyl ether, thujastandin, lariciresinol, pinoresinol were isolated from *Thuja occidentalis* xylem, besides the previously identified seven lignans. Chiral HPLC analysis of yatein indicated that the compound was optically pure. The presence of secoisolariciresinol was also identified by GC-MS analysis of the extract of *T. occidentalis* xylem. Feeding experiments of [9, 9-<sup>2</sup>H<sub>2</sub>, OC<sup>2</sup>H<sub>3</sub>]coniferyl alcohol and [7, 7-<sup>2</sup>H<sub>2</sub>, 3'-OC<sup>2</sup>H<sub>3</sub>] secoisolariciresinol into *T. occidentalis* young shoots resulted that two molecules of coniferyl alcohol were incorporated into pinoresinol and lariciresinol, and secoisolariciresinol was incorporated into lariciresinol.

1999-P09

数種の培養細胞を用いたリグナン、ポドフィロトキシンのバイオトランスフォーメーションによるリナン配糖体の調製の試み

内藤隆行、伊藤和貴、橋 燦郎

愛媛大学農学部

Trial for preparation of podophyllotoxin glucoside by biotransformation of podophyllotoxin by use of some plant cell cultures.

Takayuki Naito, Kazutaka Ito, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Production of podophyllotoxin glucoside by biotransformation of podophyllotoxin by

use of cell suspension cultures of *Gardenia jasminoides*, *Nicotiana tabacum* and *Datura innoxia* was tried. From the results of HPLC analysis of each reaction product, we found that podophyllotoxin glucoside was produced by the cultures of *D. innoxia* in the maximum yield of 4.6%. However, the glucoside could not be produced by the cultures of *G. jasminoides* and *N. tabacum*.

1999-P10

Mn(II)酸化能を有する微生物に関する研究

西中垂紀子、堤 祐司、西田友昭

静岡大学農学部

Studies on Mn( II )-oxidizing microorganisms.

Akiko Nishinaka, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: Screening of microorganisms which can oxidize Mn(II) to Mn(III) was attempted. One of such microorganism from literatures, *Leptothrix discophora* SS-1(SS-1), was examined its potential of Mn(III) formation from Mn(II). The prepared crude enzyme from SS-1 could oxidize Mn(II) to MnOx and effectively convert Mn(II) to Mn(III) in the presence of pyrophosphate as a chelator of Mn(III). Also, 336 of positive bacterial colonies were isolated from the samples collected from Taguchi mine, Japan, by their ability of MnOx formation from Mn(II) on the plate. Twenty-six colonies were further selected from 336 and their ability of Mn(III) formation is in progress.

1999-P11

白色腐朽菌が産生するマンガンペルオキシダーゼ活性化物質について

扇 剛士、鬼束愛子、近藤隆一郎、坂井克己

九州大学農学部

Production of extracellular manganese peroxidase activity-stimulating substances by white rot fungi.

Takeshi Ougi, Aiko Onitsuka, Ryuichiro Rondo, Kokki Sakai

Faculty of Agriculture, Kyusyu University

Abstract: Manganese peroxidase (MnP) is an extracellular heme protein produced by wood-rotting and litter-degrading basidiomycetes especially during secondary metabolism. MnP catalyzes the H<sub>2</sub>O<sub>2</sub>-dependent oxidation of phenolic lignin structures. We had interest in producing of extracellular MnP activity-stimulating substances by white rot fungi. *Phanerochaete sordida* YK-624 and *P. chrysosporium* were cultivated in the liquid medium, and extracellular low molecular-weight substances were prepared. Addition of extracellular substances, which is equivalent amounts of Mn to MnSO<sub>4</sub>, to the MnP reaction mixture increased the MnP activity comparing with MnP-MnSO<sub>4</sub> system. Addition of Kirk medium instead of MnSO<sub>4</sub> to the reaction mixture did not increase the MnP activity. These results suggest that white rot fungi night produce extracellular MnP activity- stimulating substances.

1999-P12 (発表中止)

1999-P13

白色腐朽菌 MZ-340 株の 18SrDNA による系統学的分類

須原弘登、近藤隆一郎、坂井克己、白石 進

九州大学大学院生物資源環境科学研究科

Taxonomy of the white rot fungus MZ-340 using 18SrDNA.

Hiroto Suhara, Ryuichiro Kondo, Kokki Sakai, Susumu Shiraishi

Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been a public concern for several decades because of their strong toxicity. We have suggested that one white rot fungus, tentatively named strain MZ-340, collected from natural forest in Japan, can degrade PCDDs and PCDFs. To identify the classification of the strain MZ-340, nucleotide sequences of the small subunit ribosomal RNA gene were examined. The strain MZ-340 was closely related to *Phanerochaete chrysosporium* or *Phlebia radiata* when searched with "DDBJ BRAST search". Subsequently phylogenetic relationship of strain MZ-340 was investigated by "Phylip package" using our sequences and data on "GenBank". Based on our current data, strain MZ-340 could be classified as family of *Corticaceae* including genus of *Phanerochaete* and *Phlebia*.

1999-P14

白色腐朽菌によるダイオキシン類の *in vitro* 分解 (III) ~MZ-340 株産生酵素の基質特異性について~

森智夫、近藤隆一郎、坂井克己

九州大学大学院生物資源環境科学研究科

*In vitro* degradation of dioxins by white rot fungi. (III). -Substrate specificity of extracellular enzyme from the fungus MZ-340.

Toshio Mori, Ryuichiro Kondo, Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: The white rot fungus strain MZ-340 was screened as the strain having dioxins-degrading ability. We have previously reported that culture filtrate from the strain MZ-340 can degrade 2,7-dichlorodibenzo-*p*-dioxin and 2,8-dichlorodibenzofuran. The purpose of present study was to examine whether biaryl compounds such as dioxins or dioxin like compounds can be degraded by the culture filtrate from the strain MZ-340. 2,7 dichlorodibenzo-*p*-dioxin, 2,8-dichlorodibenzofuran and 4,4'-dichlorobiphenyl were reacted with the filtrate, although non-chlorinated compounds, dibenzo-*p*-dioxin, dibenzofuran and biphenyl were not. Probably, chlorine-substitution will be important in this enzymatic reaction.

1999-P15

担子菌におけるケミカルストレス応答タンパク質の検索

森下大史、一瀬博文、栗原宏征、割石博之、田中浩雄

九州大学農学部

Search for the new proteins from the basidiomycetes.

Hiroshi Morishita, Hirofumi Ichinose, Hiroyuki Kurihara, Hiroyuki Wariishi, Hiroo Tanaka

Faculty of Agriculture, Kyushu University

Abstract: To investigate the mechanism of substrate recognition and metabolic response, 2-dimensional protein electrophoresis and differential display techniques were utilized. The cell free extracts prepared from fungal hyphae in the presence of the chemical stress were compared with those from non-stressed cell. Dioxins, biphenyls, and dibenzothiophenes were utilized as a chemical stress, since their metabolic pathways were at least partially elucidated. The addition of these compounds resulted in the appearance of new proteins and the expression of specific genes.

1999-P16

木材腐朽菌によるケナフパルプの漂白

大前陽子、大谷慶人、鮫島一彦

高知大学農学部

Biobleaching of kenaf bast pulp by wood rot fungi.

Yoko Ohmae, Yoshito Ohtani, Kazuhiko Smeshima

Faculty of Agriculture, Kochi University

Abstract: Biobleaching of kenaf bast pulp was tried using some wood-rot fungi screened and isolated from the field and typical ones; *Pleurotus ostreatus* and *Phanerochaete chrysosporium*. Each fungus precultured in Kirk medium was inoculated upon kenaf bast pulp and incubated statically at 29°C. The most effective fungus was OM5-1 screened in our laboratory. It has an ability to increase pulp brightness 2 times larger and to decrease kappa number 1.5 times larger than *P. chrysosporium*. It also showed higher initial Mn peroxidase activity than *P. chrysosporium*.

1999-P17

溶媒再循環プロセスによる HBS パルプ化(2)ー広葉樹材および草本類の脱リグニンー

ワヒュ・エコ・ウイドド、佐野嘉拓

北海道大学大学院農学研究科

HBS pulping with solvent-recycling process (2) – Delignification of hardwood and annual plants.

Wahju Eko Widodo, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: In order to develop a new pulping process with non-pollution and saving energy, hardwood (birch and commercial *E. globulus*) and annual plants (kenaf, palm oil wastes, rice and wheat straws, and bagasse) were subjected to delignification by HBS pulping process with high boiling-point solvents (HBS) with and without acetic acid. They were significantly delignified at 200°C for 3 h without acetic acid and for 2 h with 5-10% AcOH of the solvent. The RHBSs removed only lignin from pulping waste liquors were possible to reuse several times as pulping solvent.

1999-P18

常圧酢酸パルプ化ーパルプ廃液から得られる糖成分の考察

久保田康恵、佐野嘉拓

北海道大学大学院農学研究科

Atmospheric acetic acid pulping. –Carbohydrate in water solubles fractionated from waste liquor.

Yasue Kubota, Yoshihiro Sano

Faculty of Agriculture, Hokkaido University

Abstract: Atmospheric acetic acid pulping (AcOH pulping) is one of the organosolv pulping aimed at total utilization of biomass. Birch, todomatsu and rice and wheat straws were fractionated into pulp, lignin and water solubles by the pulping. Each water solubles were obtained in yields of 20-30% of raw material and contained monosaccharides (sugars, 40-50% of water solubles) and colored substances. The sugars were easily purified with carbon-celite, following by conversion to alditols by catalytic hydrogenolysis with Raney Nickel. The alditols purified by ion-exchange resin were analyzed.

1999-P19

自己会合性ヒドロキシプロピルリグノセルロース誘導体の溶液挙動

半崎亜希子<sup>\*1</sup>、浦木康光<sup>\*1</sup>、佐野裏拓<sup>\*1</sup>、浦川 宏<sup>\*2</sup>、安永秀計<sup>\*2</sup>、梶原莞爾<sup>\*2</sup>

<sup>\*1</sup>北海道大学大学院農学研究科、<sup>\*2</sup>京都工芸繊維大学工芸学部

Solution property of self-assembled hydroxypropylated lignocellulose derivative.

Akiko Hanzaki<sup>\*1</sup>, Yasumitsu Uraki<sup>\*1</sup>, Yoshihiro Sano<sup>\*1</sup>, Hiroshi Urakawa<sup>\*2</sup>, Hidekazu Yasunaga<sup>\*2</sup>, Kanji Kajiwara<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, <sup>\*2</sup>Faculty of Engineering and Design, Kyoto Institute of Technology

Abstract: Solution behavior of hydroxypropylated (HP) lignocellulose that was prepared from acetic acid pulp was investigated by the small angle X-ray scattering (SAXS) and the measurement of lower critical solution temperature (LCST) to clarify the self-assembly. Kratky plot of SAXS indicated that HP-lignocellulose was a rod-like polymer both in water and tetrahydrofuran as well as commercially HP-cellulose (HPC). The cross-sectional radius of gyration was found to increase with the increase in residual lignin content by Guinier plot. LCST of HP-lignocellulose was approximately 36°C, while HPC had LCST above 39°C. These results suggest that the residual lignin in the self-assembled HP-lignocellulose remarkably affected polymer structure and phase separation in the solution.

## 第 45 回 (2000.10.26-27) 愛媛大学農学部

2000-101

広葉樹シリングルリグニンの生成機構

山内一慶<sup>\*1</sup>、福島和彦<sup>\*1</sup>、安田征市<sup>\*1</sup>、浜田勝義<sup>\*2</sup>、堤祐司<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科, <sup>\*2</sup>静岡大学農学部

The biosynthetic mechanism of syringyl lignin in angiosperm

Kazuchika Yamauchi<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Katsuyoshi Hamada<sup>\*2</sup>, Yuji Tsutsumi<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>Faculty of Agriculture, Shizuoka University

Abstract: There is a great interest in the question whether sinapic acid is the true precursor of syringyl lignin or not, because the activity of 4-coumarate:CoA ligase (4CL) for sinapic acid was not detected in many angiosperms. We synthesized labeled sinapic acid-[2OMe- $d_6$ ,  $\beta$ - $d$ ] and [2OMe- $d_6$ ,  $\beta$ - $^{13}C$ ], and administered into angiosperms (*Nerium indicum* Mill. and *Robinia pseudoacacia* L.). The newly formed xylem of administered woods was analyzed by DFRC method. Labeled sinapic acid was incorporated into the syringyl lignin accompanied by all labels. Our results suggested the existence of the pathway from sinapic acid to sinapyl alcohol via sinapoyl CoA.

2000-102

コニフェリルアルコールの脱水素重合中に生成するシリングル核

斉藤香織<sup>\*1</sup>、安田征市<sup>\*1</sup>、小名俊博<sup>\*2</sup>、福島和彦<sup>\*1</sup>

<sup>1</sup>名大院生命農, <sup>2</sup>王製紙(株)森林資源研究所

Syringyl units generated during the polymerization of coniferyl alcohol

Kaori Saito<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Toshihiro Ona<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>Forestry Research Institute, Oji Paper Co. Ltd.

Syringyl (S) and *p*-hydroxyphenyl (H) units were detected in addition to guaiacyl (G) unit in thioacidolysis products of the DHP prepared from only coniferyl alcohol by peroxidase-H<sub>2</sub>O<sub>2</sub> system. We established the appropriate condition for the formation of S and H units during the polymerization of coniferyl alcohol. We also prepared DHPs from methoxyl-*d*-labeled coniferyl alcohol to clarify the mechanism for the formation of S and H units, but we could not prove the transference of methoxyl groups.

2000-103

シリングルリグニン生合成におけるシナップ酸と 4-Coumarate: Coenzyme A Ligase の役割

浜田勝義<sup>\*1</sup>、宮武亜樹子<sup>\*1</sup>、福島和彦<sup>\*2</sup>、堤祐司<sup>\*1</sup>、西田友昭<sup>\*1</sup>

\*<sup>1</sup> 静岡大学農学部、\*<sup>2</sup> 名古屋大学大学院生命農学研究科

The role of sinapic acid and 4-coumarate: coenzyme A ligase in syringyl lignin biosynthesis.

Katsuyoshi Hamada\*<sup>1</sup>, Akiko Miyatake\*<sup>1</sup>, Kazuhiko Fukushima\*<sup>2</sup>, Yuji Tsutsumi\*<sup>1</sup>, Tomoaki Nishida\*<sup>1</sup>

\*<sup>1</sup> Faculty of Agriculture, Shizuoka University, \*<sup>2</sup> Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: We investigated the involvement of sinapic acid (SA) and 4-coumarate: Coenzyme A ligase (4CL) in syringyl lignin biosynthesis. Deuterated ferulic acid (FA) [3-OD<sub>3</sub>, β-D] and SA [3,5-OCD<sub>3</sub>, β-D] were administered to poplar (*Populus alba* L.) callus cultures as precursors of lignin. The thioacidolysis analyses of the administered calluses showed that the deuterated SA was not converted to guaiacyl and syringyl lignins, while SA administration clearly increased syringyl lignin content in the callus. 4CL activity against SA was not observed in the homogenized cell, crude enzyme, and microsome preparations by an enzyme assay using <sup>14</sup>C-labeled SA. The results suggest that SA is not a precursor of syringyl lignin *per se* but induces or enhances syringyl lignin biosynthesis in the callus.

2000-104

ヒヤクニチソウ管状要素分化過程における細包外リグニン前駆体の存在とリグニン化への影響

細川麻美\*<sup>1</sup>、鈷木史朗\*<sup>2</sup>、梅沢俊明\*<sup>2</sup>、佐藤 康\*<sup>1</sup>

\*<sup>1</sup> 愛媛大学理学部、\*<sup>2</sup> 京都大学木質科学研究所、

Existence of extracellular lignin precursors and their effects on lignification during tracheary element differentiation of *Zinnia*.

Mami Hosokawa\*<sup>1</sup>, Shiro Suzuki\*<sup>2</sup>, Toshiaki Umezawa\*<sup>2</sup>, Yasushi Sato\*<sup>1</sup>

Faculty of Science, Ehime University, Wood Research Institute, Kyoto University

Abstract: We investigated how and whence monolignols are supplied to tracheary elements (TEs) undergone programmed cell death using an experimental system of TE differentiation from isolated *Zinnia* mesophyll cells. Alternations of culture condition indicated that monolignols were supplied to TEs through medium. Analyses by HPLC and GC-MS showed that coniferyl alcohol were mainly accumulated in cultured medium. The concentration of coniferyl alcohol peaked at the beginning of secondary wall thickening, decreased during secondary wall thickening, then increased again. These results indicated that lignification of TEs progressed by supply of monolignols from not only TEs themselves but also surrounding xylem parenchyma-like cells.

2000-105

アスパラガス培養細胞の産生する *cis*-ヒノキレジノールの生合成機構について

鈴木史朗、梅沢俊明、島田幹夫

京都大学木質科学研究所

The biosynthesis of *cis*-hinokiresinol produced by cultured cells of *Asparagus officinalis* L.

Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: The biosynthesis of a norlignan, *cis*-hinokiresinol, was studied by feeding of labelled compounds into cultured cells of *Asparagus officinalis* L. treated with fungal elicitor. The SIM-MS analysis showed that two <sup>13</sup>C atoms were incorporated into a single molecule of *cis*-hinokiresinol when [7-<sup>13</sup>C<sub>1</sub>]cinnamate and [8-<sup>13</sup>C<sub>1</sub>]cinnamate were administered individually to the cells, while only one <sup>13</sup>C atom originated from [9-<sup>13</sup>C<sub>1</sub>]cinnamate was incorporated into the compound. The NMR analysis of *cis*-hinokiresinol produced by the cells fed with [9-<sup>13</sup>C<sub>1</sub>]cinnamate revealed the incorporation of a single <sup>13</sup>C atom into the 9-position of *cis*-hinokiresinol. The cells administered with 4-[8-<sup>13</sup>C<sub>1</sub>, ring-<sup>13</sup>C<sub>6</sub>]coumarate produced *cis*-[<sup>13</sup>C<sub>14</sub>]hinokiresinol. These results unequivocally

indicated for the first time that *cis*-hinokiresinol was formed by the coupling of two phenylpropanoid monomer units with the loss of one carbon of the 9-position of the monomer.

2000-106

*Sphingomonas paucimobilis* SYK-6 株のリグニン代謝に関わる脱メチル化酵素機能の多様性と遺伝子配置

園木和典、大塚祐一郎 彰 学、政井英司、福田雅夫、片山義博  
東京農工大学大学院 BASE、長岡技術大学工学部

An enzymatic diversity involved in the O demethylation of lignin metabolism and the gene arrangement in *Sphingomonas paucimobilis* SYK-6.

Tomonori Sonoki, Yuichiro Otuka, Xue Peng, Eiji Masai, Masao Fukuda, Yoshihiro Katayama

\*1Graduate school of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, Nagaoka University of Technology

Abstract: *Sphingomonas paucimobilis* SYK-6, a bacterium that can grow on 5,5'-dehydrodivanillic acid (DDVA) as a sole carbon source, and can also grow on several dimeric model compounds of lignin. This means that this bacterium has various enzyme systems for getting energy from poor degrading compounds such as lignin. *S. paucimobilis* SYK-6 has the O demethylation systems upon three kinds of substrates; DDVA, syringate, and vanillate. We succeeded in detecting enzyme activity and molecular cloning involved in DDVA specific O demethylation and syringate and vanillate specific O demethylation. The biochemical analysis of O demethylation systems revealed that the O demethylation system of DDVA was oxygenase system and that of syringate and vanillate was tetrahydrofolate dependent methyltransferase system. In the genome of SYK-6, the biphenyl specific O demethylase gene and dioxygenase involved in ring fission located in the neighborhood.

2000-107

担子菌におけるダイオキシンストレス応答遺伝子

栗原宏征、割石博之、田中浩雄

九州大学大学院生物資源環境科学研究科

Dioxin stress responsible genes from lignin-degrading basidiomycete.

Hiroyuki Kurihara, Hiroyuki Wariishi, Hiroo Tanaka

Graduate School of Bioresources and Bioenvironmental Sciences, Kyushu University

Abstract: To survey the enzymes and genes involved in fungal degradation of dioxin derivatives, the effect of exogenous dibenzo-*p*-dioxin on extracellular enzyme activities and gene transcription were studied. Lignin peroxidase activity in the culture medium of white-rot fungus *Phanerochaete chrysosporium* increased upon the addition of dibenzo-*p*-dioxin, strongly suggesting the involvement of LiP in the oxidation of this compound. A series of dioxin stress responsible genes were detected using a differential display RT-PCR technique. Several cDNAs of those responsible genes (*FDD-1* to *-6*) were further characterized. The full length cDNA of *FDD-1* was determined and sequenced, indicating that its deduced amino acid sequence showed a high homology to that of quinone oxidoreductase. The expression of this gene was confirmed when dibenzo-*p*-dioxin and catechol were added but not when dibenzofuran was added. The protein encoded by *FDD-1* might play an important role in the reduction of LiP-derived quinone products to the corresponding phenolic compounds for further metabolism.

2000-108

担子菌類の汚染物質分解遺伝子を導入した植物の分子育種と持続的環境修復に関する研究

池田成一郎<sup>\*1</sup>、園木和典<sup>\*1</sup>、飯付洋介<sup>\*2</sup>、早川敏夫<sup>\*3</sup>、金原和秀<sup>\*3</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 工業技術院資源環境技術総合研究所、<sup>\*3</sup> JR 総合技術研究所

Studies on molecular breeding of plants with fungal ability degrades of environmental pollutants and continuous remediation.

Seiichiro Ikeda<sup>\*1</sup>, Tomonori Sonoki<sup>\*1</sup>, Yosuke Iimura<sup>\*2</sup>, Toshio Hayakawa<sup>\*3</sup>, Kazuhide Kinbara<sup>\*3</sup>, Sinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>National Institute for Resources and Environment, <sup>\*3</sup>Railway Technical Research Institute.

Abstract: Plants offer many advantages over bacteria as agents for bioremediation; however, they typically lack the degradative capabilities of specially selected bacterial strains. Innate biodegradative abilities of plants are less impressive than those of adapted bacteria and fungi, but these disadvantages are balanced by the large amounts of plant biomass that can easily be sustained in the field. Transgenic plants expressing microbial degradative enzymes could combine the advantages of both systems. To investigate this possibility, we generated transgenic plants expressing Manganese Peroxidase(MnP), an enzyme derived from *Coliolum versicolor*. In comparison with control, transgenic callus showed high MnP activity.

2000-109

リグニンの $\beta$ -aryl ether 結合の特異的開裂機能を有する新規糸状菌 2BW-1 株の機能及び酵素学的研究

大塚裕一郎、園木和典、片山義博

東京農工大学大学院 BASE

Detection and characterization of new fungous enzyme catalyzing cleavage of guaiacylglycerol- $\beta$ -aryl ether bond.

Yuichiro Ohtsuka, Tomonori Sonoki, Yoshihiro Katayama

<sup>\*1</sup>Graduate school of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology

Abstract: Fungus lignin degradation has studied to upspecific degradation from the viewpoint of lignin. The specific degradation of low molecular lignin has been studied in soil bacterium while that of high molecular lignin isn't yet detected. We focused in the fungi world that have special extracellular deqvqge fmdnleavage function. In this report, we succeeded isolation the fungus, 2BW-1 strain, that has specifical  $\beta$ -aryl ether cleavage function. This function was observed at the extracellular fraction. In this fraction, thee guaiacylglycerol- $\beta$ -O-guaiacyl (GOG) was converted into the guaiacylglycerol. It is the new fungus specifical lignin degrading function.

2000-110

耐塩性白色腐朽菌に関する研究(III):耐塩性白色腐朽菌 MG-60 株が産生する MnP の特性

李 シン、近藤隆一郎、坂井克己

九州大学大学院生物資源環境科学研究科

Studies on hypersaline-tolerant white-rot fungi. (III). Characterization of manganese peroxidase from a marine fungus MG-60.

Xin LI, Ryuichiro Kondo, Kokki Sakai

Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: Characterization of MnPs secreted by a fungus, MG-60 that was incubated at 0% and 3% sea salts concentrations, was reported and the purified MnPs were represented as MnP-0 and MnP-3, respectively, in this paper. The MnPs were highly tolerant to sea salts and NaCl. The

optimum pH and temperature of MnP-0 was 4 and 65°C, respectively, while, for MnP-3, optimum pH was 3 and optimum temperature was 60°C.

2000-111

マンガンペルオキシダーゼ活性に影響を及ぼす担子菌菌体外物質について

扇 剛士、近藤隆一郎、坂井克己

九州大学大学院生物資源環境科学研究科

The extracellular manganese peroxidase activity-stimulating substances produced by basidiomycetes.

Takeshi Ougi, Ryuichiro Kondo, Kokki Sakai

Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: Manganese peroxidase (MnP) is an extracellular heme protein produced by wood-rotting and litter-degrading basidiomycetes especially during secondary metabolism. MnP catalyzes the H<sub>2</sub>O<sub>2</sub>-dependent oxidation of phenolic lignin structures. We have focused in extracellular MnP activity-stimulating substances produced by white rot fungi. The best-studied lignin-degrading fungus, *Phanerochaete chrysosporium* was cultivated in the liquid medium, and extracellular MnP activity-stimulating substances were prepared. Addition of extracellular substances increased the MnP activity comparing with MnP-MnSO<sub>4</sub> system even in succinate buffer. GPC analyses show the possibility that extracellular substances have absorption at 280nm.

2000-112

ラッカーゼ・1-HBT 系による非フェノール性 β-O-4 型リグニンモデル化合物の分解機構の解析

中川 誠、河合真吾、大橋英雄

岐阜大学農学部

Degradation mechanism of non-phenolic β-O-4 lignin model compound by laccase-1-HBT system.

Makoto Nakagawa, Shingo Kawai, Hideo Ohashi

Faculty of Agriculture, Gifu University

Abstract: In the previous work, we demonstrated that *Trametes versicolor* laccase catalyzed not only Cα-Cβ cleavage, Cα oxidation and β-ether cleavage but also aromatic ring cleavage of a non-phenolic β-O-4 lignin model dimer, 1,3-dihydroxy-2-(2,6-dimethoxyphenoxy)-1-(4-ethoxy-3-methoxyphenyl)propane (i), in the present of 1-HBT. This paper reports the incorporation experiments of <sup>18</sup>O from H<sub>2</sub><sup>18</sup>O and <sup>18</sup>O<sub>2</sub> into the degradation products of substrate (i) catalyzed by laccase-1-HBT system. Furthermore, the degradation mechanisms for non-phenolic β-O-4 lignin model dimer by this system are discussed.

2000-113

白色腐朽菌 *Ceriporiopsis subvermispora* によるポリイソプレノイドの分解

佐藤 伸、榎 牧子、本田与一、渡辺隆司、桑原正章

京都大学木質科学研究所

Degradation of polyisoprenoids by white rot fungus *Ceriporiopsis subvermispora*.

Shin Sato, Makiko Enoki, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: Vulcanized natural rubber sheet was intensively degraded on wood meal cultures by a selective white rot fungus, *Ceriporiopsis subvermispora*, while *Dichomitus squalens* was not able to decompose the rubber sheet under the same culture condition. *C. subvermispora* also decomposed synthetic polyisoprenoids, styrene-butadiene rubber (SBR) and ethylene-propylene rubber (EP) in

addition to natural polyisoprene isolated from natural rubber latex on wood cultures. Structural changes of the fungal treated polyisoprenoids were analyzed.

2000-114

MnP-脂質過酸化複合系による多環式芳香属炭化水素類の酸化

松浦好高<sup>\*1</sup>、長野和種<sup>\*2</sup>、堤 祐司<sup>\*1</sup>、西田友昭<sup>\*1</sup>

<sup>\*1</sup> 静岡大学農学部、<sup>\*2</sup> 名古屋大学大学院生命農学研究科

Oxidation of polycyclic aromatic hydrocarbons by MnP-lipid peroxidation system.

Yositaka Matsuura<sup>\*1</sup>, Kazutane Nagano<sup>\*2</sup>, Yuji Tsutsumi<sup>\*1</sup>, Tomoaki Nishida<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Shizuoka University, <sup>\*2</sup> Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: We investigate the reaction mechanisms in the oxidation of polycyclic aromatic hydrocarbons by a MnP-mediated lipid peroxidation system. In the system containing 100 mU/ml of MnP, linoleic acid was rapidly consumed and produced active radical species to react with anthraene (AT), consequently a decrease of AT followed to almost a pseudo-first order reaction. The oxidation rates of linoleic acid and AT were not largely affected by the reduction of MnP concentration down to 25 mU/ml in the system. A reaction with very low MnP concentration (2.5 mU/ml) in the system suggests that the MnP-mediated lipid peroxidation to produce active radical species is composed of at least two reactions: the first step is very fast and probably the formation of peroxidized-lipid as intermediates, and the next is the formation of active radical species from intermediates.

2000-115

ペルオキシダーゼ活性を抑制した組換え樹木のリグニン構造

諸星紀幸<sup>\*1</sup>、李 亜紅<sup>\*1</sup>、並木理卓<sup>\*1</sup>、西窪伸之<sup>\*1</sup>、梶田真也<sup>\*1</sup>、辻 幸子<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 名古屋大学大学院生命農学研究科

Lignin chemical structure of transgenic poplar controlling the peroxidase activity.

Noriyuki Morohoshi<sup>\*1</sup>, Li Yahong<sup>\*1</sup>, Ritaku Namiki<sup>\*1</sup>, Nobuyuki Nishikubo<sup>\*1</sup>, Shinnya Kajita<sup>\*1</sup>, Yukiko Tsuji<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Bio-application and Systems engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: The objective of our research was to form a super tree using new biotechnological and genetic engineering techniques. The primary aim was to produce a tree with a lower lignin content by controlling lignin biosynthesis genes using antisense RNA. The isolation and sequencing of *prx43a* involved in lignification from hybrid aspen (*Populus kitakamiensis*) was achieved. The transgenic poplars had lower total peroxidase activity compared with that of the control. After peroxidase isozyme analysis by the isoelectric focusing, it was clear that a peroxidase band (pI 3.8) disappeared in the transgenic plants. The lignin content in transgenic plants decreased 20-50% compared with control parts when the potassium permanganate oxidation method was used. A characteristic of the lignin chemical structure in transformants are to have more syringyl units, beta-O-4 structures and condensed units. The decrease of syringyl units and lignin contents in the primary xylem tissue of transformant (POX27) were also observed by the ultraviolet microscopy.

2000-116

酸化的脱リグニン過程でのβ-O-4 型側鎖構造の変化について

杉本倫子、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Change in side-chain of β-O-4 structure during oxidative degradation of lignin.

Tomoko Sugimoto, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: By the ozonation method, erythro and threo (E/T) ratio of arylglycerol- $\beta$ -aryl ether ( $\beta$ -O-4) structure can be obtained as a ratio between two ozonation products, erythronic and threonic acids. Previously, when wood samples were delignified by NaClO<sub>2</sub> treatment, no significant change was observed in E/T ratio of residual lignin. In order to confirm the reason for this, MWL was treated with NaClO<sub>2</sub>, and changes in side-chain part ( $\beta$ -O-4 structure) of lignin were observed by ozonation method. NaClO<sub>2</sub> treated MWL showed almost the same E/T ratio as starting MWL, indicating that delignification reaction proceeded homogeneously during NaClO<sub>2</sub> treatment. When MWL was reduced by NaBH<sub>4</sub>, the yield of both acids increased. This increase is due to the reduction of  $\beta$ -O-4 structure that possesses  $\alpha$ -carbonyl structure, but since the reduction of NaBH<sub>4</sub> was stereo-preferential, the increase in threonic acid was greater than erythronic acid. When this NaBH<sub>4</sub>-reduced MWL (red-MWL) was treated with NaClO<sub>2</sub>, the yields of both acid decreased but not significantly. Probably, oxidatively cleaved aromatics during NaClO<sub>2</sub> treatment can still give erythronic and threonic acids by ozonation if they carry  $\beta$ -O-4 structure. But when NaBH<sub>4</sub> reduction was conducted after NaClO<sub>2</sub> treatment, the yield of ozonation product decreased significantly. The reason for this is probably that the reduction of cleaved aromatics would change these structures into structure that could not produce erythronic and threonic acids by ozonation method. These NaClO<sub>2</sub> treatments of red-MWL were conducted in aerobic and anaerobic atmosphere, but no significant difference was observed between these two. At least in this reaction condition, the presence of oxygen does not affect the NaClO<sub>2</sub> treatment of (red-)MWL.

2000-117

リグニン中の $\beta$ -O-4型側鎖構造の光学活性に関する研究

秋山拓也<sup>\*1</sup>、松本雄二<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、石津 敦<sup>\*1</sup>、真柄謙吾<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 森林総合研究所

Studies on the optical activities of  $\beta$ -O-4 structure in lignin by ozonation method.

Takuya Akiyama<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>, Kengo Magara<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup> Forestry and Forest Products Research Institute

Abstract: Erythronic acid and threonic acid were obtained from corresponding *erythro* and *threo* forms of arylglycerol- $\beta$ -aryl ether structure in lignin by ozonation of Birch wood meal. These acids obtained from lignin keep the stereo structure of side-chain part of  $\beta$ -O-4 ether structure. Erythronic and threonic acids were separated by HPLC and were collected, respectively. The fraction of erythronic acid was subjected to HPLC analysis, and the optical activity was measured by on-line optical rotation detector. The optical activity of threonic acid was also measured. It was confirmed that both *erythro* and *threo* forms of arylglycerol- $\beta$ -guaiacyl ether structure consist of two enantiomers. It was strongly suggested that the *erythro* forms of arylglycerol- $\beta$ -guaiacyl ether structure is optically inactive (enantiomer excess (e.e.) < 3.5%). As to threonic acid, because of the incompleteness of purification, maximum e.e. was rather high but was still less than 10%.

2000-118

熱分解ガスクロマトグラフィーによるシナムアルデヒドを含むモノリグノール比の解析

園田哲也<sup>\*1</sup>、小名俊博<sup>\*1</sup>、横井裕明<sup>\*2</sup>、石田康行<sup>\*2</sup>、大谷 肇<sup>\*2</sup>、柘植 新<sup>\*2</sup>

王子製紙株式会社森林資源研究所、名古屋大学大学院工学研究科

Characterization of monolignol ratio including cinnamaldehydes by pyrolysis-gas chromatography.

Tetsuya Sonoda<sup>\*1</sup>, Toshihiro Ona<sup>\*1</sup>, Hiroaki Yokoi,<sup>\*2</sup> Yasuyuki Ishida<sup>\*2</sup>, Hajime Ohtani<sup>\*2</sup>, Shin Tsuge<sup>\*2</sup>

\*<sup>1</sup>Forestry Research institute, Oji Paper Co. Ltd., \*<sup>2</sup> Graduate School of Engineering, Nagoya University  
Abstract: It is difficult to determine cinnamaldehyde components in lignin accurately by pyrolysis-gas chromatography (Py-GC) because the secondary formation of cinnamaldehydes are considered to occur from the cinnamyl alcohol components in lignin during pyrolysis. In this work, we examined the compositional analysis of monolignols including cinnamaldehydes in various DHPs and woods using pre-acetylation before Py-GC in order to prevent the secondary formation of cinnamaldehydes during pyrolysis. On the basis of the characteristics peaks on the pyrograms, the monolignol ratios in various DHPs determined with taking cinnamaldehydes into consideration were in excellent agreement with those in the DHP preparation.

2000-119

反応熱脱着ガスクロマトグラフィーによる木材中の抽出成分の迅速分析

横井裕明<sup>\*1</sup>、中瀬敬二<sup>\*1</sup>、後藤邦佳<sup>\*1</sup>、石田康行<sup>\*1</sup>、大谷 肇<sup>\*1</sup>、柘植 新<sup>\*1</sup>、園田哲也<sup>\*2</sup>、小名俊博<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院工学研究科、<sup>\*2</sup>王子製紙株式会社森林資源研究所

Rapid characterization of wood extractives by reactive thermal desorption-gas chromatography.

Hiroaki Yokoi<sup>\*1</sup>, Takahito Nakase<sup>\*1</sup>, Kuniyoshi Goto<sup>\*1</sup>, Yasuyuki Ishida<sup>\*1</sup>, Hajime Ohtani<sup>\*1</sup>, Shin Tsuge<sup>\*1</sup>, Tetsuya Sonoda<sup>\*2</sup>, Toshihiro Ona<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Engineering, Nagoya University, <sup>\*2</sup>Forestry Research institute, Oji Paper Co. Ltd.

Abstract: A novel rapid method to characterize wood extractives was developed on the basis of reactive thermal desorption-gas chromatography (RTD-GC) in the presence of an organic alkali, tetramethylammonium acetate ( $(\text{CH}_3)_4\text{N}^+\text{OCOCH}_3^-$ ; TMAAc). The reactive thermal desorption at 200°C using TMAAc allowed highly sensitive detection of wood extractives such as fatty acids, steroids and phenols in *Eucalyptus camaldulensis* as their methyl derivatives on the resulting pyrograms without using any cumbersome pretreatments such as solvent extraction. The distribution of fatty acids in extractives was able to estimate by RTD-GC using powdered wood samples as received with relative standard deviations of around 5%. The observed result was in good agreement with that determined using acetone solubles.

2000-特別講演

今後の植物の遺伝子組み換え

林 秀則

愛媛大学理学部

Invited Lecture: Future aspects in genetic engineering of plants.

Hidenori Hayashi

Department of Chemistry, Ehime University

Abstract: Gene engineering of stress tolerance in plants is powerful technique which would be helpful to improve the crop productivity and to recover the damaged environment. So far target genes suitable for this purpose have been searched from a variety of organisms and used for plant transformation. In addition to these preexisting gene, more potential genes would be available if we understand the molecular mechanism of each gene product and design proteins having enhanced function by molecular engineering. In this lecture, I will demonstrate an example of gene engineering to enhance the salt tolerance in plant with the gene for synthesis of a compatible solute as well as our approach in the molecular engineering of proteins responsible for heavy metal tolerance in cyanobacteria.

2000-201

MWL 抽出残渣からのリグニンの溶出挙動

廣沢修一、中坪文明

京都大学大学院農学研究科

The behavior of extraction of lignin from wood meal after extraction of milled wood lignin.

Shuichi Hirotsawa, Fumiaki Nakatsubo

Graduate School of Agriculture, Kyoto University

Abstract: At present, milled wood lignin (MWL) is mainly used to investigate chemical structure of lignin. But the MWL is not representative of the total lignin component. Therefore, elucidation of chemical structure of lignin in the wood meal after extraction of the MWL (WMEM) is important. In this study, lignin in the WMEM was fractionated by extractions with solvents for polysaccharides (hemicellulose, cellulose). Alkali extraction was carried out for the purpose of extraction of hemicellulose and lignin. Then, cellulose and lignin was extracted with LiCl/N, N-dimethylacetamide (DMAc). Determination of lignin contents, nitrobenzene oxidation and sugar analyses were carried out to elucidate behaviors of polysaccharides and lignin during extractions.

2000-202

非フェノール性  $\alpha$ -O-アルキル  $\beta$ -O-4 型シリングルリグニンモデルのエリスロ・スレオ体の NMR と酸加水分解過程の速度論的解析

岸野正典\*<sup>1</sup>、大井 洋\*<sup>2</sup>、大原誠資\*<sup>3</sup>

\*<sup>1</sup> 北海道立林産試験場、\*<sup>2</sup> 筑波大学農林工学系、\*<sup>3</sup> 森林総合研究所

NMR of erythro and threo forms of nonphenolic  $\alpha$ -O-alkyl  $\beta$ -O-4 type syringyl lignin model and kinetics of their acid hydrolysis.

Masanori Kishino, Hiroshi Ohi, Seiji Ohara

Hokkaido Forest Products Research Institute, Institute of Agricultural and Forest Engineering, University of Tsukuba, Forestry and Forest Products Research Institute

Abstract: NMR chemical shifts of erythro and threo forms of  $\alpha$ -ethyl ether derivatives of veratrylglycerol- $\beta$ -syringyl ether (VSE: 3-(3,4-dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-ethoxypropan-1-ol) were assigned on the basis of the kinetics for acid hydrolysis of each diastereomer of VSE into the diastereomers mixture of veratrylglycerol- $\beta$ -syringyl ether (VS: 1-(3,4-dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol). One VSE diastereomer eluted earlier by HPLC and the other diastereomer were named VSE<sub>1</sub> and VSE<sub>2</sub>, respectively. The value of  $z_1$  defined as a molar ratio (VS threo to VSE<sub>1</sub>) at which VSE<sub>1</sub> gave VS threo during the acid hydrolysis was found to be 1.000. The value of  $z_2$  for VSE<sub>2</sub> giving VS erythro isomer of VS was 0.841. This indicates that VSE<sub>1</sub> is the erythro form of VSE. In addition, coupling constants ( $J_{\alpha\beta}$ ) for both VSE<sub>1</sub> (erythro VSE) and VSE<sub>2</sub> (threo VSE) were 7.0Hz, although those for erythro and threo forms of VS were 3.7 Hz and 7.5Hz, respectively. This indicates that conformations of VSE are changed by introduction of  $\alpha$ -ethyl group into VS.

2000-203

遺伝子組換えタバコから得られる木部組織のパルプ蒸解生性

梶田真也\*<sup>1</sup>、石藤雅俊\*<sup>2</sup>、原 晋一\*<sup>2</sup>、川端治彦\*<sup>2</sup>、諸星紀幸\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学大学院 BASE、\*<sup>2</sup> 三菱製紙株式会社、

Pulping characteristics of xylem materials from transgenic tobacco plants.

Shinya Kajita, Masatoshi Ishifuji, Shin-ich Hara, Haruhiko Kawabata, Noriyuki Morohoshi

Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Mitsubishi Paper Mills Limited,

Abstract: 4-Coumarate:CoA ligase (4CL) is a phenylpropanoid biosynthetic enzyme that converts hydroxycinnamic acids into corresponding CoA esters. Recently, we produced transgenic

tobacco plants with a chimeric gene for 4CL. The activity of 4CL and lignin content in the plants were depressed by effect of the introduced gene. In this Study, we found that tobacco chips, the xylem

materials from the transgenic plants, was delignified more extensively than those from controls in Kraft pulping process. This result indicates that genetic engineering of lignin biosynthesis with modulation of 4CL activity is an efficient tool for production of new wood materials.

2000-204

HBS パルプ化-RHBS の脱リグニン促進効果

梶本純子、佐野嘉拓

北海道大学大学院農学研究科

HBS pulping. -Acceleration effect of RHBS on delignification.

Junko Kajimoto, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: HBS pulping with saving-energy and non-pollution was investigated using aqueous solvents (HBS) with boiling point of about 200°C. Todomatsu and birch chips were satisfactorily pulped with the pulping process. RHBS recovered only high molecular-weight lignin from spent liquors were reused several times as a pulping solvent, though it consisted of sugars, modified sugars, low molecular-weight lignin and so forth as minor components in addition of a main material HBS. RHBS was a more excellent pulping solvent than pure HBS. The accelerated effect of RHBS on the delignification resulted from aldoses existed in RHBS. Both delignification with HBS and RHBS obeyed two pseudo first-order kinetics, bulk and final phases, respectively. The rate constant of the bulk phase with RHBS was about 1.5 times that with HBS. We name the delignification of lignin with aldoses "aldosolysis". When heated with aqueous neutral solvent at temperatures of above 200°C, the depolymerization of lignin takes place by homolysis, though it is accelerated by aldolysis.

2000-205

HBS パルプ化 - $\beta$ -O-4 モデル化合物の反応(2) -

岸本崇生、佐野嘉拓

北海道大学大学院農学研究科

HBS pulping. - Reaction of  $\beta$ -O-4 type lignin model compounds. (2).

Takao Kishimoto, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: We have been proposed that phenolic  $\beta$ -aryl ethers in lignins are cleaved homolitically via the formation of quinone methide intermediates under HBS (high-boiling solvent) pulping conditions. In order to confirm the delignification mechanism, a phenolic  $\beta$ -O-4 type lignin model compound, guaiacylglycerol- $\beta$ -guaiacyl ether (GG) was treated with 70 wt % aq 1,4-butanediol solution at 180 °C. Thirteen compounds including 4 monomers, 6 dimers, 2 trimers and 1 tetramer were isolated from the reaction products. Most of those oligomeric products were generated by recombination of phenoxy radicals formed by homolysis of the  $\beta$ -aryl ether. These results support that phenolic  $\beta$ -O-4 linkages in lignin are cleaved by radical mechanism under HBS pulping conditions.

2000-206

リグニン芳香核の酸化的開裂に伴う構造変化 -生成する低分子カルボン酸類の起源構造-

角田靖典、新谷博幸、飯塚堯介

東京大学大学院農学生命科学研究科

Structural changes of lignin at oxidative degradation of aromatic rings. –Origin of low molecular weight carboxylic acids.

Yasunori Tsunoda, Hiroyuki Shintani, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Hardwood kraft lignin was treated with alkaline oxygen (1 mol/L NaOH, 0.3 MPa, 70°C, 8 hours) in H<sub>2</sub>O, H<sub>2</sub>O–D<sub>2</sub>O (1:1) and D<sub>2</sub>O. <sup>13</sup>C–NMR spectra of these three samples indicated the production of many kinds of low molecular weight compounds, especially a lot of carboxylic acids, and introduction of deuterium atoms to their compounds, although quantitative evaluation of each compound or structure was not accomplished. When alkaline oxygen treated samples in H<sub>2</sub>O were heated in D<sub>2</sub>O/NaOD at 70°C for 8 hours, further structural change of some compounds were indicated by <sup>13</sup>C–NMR.

2000–207

酸処理・過酸化水素漂白を用いるクラフトパルプの低二酸化塩素添加・無塩素漂白

大井 洋

筑波大学農林工学系

Non-chlorine bleaching of kraft pulp with small addition of chlorine dioxide using acid treatment and peroxide beaching.

Hiroshi Ohi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Non-chlorine bleaching of hardwood kraft pulp (LUKP) with a small addition of chlorine dioxide was investigated. Acid (A) treatment conducted at pH2–2.5 and 40–80°C for 30–120min was proposed as the pre-treatment of peroxide (P) beaching. By the A treatment, manganese could be reduced and removed significantly. Kappa numbers of pulp were decreased slightly by the A treatment. The P bleaching at 105°C could be improved by stabilization of manganese (II) in pulp. Dioxins and coplanar PCBs from LOKP bleaching with a very large excess of chlorine dioxide were determined. Formation of 2,3,7,8–TCDD and PCBs was at a little higher level than the minimum level, but 2,3,7,8–TCDF was distinctly determined. A possibility that an excess of chlorine dioxide may cause TCDFs formation was shown. Then, the sequences using the A–P bleaching and a small addition of chlorine dioxide were developed; O–A–P–D, O–A–P–D–P<sub>2</sub>, A–P–A–P–D, A–P–D–P<sub>2</sub>–D, A–P–H–D–P<sub>2</sub>, and O–A–P–A–P<sub>2</sub>, A–P–A–P for totally chlorine free bleaching of LUKP.

2000–208

リグニンの脱水素重合反応に対する分子軌道法によるコンピュータシミュレーション

重松幹二、小林孝行、杉野哲也、棚橋光彦

岐阜大学農学部

Computer simulation by molecular orbital calculation on the dehydrogenative polymerization of lignin.

Mikiji Shigematsu, Takayuki Kobayashi, Tetsuya Sugino, Mitsuhiko Tanahashi

Faculty of Agriculture, Gifu University

Abstract: Solvent effect on the dehydrogenative polymerization of lignin was computer-simulated by semi-empirical molecular orbital calculation, MOPAC2000. The simulation was divided into three stages and analyzed; 1) one electron oxidation of monolignols catalyzed by horseradish peroxidase (HRP) analyzed by HOMO energy level, 2) spin density and atomic charge of reactable atoms, 3) transition state and activation enthalpy at radical coupling reaction. All the results of these simulations qualitatively agreed with the experimental results about solvent effect,

i.e., the activity of HRP to monolignols, and the increased formation of  $\beta$ -O-4 linkage in a nonpolar solvent.

2000-209

分子軌道計算によるフェノール化合物のホルムアルデヒドとの反応性予測

光永 徹<sup>\*1</sup>、Anthony H. Conner<sup>\*2</sup>、Charles G. Hill Jr<sup>\*3</sup>.

<sup>\*1</sup> 三重大学生物資源学部、<sup>\*2</sup>USDA-Forest Service, Forest Products Laboratory、<sup>\*3</sup>College of Engineering, University of Wisconsin

Predicting the reaction of formaldehyde with phenols by molecular orbital computation.

Tohru Mitsunaga<sup>\*1</sup>、Anthony H. Conner<sup>\*2</sup>、Charles G. Hill, Jr<sup>\*3</sup>

<sup>\*1</sup>Faculty of Bioresources, Mie University、<sup>\*2</sup>USDA-Forest Service, Forest Products Laboratory、<sup>\*3</sup>Department of Chemical Engineering, College of Engineering, University of Wisconsin

Abstract: Computational chemistry has been used to study the relationship between the reactivity of a number of phenolic compounds with formaldehyde in an aqueous, alkaline system, and charges calculated for reactive sites on the aromatic ring of the phenolic compound. Atomic-charges for each phenolic compound were calculated by *ab initio* methods at the RHF/6-31+G level of theory using the ChelpG method. Reaction rate constants were determined from measurements of the concentrations of the phenolic compounds and formaldehyde as functions of time. The charge per reactive site was estimated by summing the charges at all the reactive sites on the phenolic ring and dividing by the number of reactive sites. A strong correlation was observed between the reactivity per reactive site and the average charge per reactive site.

2000-210

超臨界メタノールによる木質系バイオマスの化学変換 –針葉樹と広葉樹の比較–

南 英治、大貫英範、坂 志朗

京都大学大学院エネルギー科学研究科

Chemical conversion of woody biomass in supercritical methanol. –Comparisons between softwood and hardwood.

Eiji Minami, Hidenori Onuki, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: The supercritical methanol biomass conversion system with batch-type reaction vessel was applied to study the chemical conversion of sugi (*Cryptomeria japonica*) and buna (*Fagus crenata*) woods to useful chemicals. As a result, more than 90% of sugi and buna woods were decomposed and liquefied in methanol for 30min supercritical treatment at 350°C–43MPa. In addition, buna wood was easier to be liquefied in methanol than sugi at 270°C–27MPa. It was further indicated for the methanol-insoluble residues that observed differences are mainly originated from intrinsic ones in lignin structure between softwood and hardwood.

2000-211

亜臨界水及び超臨界水による木材の化学変換 –リグニンの分解–

江原克信、坂 志朗

京都大学大学院エネルギー科学研究科

Chemical conversion of wood by subcritical or supercritical water. –Degradation of lignin.

Katsunobu Ehara, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: Chemical conversion of buna wood (*Fagus crenata* Blume) was made in subcritical and supercritical water (>22.1MPa, >374°C) to study liquefaction mechanism of wood. The treated wood

was fractionated into the water-soluble portion, methanol-soluble portion, and methanol-insoluble residues. In this study, a characterization of the lignin was focused on the methanol-soluble portion. The obtained methanol-soluble portion showed to be rich in lignin and more oxidative with more phenolic hydroxyl groups than milled wood lignin (MWL). The alkaline nitrobenzene oxidation analyses of the lignin in methanol-soluble and methanol-insoluble portions exhibited a decrease of oxidation products under supercritical water treatment. These observations suggested that a preferential degradation of the ether linkages of lignin occurred in supercritical water.

2000-212

スギ樹皮のポリエチレングリコール・バイサルファイト法による液化

上野智子、耿 興蓮、芦谷竜矢、親泊政二三、坂井克己

九州大学大学院生物資源環境科学研究科

Liquefaction of sugi (*Cryptomeria japonica* D. Don) bark by Polyethyleneglycol-bisulfite method.

Tomoko Ueno, Xinglian Geng, Tatsuya Ashitani, Masafumi Oyadomari, Kokki Sakai

Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: Polyethyleneglycol-bisulfite treatment was applied to the liquefaction of inner and outer barks of sugi. The optimal temperature of the treatment was 250°C. The longer liquefaction time resulted in the higher solubilization of inner bark. In the case of outer bark, condensation of lignin and/or tannin appeared to occur during treatments for 60min and longer. The concentration of aqueous sodium bisulfite solution exhibited no influence on solubilization of inner bark. Higher solubilization of outer bark was obtained in higher concentration of the bisulfite solution. This result suggests that sodium bisulfite caused sulfonation of lignin and condensed tannin which are contained in larger amounts in outer bark than in inner bark.

2000-213

含糖型ポリウレタンの熱的および機械的性質に対するリグニン添加の影響

畠山兵衛<sup>\*1</sup>、浅野育洋<sup>\*1</sup>、廣瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>工業技術院物質研究所、<sup>\*3</sup>大妻女子大学家政学部

Influence of lignin on thermal and mechanical properties of polyurethanes containing saccharides.

Hyo Hatakeyama<sup>\*1</sup>, Y Asano<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Fukui Institute of Technology, <sup>\*2</sup>National Institute of Materials and Chemical Research, <sup>\*3</sup>Otsu Women's University

Abstract: Polyurethane (PU) foams with various lignin and saccharides contents were prepared by changing the ratio between kraft lignin (KL) and molasses (ML) contents in polyethylene glycol ( $M_w = ca. 200$ ). Thermal and mechanical properties of the above polyurethanes (PU's) were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous TG and Fourier-transformed infrared spectrometry (TG-FTIR) and mechanical measurements. Glass transition temperatures ( $T_g$ 's) of the PU's decreased with increasing KL/ML ratio. However, thermal degradation temperatures ( $T_d$ 's) increased with increasing KL/ML ratio. The amount of thermal degradation products having characteristic functional groups changed according to the temperature.

2000-214

相分離システムによる草本系リグノフェノール誘導体の誘導

関 範雄<sup>\*1</sup>、伊藤国徳<sup>\*1\*2</sup>、船岡正光<sup>\*2</sup>

<sup>\*1</sup>岐阜県生活技術研究所、CREST,JST、<sup>\*2</sup>三重大学生物資源学部、CREST,JST

Synthesis of lignophenol derivatives from herbaceous lignocellulosics through phase-separation system.

Norio Seki<sup>\*1</sup>, Kuniyasu Itoh<sup>\*1\*2</sup>, Masamitsu Funaoka<sup>\*2</sup>

<sup>\*1</sup>Gifu Prefectural Human Life Technology Research Institute, <sup>\*2</sup>Faculty of Bioresources, Mie University

Abstract: Lignophenol derivatives were synthesized from various herbaceous lignocellulosics, using phase-separation system that was composed of phenol derivatives and concentrated acid, and their characteristics were investigated. Their yields were higher with mild concentrated acid treatment during this system, compared with that of softwood. Although lignophenol derivatives from herbs had similar basic characteristics to that from woods, some characteristics of which slightly differed with their originating species and woods. These differences would be due to the difference in the network structure of native lignin, the distribution and quantity of ether linkages, and the degree of condensation.

2000-215

両親媒性物質に親和性を示す酢酸リグニンヒドロゲルの調製

西田光邦、浦木康光、佐野嘉拓

北海道大学大学院農学研究科

Preparation of acetic acid lignin hydrogel with affinity for amphiphilics.

Mitsukuni Nishida, Yasumitsu Uraki, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: Acetic acid lignin (AL) prepared by the atmospheric acetic acid pulping of birch was found to form hydrogel by the reaction with polyethylene glycol diglycidyl ether (PE) as a cross-linker under alkaline conditions. In this study, the gelation time and the adsorption ability of the gel to cationic surfactants were investigated to clarify the properties of novel lignin gels. The gel formation depended on amounts of glycidyl group in PE and reaction temperatures. AL hydrogel remarkably adsorbed cationic surfactants with long alkyl chains, but the surfactants with the short chain was not adsorbed. This result suggests that the adsorption was mainly caused from hydrophobic interaction between AL domain of gel and alkyl chain of surfactant.

2000-特別講演

リグニン研究とケナフ栽培利用研究の接点について

鮫島一彦

高知大学農学部

Invited Lecture: About the overlapping points of lignin research and kenaf cultivation and utilization research.

Kazuhiko Sameshima,

Faculty of Agriculture, Kochi University

Abstract: Kenaf (*Hibiscus cannabinus*, in some case a variety of *Hibiscus sabdariffa* is included) is a fiber plant which is traditionally used for making rope, bag and other fiber products. It is now, however, widely recognized that kenaf could be one of the possible plants to fight to realize a new fiber production and utilization system for the future in many places in the world. After the industrial revolution wood has been recognized as a fiber plant and used for pulp and paper making and other purposes for large-scale production. It is still true but other fiber plant like kenaf should be utilized as a supplemental fiber for many purposes. Because the population increases, environmental problems and other modern problems could be solved in part by using kenaf as useful plant for human being. Lignin research has been mostly concentrated on wood utilization, but the methods will be adopted to kenaf research and development. It grows fast and have low lignin and silica content, and it might be easier for lignin researchers to find useful methods for kenaf versatile utilization.

2000-P01

リグニンモデル化合物を用いた超臨界メタノールでのリグニンの反応性

辻野潤一郎、河本晴雄、坂 志朗

京都大学大学院エネルギー科学研究科

Reactivity of lignin in supercritical methanol studied with some lignin model compounds.

Junichiro Tsujino, Harui Kawamoto, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: Behaviors of lignin in supercritical methanol were studied by using lignin model compounds. As a result, both guaiacyl and syringyl types of aromatic rings and biphenyl type structures were very stable under supercritical condition of methanol. However,  $\beta$ -ether linkage in the phenolic  $\beta$ -O-4 model compound was cleaved rapidly into guaiacol and coniferyl alcohol which was further converted to its  $\gamma$ -methyl ether. Non-phenolic  $\beta$ -O-4 model compound was, on the other hand, converted initially into its  $\alpha$ -methyl ether and further degraded to produce guaiacol. Such a continuous decomposition can suggest that the supercritical methanol treatment is very effective to depolymerize lignin into the lower molecular products. These lines of evidence imply that new phenolic residues of lignin are continuously formed and decomposed repeatedly in supercritical methanol mainly by the cleavage of the dominant  $\beta$ -ether structure in lignin.

2000-P02

非塩素漂白過程における $\alpha$ -カルボニル型リグニン構造の挙動 I. 重水素ラベルとニトロベンゼン酸化を組み合わせた定量法

友田生織、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Formation and degradation of  $\alpha$ -carbonyl structure in lignin during chlorine free bleaching. I. Method to estimate the  $\alpha$ -carbonyl content in lignin remaining in pulp.

Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: It is generally assumed that  $\alpha$ -carbonyl structure is one of the key structures which govern the reactivity of lignin towards non-chlorine bleaching. We developed a method to evaluate the content of  $\alpha$ -carbonyl structure in residual lignin without isolating the lignin from the pulp. This method is based on a finding that a deuterium atom introduced to  $\alpha$ -position by a  $\text{NaBD}_4$  reduction of  $\alpha$ -carbonyl structure could be retained in aldehyde when nitrobenzene oxidation was applied under mild condition. Under the modified reaction condition of nitrobenzene oxidation, the retention of  $\alpha$ -D in a model compound was about 70%.

2000-P03

GC法によるメトキシ基の定量法の再評価(2)-漂白パルプのリグニンメトキシ基の定量-

後藤仁志<sup>\*1</sup>、幸田圭一<sup>\*2</sup>、松本雄二<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 北海道大学大学院農学研究科

Determination of methoxyl content with GC method.(2). -Determination of lignin methoxyl content in bleached pulp.

Hitoshi Goto<sup>\*1</sup>, Keiichi Koda<sup>\*2</sup>, Yuji Matsumoto<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Graduate School of Agriculture, Hokkaido University

Abstract: Several types of lignin model compounds were subjected to HI treatment under various conditions and the yield of methyl iodide was determined. Methyl iodide formation from a

compound with electron donating group was faster than that with electron withdrawing group. Not only the iodide concentration but also the acid concentration significantly affected the formation rate of methyl iodide. All these results seemed to be explained well by a hypothesis that the protonation to the oxygen atom of methoxyl group plays a decisive role in the cleavage of this group by HI. The ability of carbohydrate as Lewis base to consume acid could partly explain the interfering effect of the carbohydrate on the methyl iodide formation from a model compound, which could be explained also by a consumption of iodide by carbohydrates.

2000-P04

木材炭化に伴う抽出成分の構造変化

渡辺泰高<sup>\*1</sup>、光永 徹<sup>\*1</sup>、中原光一<sup>\*2</sup>

<sup>\*1</sup> 三重大学生物資源学部、<sup>\*2</sup> サントリー株式会社基礎研究所

Structural changes of extractives by carbonization of wood.

Yasutaka Watanabe<sup>\*1</sup>, Tohru Mitsunaga<sup>\*1</sup>, Koichi Nakahara<sup>\*2</sup>

<sup>\*1</sup>Faculty of Bioresources, Mie University, <sup>\*2</sup> Institute for Fundamental Research, Suntory Ltd.,

Abstract: Constitutional analysis of the components extracted with 60% aqueous ethanol from the carbonized or heated (180°C) white oak (*Quercus alba* L.) wood were investigated. The yield of the extractives from carbonized or heated wood was almost the same with untreated wood, but the color of the solution from treated wood showed light brown and its color became dark brown as the function of time. Gallic acid, syringic acid, vanillic acid, vanillin, syringaldehyde and ellagic acid were contained in the extractives of wood with and without carbonization. On the other hand, the yields of these compounds from carbonized wood meal were 1.6–6.3 times of untreated meal. In addition, 5-hydroxymethylfurfural and sinapaldehyde were formed from treated wood and wood meal.

2000-P05

フェノール性  $\beta$ -O-4 型リグニンモデル化合物の熱分解

堀越 直、河本晴雄、坂 志朗

京都大学大学院エネルギー科学研究科

Thermal degradation of phenolic  $\beta$ -O-4 lignin model compounds

Sunao Horigoshi, Haruo Kawamoto, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: Effects of C $\alpha$  and C $\gamma$  structures on the cleavage of the  $\beta$ -ether during thermal degradation of lignin were studied by the reactivity of four phenolic  $\beta$ -O-4 lignin model compounds under atmospheric nitrogen at 400°C for 1 min. As a result, the reactivity varied greatly with the C $\alpha$  and C $\gamma$  structures (C $\gamma$ : CH<sub>2</sub>OH  $\gg$  CH<sub>3</sub>, C $\alpha$ : C=O  $\gg$  CH<sub>2</sub>OH $\equiv$ CH<sub>3</sub>). Mechanism of thermal degradation of the  $\beta$ -ether is discussed with these results; C $\gamma$ -OH plays an important role in the  $\beta$ -ether cleavage, while neighboring group participation of C $\alpha$ -OH and a quinonemethide intermediate formed by elimination of this hydroxyl group are not important in the mechanism.

2000-P06

水蒸気圧縮処理による樹液抽出法の開発(II)

棚橋光彦<sup>\*1</sup>、鈴木正史<sup>\*1</sup>、神谷 恵<sup>\*1</sup>、志智千賀子<sup>\*1</sup>、小林孝行<sup>\*1</sup>、京盛健一<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学農学部、<sup>\*2</sup> 岐阜大学工学部

Development of a sap extraction method associated with the compressive molding process. (II).

Mitsuhiko Tanahashi<sup>\*1</sup>, Masashi Suzuki<sup>\*1</sup>, Megumi Kamiya<sup>\*1</sup>, Chikako Shicchi<sup>\*1</sup>, Takayuki Kobayashi<sup>\*1</sup>, Ken-ichi Kyomori<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Gifu University, <sup>\*2</sup>Faculty of Engineering, Gifu University

Abstract: We have developed a compressive molding process, which converts thinnings or the growth of miscellaneous hardwood species to useful materials. However, sap is disposed of together with wastewater in this process. In this study, utilization of the sap for new industrial materials was investigated. Composition analysis of the sap from white birch, detected the presence of sinapylalcohol and coniferylalcohol. In another study, 5-hydroxymethylfurfural was identified from leaves of Japanese cedar. These compounds will be useful as industrial materials. Furthermore revised settings in the apparatus could yield hydrocarbon compounds which are useful as liquid fuels.

2000-P07

ケナフ靱皮繊維のパルプ化温度に関する研究  
金森季一、ビブチ・B・マズンダル、大谷慶人、鮫島一彦  
高知大学農学部

Studies on kenaf bast pulping temperature.  
K. Kanamori, B. B. Mazumder, Y. Ohtani and K. Samesima  
Faculty of Agriculture, Kochi University

Abstract: The relationship between viscosity and cooking temperature in kenaf bast soda-pulping, at 100°C, 120°C, 140°C was examined. The bleaching after soda-pulping was also tried. Kenaf variety of Zhejiang-1 grown in Kochi was used as bast sample. The soda-pulping was made after ammonium oxalate pretreatment. Sodium hypochlorite and chlorine dioxide were used for bleaching experiment. Yield, Kapper number, viscosity, and brightness were measured. Kappa number didn't decrease much at 100°C and 120°C but started to decrease at 140°C. In contrast viscosity decreased proportionally to cooking temperature increase. In bleaching, sodium hypochlorite showed maximum brightness, but that of chlorine dioxide increased proportionally to the dosage.

2000-P08

HBS パルプ化 一回転式オートクレーブによるシラカンバのパルプ化  
長岡秀明、梶本純子、佐野嘉拓  
北海道大学大学院農学研究科

HBS pulping-pulping of birchwood by rotating autoclave.  
Hideaki Nagaoka, Junko Kajimoto, Yoshihiro Sano.  
Graduate School of Agriculture, Hokkaido University

Abstract: HBS pulping of birch wood with PG in a rotating autoclave was carried out at 200°C, for 1 to 2 h. Pulping spent liquors were separated into lignin and RPG. RPG consisted of low molecular lignin products, ugars and modified sugar products in addition to PG as a main material. The results on the yields of pulp, pulp residual lignin (KL) and lignin showed that PG and RPG were good pulping solvents corresponding to butanediols (BDOL) and RBDOL, though RPG and RBDOL were better solvents than PG and BDOL. The strength properties of PG pulp were inferior to those of corresponding kraft pulp, but comparable to those of BDOL and other organosolv pulps.

2000-P09

常圧酢酸法によるバイオマス成分の効率的総合利用  
佐野嘉拓、中野潤也、久保田康恵、浦木康光  
北海道大学大学院農学研究科

Total utilization of biomass with efficiency with atmospheric acetic acid process.- Separation of birch components using a large-scale extractor.  
Yoshihiro Sano, Jyunya Nakano, Yasue Kubota, Yasumitsu Uraki  
Graduate School of Agriculture, Hokkaido University

Abstract: Birch was separated into wood, outer bark and inner bark fractions. Ten kg of chips prepared from the wood fraction was refluxed with 90% AcOH containing a small amount of H<sub>2</sub>SO<sub>4</sub> for 1–3 h by use of all extractor of 100L capacity to be divided into pulp, lignin and water solubles. Xylose was isolated and purified from the water solubles to convert to xylitol. The outer bark fraction (3.4 kg) was refluxed with absolute AcOH by the same extractor to extract betulin.

2000–P10

樹皮のグリコール–バイサルファイト法による液化反応の解析

芦谷竜矢、上野智子、坂井克己

九州大学大学院生物資源環境科学研究科

Reaction of liquefaction of bark by glycol–bisulfite method.

Tatsuya Ashitani, Tomoko Ueno, Kokki Sakai

Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: Liquefaction of bark by glycol–bisulfite method was analyzed. Especially, conversion of polyphenolic components under the liquefaction condition was examined. Catechin as tannin monomer and quebracho tannin were treated with ethylene glycol and aqueous sodium bisulfite at 250°C. The products were extracted by water and ethyl acetate. Catechol was detected as a common product by GC–MS analysis of the ethyl acetate soluble parts obtained from the treatment of catechin and quebracho tannin. From IR spectra, it was assumed that solvent–insoluble precipitate was polymerization products of low molecule phenolic compounds like catechol.

2000–P11

酢酸リグニン–古紙混合物の押し出し成形と活性炭化

浦木康光、岡野祥平、久保智史、佐野嘉拓、

北海道大学大学院農学研究科

Extrusion molding of a mixture of acetic acid lignin and waste paper, and its conversion to activated carbon moldings.

Yasumitsu Uraki, Shohei Okano, Satoshi Kubo, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: An aim of study is to prepare activated carbon (AC) moldings, such as pellet and sheet, from the mixture of acetic acid lignin and waste newspaper continuously. The continuous molding of the mixture even with 10% of the infusible newspaper was carried out by extrusion molding using single screw extruder equipped with mono hole nozzle in a diameter of 3 mm and T–die as dice for preparing long pellet and sheet, respectively. Such moldings were converted to AC moldings by steam activation. The sheet prepared by the extruder required longer activation time than that by thermal compression method to produce the AC with more than 900 m<sup>2</sup>/g of specific surface area.

2000–P12

免疫法によるスギ心材成分の標識 3. 抗アガサレジノール血清の認識選択性

長崎剛士<sup>\*1</sup>、安田征市<sup>\*1</sup>、今井貴規<sup>\*1</sup>、高橋孝悦<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>山形大学農学部

Immunolabeling of heartwood extractives in *Cryptomeria japonica*. 3. Recognition selectivity of anti–agatharesinol serum.

Takeshi Nagasaki<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Takanori Imai<sup>\*1</sup>, Koetsu Takahashi<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>School of Agriculture, Yamagata University

Abstract: Recognition selectivity of the previously prepared anti–agatharesinol serum was

examined by competitive inhibition-ELISA using various kinds of wood extractives as competitors. The antiserum had the highest reactivity with agatharesinol among the used extractives. The antiserum was able to differentiate between norlignans according to slight differences in their chemical structures, and reactivities of the extractives other than norlignan were much lower. Competitive inhibition-ELISA using agatharesinol derivatives as well as various norlignans indicated that the antiserum required 1,3-bis-(*p*-hydroxyphenyl)-propene structural unit of agatharesinol for the antigen-antibody reaction and that hydroxylation pattern on one aromatic ring (referred to "B ring") influenced seriously the reactivity.

2000-P13

ペルオキシダーゼアイソザイムの基質認識の差異とシリングルリグニン生合成における役割

青山 渉、松村茂起、堤 祐司、西田友昭

静岡大学農学部

Substrate utilization toward monolignols of peroxidase isoenzymes and their involvement in syringyl lignin biosynthesis.

Wataru Aoyama, Shigeki Matsumura, Yuji Tsutsumi, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: A peroxidase, SyPO, isolated from the cell walls of poplar callus culture is capable to utilize sinapyl alcohol as substrate most effectively in plant isoperoxidases. In this paper, we compared the ability of SyPO in oxidation and polymerization of sinapyl alcohol to other peroxidases, such as horseradish peroxidase (HRP) and the other isoperoxidase, GPO-2, that was also isolated from the cell walls of poplar callus culture. The results showed that the two peroxidases, HRP and GPO-2 could also oxidize sinapyl alcohol in the presence of coniferyl alcohol, however, these peroxidases could not produce a dehydrogenative polymer from sinapyl alcohol and its oligomer compared to that SyPO could do. The surface plasmon resonance analysis suggests that only SyPO can bind to the oligomer of sinapyl alcohol.

2000-P14

担子菌によるジフェニルエーテル化合物の分解機構

平塚宣博、割石博之、田中浩雄

九州大学大学院生物資源環境科学研究科

Nobuhiro Hiratsuka, Hiroyuki Wariishi, Hiroo Tanaka

Graduate School of Bioresources and Bioenvironmental Sciences, Kyushu University

Abstract: A series of diphenyl ether compounds were effectively degraded by the white-rot fungus, *Coriolus versicolor*. 4-Chlorodiphenyl ether was degraded to produce 4-chlorophenol via the intermediate formation of 4-chloro-4'-hydroxydiphenyl ether. Diphenyl ether was also hydroxylated to form 4-hydroxydiphenyl ether which was further metabolized. Piperonyl butoxide, a typical inhibitor for cytochrome P450, effectively inhibited the hydroxylation of diphenyl ethers. The quantitative recovery of the starting substrates was also confirmed in the presence of piperonyl butoxide, strongly suggesting that the initial step of the metabolic pathways might be the hydroxylation reaction. On the other hand, 4-amino- and 4-hydroxydiphenyl ethers were oxidized by extracellular phenoloxidases.

2000-P15

18SrDNAによる有用白色腐朽菌株の同定

須原弘登<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>、坂井克己<sup>\*1</sup>、前川二太郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>(財)菌蕈研究所

Identification of valuable white rot fungi by 18SrDNA sequences.

Hiroto Suhara<sup>\*1</sup>, Ryuichiro Kondo<sup>\*1</sup>, Kokki Sakai<sup>\*1</sup>, Nitaro Maekawa<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>The Tottori Mycological Institute

Abstract: Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been a public concern for several decades because of their strong toxicity. We have suggested one white rot fungus, strain MZ-340, collected from natural forest in Japan, is able to degrade highly-chlorinated PCDDs and PCDFs. We did not have enough information except that it belongs to white rot fungus. Therefore nucleotide sequences of the small subunit ribosomal RNA gene were used to identify strain MZ-340. Strain MZ-340 was suggested to belong to genus *Ceriporia* with DNA analysis data. Subsequently, morphological observation was done. The observation also supported that strain MZ-340 belongs to genus *Ceriporia*.

2000-P16

遺伝子組み換え微生物バイオリアクターを用いたリグニン芳香核構造からの新規ポリアミド型機能性高分子材料の生産

片山義博<sup>\*1</sup>、西川誠司<sup>\*2</sup>、政井英司<sup>\*1</sup>、福田雅夫<sup>\*3</sup>、重原淳孝<sup>\*4</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>株式会社コスモ総合研究所、<sup>\*3</sup>長岡技術科学大学工学部、<sup>\*4</sup>東京農工大学工学部

The production of the new polyamide type polymer materials from lignin aromatic structure using gene recombination of microorganism.

Yoshihiro Katayama<sup>\*1</sup>, Seiji Nishikawa<sup>\*2</sup>, Eiji Masai<sup>\*1</sup>, Masao Fukuda<sup>\*3</sup>, Atsutaka Shigehara<sup>\*4</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and System Engineering, Tokyo University of Agriculture & Technology, <sup>\*2</sup>Cbsmo Research Institute, <sup>\*3</sup>Department of Bioengineering, Nagaoka University of Technology, <sup>\*4</sup>Faculty of Technology, Tokyo University of Agriculture and Technology

Abstract: We are currently investigating biotransformation process based on the catabolism of various dimeric lignin compounds by *Sphingomonas pausimobilis* SYK-6, which proceed via protocatechuate meta cleavage pathway. 2-pyrone-4,6-dicarboxylic acid (PDC) is a characteristic intermediate of the protocatechuate meta cleavage pathway. We have prepared the mutant with defective in PDC hydrolase by gene replacement technique ( $\Delta$ lig I), by which we have succeeded in producing the PDC in the high yield (ca. 90%) from the low-molecular weight lignin mixture. Since PDC has the unique molecular structure and the polymer made from PDC is expected to have the new function as optical material, we prepared new polyamide type polymer by the interfacial polymerization reaction with hexamethylene diamine.

2000-P17

白色腐朽菌 *Phanerochaete sordida* YK-624 株における ferrireductase 産生について

伊藤敬訓、平井浩文、西田友昭

静岡大学農学部

Production of ferrireductases by white-rot fungus *Phanerochaete sordida* YK-624.

Takanori Itoh, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: We examined the production of ferrireductase by white-rot fungus *Phanerochaete sordida* YK-624. High level of ferrireductase activity was observed in nitrogen-sufficient culture compared with nitrogen-limited culture. Ferrireductase was produced under the culture containing Fe, although it was well-known that ferrireductase by yeast was produced only in Fe-deficient culture. The addition of Mn(IV) to the culture induced the production of both manganese peroxidase

and ferrereductase as same level as the addition of Mn(II) did. These result suggest that ferrereductase plays an important role in the reduction of Mn(IV) to Mn(II).

2000-P18

ユリノキの組織培養によるシリンガレジノールの生成

山地裕二、原 敬治、伊藤和貴、橘 燦郎

愛媛大学農学部

Formation of syringaresinol in *Liriodendron tulipifera* by callus cultures.

Yuji Yamaji, Takaharu Hara, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Calli were induced from the leaves of young trees of Yurinoki, *Liriodendron tulipifera*, on Gamborg's B5 medium supplemented with 2,4-diclllorophenoxyacetic acid and kinetin, and subcultured on the same medium. High-performance liquid chromatographic analysis of the extractives of calli revealed that the calli produced syringaresinol.

2000-P19

天然からスクリーニングした菌によるダイオキシン類のバイオレメディエーション

清田幸徳、児山友彦、伊藤和貴、橘 燦郎

愛媛大学農学部

Bioremediation of dioxins by selected fungi from natural world.

Yukinori Kiyota, Tomohiko Koyama, Kazutaka Ito, Sanrou Tachibana

Faculty of Agriculture, Ehime University

Abstract: Bioremediation of dioxins (PCDD/Fs) contaminated in a paddy soil by fungus PL1 selected by a screening method from the natural world was conducted. The fungus degraded about 90% of the dioxins in the soil when 7% of the fungus was added to the soil and incubated for 30 days. The degradation rate of PCDD/Fs increased with increase in added amount of the fungus. On the contrary, the value of toxicity equivalency quantity (TEQ) in the treated soils deceased with increase in added amount of the fungus because of degradation of PCDD/Fs. Furthermore, the degradation rate of PCDD/Fs in the soil by the bioremediation was improved by addition of a surfactant. The results suggest that bioremediation of dioxins contaminated soils by selected fungi by a screening method is possible.

2000-P20

ダイオキシン分解能を有する菌による焼却灰中のダイオキシン類の分解

古賀道房、伊藤和貴、橘 燦郎

愛媛大学農学部

Degradation of dioxins in incinerated ashes by some fungi having ability for degradation of dioxins.

Michifusa Koga, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Microbial degradation of octachlorodibenzo-*p*-dioxin (OCDD) by three fungi (*Coprinus* sp., *Pycnoporus* sp. and *Lyophyllum* sp.) having ability for degradation of dioxins selected by a screening method from the natural world was conducted in a liquid medium. The three fungi degraded from about 35% to 45% of OCDD for 30 days. And bioremediation of dioxins (PCDD/Fs) in an incinerated ash by three fungi selected by the screening method was conducted in a solid medium. The three fungi degraded from about 40% to 50% of PCDD/Fs. The results suggest that purification of PCDD/Fs in incinerated ashes by the bioremediation with the selected fungi is possible.

## 第 46 回 (2001.11.1-2) 京都大学木質科学研究所

2001-101

TIZ 法によるリグニン-糖モデル化合物(DHP-Sugar)の分解

片平 類、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

The degradation of DHP-sugar model compound by the TIZ method.

Rui Katahira, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Graduate school of Agriculture, Kyoto University

Abstract: TIZ method is an useful method to cleavage  $\beta$ -O-4 bond in lignin quantitatively without any secondary condensation reaction. And in this method, most of  $\alpha$ -structure of lignin can be maintained. In this study, at first TIZ method was modified. TIZ method requires three reaction steps (Tosylation, Iodination and Zn treatment). It was found that iodination and Zn treatment could be carried out in one pot. Second, the modified TIZ method was applied to the degradation of DHP-sugar and Loblolly pine MWL. In the degradation products, compound 5 ( $R_2$ : Ac) was not found. But, the hydrogenation of the products gave compound 6 ( $R_3$ : H). It suggested that most of  $\alpha$ -structure of  $\beta$ -O-4 structure parts in lignin were substituted.

2001-102

樹幹内における  $\beta$ -O-4 型側鎖立体構造の不均一性

秋山拓也、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Heterogeneities of *erythro* and *threo* forms of  $\beta$ -O-4 structures in lignin.

Takuya Akiyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: The ratio of *erythro* and *threo* forms of  $\beta$ -O-4 structures (E/T ratio) and methoxyl group content in tension wood parts of yellow poplar were higher than those in normal wood parts. The distribution of *erythro* and *threo* forms of  $\beta$ -O-4 structures is not homogeneous, and is in fairly good agreement with that of syringyl and guaiacyl units. It was indicated that the methoxyl group is one of the factors which affects the diastereoface-differentiating water addition to quinone methides.

2001-103

GC 法によるメトキシル基の定量法の再評価(3)-メトキシル基解裂反応の機構の解析と共存する炭水化物の影響-

後藤仁志<sup>\*1</sup>、幸田圭一<sup>\*1\*2</sup>、松本雄二<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*1</sup> 北海道大学大学院農学研究科

Determination of methoxyl content with GC method. (3). -Analysis of the reaction mechanism of methoxyl cleavage and the effect of co-existing carbohydrate.

Hitoshi Goto<sup>\*1</sup>, Keijichi Koda<sup>\*1\*2</sup>, Yuji Matsumoto<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Graduate School of Agriculture, Hokkaido University

Abstract: Reaction mechanism and possible interfering effects caused by the presence of carbohydrates for the methoxyl determination by hydroiodic acid were investigated. The formation rate of methyl iodide from carbohydrates was quantitatively analyzed, and it was suggested that methyl iodide could arise from carbohydrate even when the carbohydrates did not contain a direct

precursor for methyl iodide. It was also confirmed that the presence of carbohydrates depress the formation rate of methyl iodide from lignin methoxyl group. Therefore, the presence of carbohydrates could result both in overestimation and underestimation of methoxyl group depending on the amount of carbohydrates. Hammett plot of substituent effect of side-chain part on the methyl iodide formation suggested SN2cA reaction mechanism for guaiacyl models but no clear relation was observed for syringyl models.

2001-104

TOF-SIMSによるリグニン構造解析

福島和彦<sup>\*1</sup>、山内一慶<sup>\*1</sup>、斉藤香織<sup>\*1</sup>、辻 幸子<sup>\*1</sup>、安田征市<sup>\*1</sup>、高橋元幾<sup>\*2</sup>、星 孝弘<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>アルバック・ファイ株式会社

Analysis of lignin structures by TOF-SIMS.

Kazuhiko Fukushima<sup>\*1</sup>, Kazuchika Yamauchi<sup>\*1</sup>, Kaori Saito<sup>\*1</sup>, Yukiko Tsuji<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Motoki Takahashi<sup>\*2</sup> and Takahiro Hoshi<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>ULVAC-PHI. Inc., Japan

Abstract: The structure of lignin was investigated by TOF-SIMS. Pine milled wood lignin (MWL) gave some secondary ions which seemed to correspond to guaiacyl lignin fragments. In this study, these secondary ions could be attributed to the typical guaiacyl fragments by labeling experiment of DHP. Deuterium labeled DHP prepared from coniferyl alcohol- $[\gamma\text{-D,D, -OCD}_3]$  was subjected to TOF-SIMS analysis. In addition to two major peaks of C<sub>6</sub>-C<sub>1</sub> structures, some secondary ions with C<sub>6</sub>-C<sub>3</sub> structures were also found in the mass spectra of MWL and DHP.

2001-105

熱分解マスマスペクトロメトリーによるリグニンの分析(II): 腐朽過程における化学構造の差異

中川明子、砂原 寛、黒田健一

筑波大学農林工学系

Analysis of lignin by pyrolysis-mass spectrometry. (II). Difference of chemical structure during the decaying process.

Akiko Nakagawa-izumi, Hiroshi Sunahara, Ken-ichi Kuroda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Sugi woods were decayed by brown-rot fungi (*Fomitopsis palustris*) and white-rot fungi (*Trametes versicolor*). The minute samples (<1pg) from the surface and inner parts of the decayed woods were pyrolyzed at 500°C for 4s. The products were immediately to a mass-spectrometer and ionized at 20eV. The MS spectra were analyzed by the principal components analysis (PCA). Py-MS and PCA showed (1) the differences in the samples obtained from the surface and inner parts and (2) the differences rotting process by brown-rot fungi and white-rot fungi.

2001-106

反応熱脱着ガスクロマトグラフィーによる木材中のフェノール性抽出成分の解析

横井裕明<sup>\*1</sup>、後藤邦佳<sup>\*1</sup>、石田康行<sup>\*1</sup>、大谷 肇<sup>\*1</sup>、柘植 新<sup>\*1</sup>、園田哲也<sup>\*2</sup>、小名俊博<sup>\*2</sup>

<sup>\*2</sup>名古屋大学大学院工学研究科、<sup>\*2</sup>王子製紙株式会社森林資源研究所

Characterization of phenolic wood extractives by reactive thermal desorption-gas chromatography  
Hiroaki Yokoi<sup>\*1</sup>, Kuniyoshi Goto<sup>\*1</sup>, Yasuyuki Ishida<sup>\*1</sup>, Hajime Ohtani<sup>\*1</sup>, Shin Tsuge<sup>\*1</sup>, Tetsuya Sonoda<sup>\*2</sup>, Toshihiro Ona<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Engineering, Nagoya University, <sup>\*2</sup>Forestry Research Institute, Oji Paper Co. Ltd.,

Abstract: Reactive thermal desorption-gas chromatography (RTD-GC) in the presence of organic alkali was applied to the rapid characterization of phenolic extractives in *Eucalyptus* samples. By the use of tetramethylammonium acetate (TMAAc) as the organic alkali the methyl derivatives of the phenolic acids were expectedly observed on the chromatogram formed through RTD. However, they were concluded to be formed from the extractives together from partial pyrolysis of lignin. This fact suggested that the accurate determination of the phenolic extractives were difficult. Thereupon by using tetrabutylammonium hydroxide (TBAH), the phenolic acids in the extractives without methoxyl group were converted into their perbutyl derivatives, which were clearly discriminated from lignin or the extractives with methoxyl group. Based on the peak intensities of the perbutylated phenolic acids observed on the chromatograms, the contents of the phenolic extractives without methoxyl group were rapidly estimated without using any cumbersome pretreatments of samples such as solvent extraction.

2001-107

Keynote: Monolignol biosynthesis in trees: Recent findings and paths for the future.

Vincent L. Chiang

Michigan Technological University

Abstract: We have discovered novel genes that regulate syringyl monolignol biosynthesis in angiosperms and demonstrated that the diversion of guaiacyl monolignol intermediates into syringyl types takes place at coniferaldehyde mediated by coniferaldehyde 5-hydroxylase (CAld5H), 5-hydroxyconiferaldehyde *O*-methyltransferase (AldOMT) and sinapyl alcohol dehydrogenase (SAD). These discoveries together with our early demonstration that monolignol pathway 4-coumarate: coenzyme A ligase (Pt4CL1) controls lignin accumulation provided us clues to simultaneously increasing lignin S/G ratio and reducing lignin content in trees by concurrent manipulation of the expression of genes encoding these enzymes. New insights derived from these discoveries to genetic engineering of syringyl lignin in conifers will also be discussed.

2001-108

樹木ポプラにおけるリグニン合成量の遺伝子工学的調節

熊谷大地、川合伸也

東京農工大学農学部

Regulation of lignin synthesis by genetic manipulation from *Populus kitakamiensis*.

Daichi Kumagai, Shinya Kawai

Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: It was reported that tobacco LIM protein bound to Pal-box which was a *cis*-acting element for gene expression involved in phenylpropanoid biosynthesis. Thus we have cloned and sequenced a cDNA clone, named *klim*, from young leaves of *Populus kitakamiensis*. The deduced amino acid sequence showed a high identity to other plant LIM proteins which had zinc finger motifs. We also cloned the 5'-flanking region of *klim* from genomic DNA by inverted PCR. We found several zinc finger binding motifs in 1,094 bp of the 5'-flanking region. This motif also existed in the 5'-nontranslational region of *klim* cDNA. It suggested that LIM protein might regulate itself.

2001-109

ペルオキシダーゼ過剰発現による除草剤耐性付加

田村 健、寺尾 俊、柳崎 真輝、高橋順子、川合伸也

東京農工大学農学部

Plant peroxidase over-production in tobacco induces herbicide-tolerance.

Takeshi Tamura, Shun Terao, Masaki Yanazaki, Yoriko Takahashi, Shinya Kawai  
Faculty of Agriculture, Tokvo University of Agriculture and Technology

Abstract: The aspen gene, *prxA3a*, encoding an anionic peroxidase, was over-expressed in transgenic tobacco plants. This gene had been isolated from *Populus kitakamiensis* and characterized that it contributed to lignin-biosynthesis. Peroxidase expression cassette was under the control of CaMV35S promoter. These transgenic plants increased herbicide-tolerance against paraquat, DCMU and atrazin, in leafdisk assay, without the accumulation of lignin. Such resistant plants also had more SOD activities than those of wild-type plants. These indicated that the over-expression of *prxA3a* induced plants the protection from oxidative damage caused by paraquat and DCMU.

2001-P01

高粘度ケナフ靱皮パルプの製造に関する研究(2)シュウ酸アンモニウム前処理とパルプ品質の関係

渡辺大輔、大谷慶人、鮫島一彦

高知大学農学部

Studies on production of high viscosity kenaf bast pulp. (2). Relationship between ammonium oxalate pretreatment and pulp quality.

Daisuke Watanabe, Yoshito Ohtani, Kazuhiko Sameshima

Faculty of Agriculture, Kochi University

Abstract: To confirm the importance of ammonium oxalate (Amox) pretreatment before the pulping at normal pressure, the soda pulpings with or without Amox pretreatment were compared. Whole kenaf stem was harvested, and debarked by hand, and air dried. Amox pretreatment was carried out on the bast of 10cm in 0.5% Amox. Soda pulping was performed in 10,15,20,25% NaOH for 1 hour. The yield of soda kenaf bast pulp without Amox pretreatment was higher than that of Amox pretreated one. This indicates that there exist some material which can be removed by the Amox pretreatment but not in the soda cooking. Viscosity was higher in Amox treated pulp in low NaOH concentrations. Pectin in soda pulp with the Smox pretreatment was about half of that in the pulp without Amox pretreatment. It was confirmed that Amox pretreatment is important if a pulp with lower impurities is required, but high viscosity pulp can be produced without Amox pretreatment although the level of viscosity is a little lower.

2001-P02

クラフトパルプの二酸化塩素漂白におけるダイオキシン類の生成機構

大井 洋<sup>\*1</sup>、細谷修二<sup>\*2</sup>、真柄謙吾<sup>\*2</sup>

<sup>\*1</sup>筑波大学農林工学系、<sup>\*2</sup>森林総合研究所

Mechanism of dioxins formation during chlorine dioxide bleaching of kraft pulp.

Hiroshi Ohi<sup>\*1</sup>, Shuji Hosoya<sup>\*2</sup>, Kengo Magara<sup>\*2</sup>

<sup>\*1</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba, <sup>\*2</sup>Forestry and Forest Products Research Institute

Abstract: Kraft pulp and sulfite pulp bleaching mills using chlorine, chlorine dioxide (D) and other chlorinated compounds are under surveillance of the dioxins regulation. The bleaching mills are regarded as "notified establishments" which should pollute water quality. According to it, a limit for emissions of dioxins and PCBs to environmental water from the mills is less than 10pg-TEQ<sup>WHO1998</sup>/L. The limit should be considered ten times as that of environmental water quality (1pg-TEQ/L). One of questions is that water qualities of process sewers in chlorine dioxide bleaching (ECF) mills are less than the environmental water quality (1pg-TEQ/L), or not. Objectives of this study are to clarify

the dioxins level of ECF mill sewers and to know more about mechanism of dioxins formation during chlorine dioxide bleaching of oxygen-delignified hardwood kraft pulp (LOKP) on a basis of the analysis level for the environmental water quality. Laboratory bleaching was carried out using a mill LOKP(kappa number 9.8), chlorine dioxide from a mill R8 generator and drink water in a laboratory high-share mixer. Active chlorine factors were in the range of 0.14-1.14. The total TEQs are less than 15ppq for the D treated and D and alkali-extracted (E) pulps and less than 0.0057pg-TEQ/L for the D and E spent liquors. In both cases, 2,3,7,8-TCDD and TCDF were not detected.

2001-P03

アルカリ系蒸解過程におけるリグニン側鎖構造の変化

永谷宏幸、杉元倫子、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Change of lignin side-chain structure during soda- and kraft-pulping.

Hiroyuki Nagatani, Tomoko Sugimoto, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Glyceric acid was obtained as a predominant product by ozonation of both kraft pulp residual lignin and dissolved lignin. The yield ratio between glyceric acid and tetrionic acids (erythronic and threonic) becomes higher with the progress of delignification. Quantitative analysis of the yield of those ozonation products suggested that glyceric acid originates from certain structure(s) which originally present in wood lignin, although structures modified during pulping reaction could also contribute to the formation of this acid.

2001-P04

パルプ残存リグニンの単離とその性状に関する研究 一過ヨウ素酸塩前処理を用いたパルプ残存リグニンの単離一

相見 光、飯塚堯介

東京大学大学院農学生命科学研究科

Isolation of residual lignin from unbleached hardwood kraft pulp by a pretreatment with mild periodate treatment.

Hikaru Aimi, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo,

Abstract: It is very important to elucidate the structural feature of residual lignin to understand the reason why it is not removed from pulp during cooking. In order to isolate the residual lignin from pulp, two methods are, at the present, widely used: that is, acidolytic treatment and enzymatic treatment. In this study, we investigated the isolation method of residual lignin by a mild periodate pretreatment. By this treatment, the rings of sugar units in pulp will be opened and the sugar chains will have more flexible conditions. We expect to obtain the residual lignin at higher yield by the subsequent extraction of the treated pulps. When the diazomethane treated pulp was mildly treated with periodate and was extracted with aqueous alkali in the presence of  $\text{NaBH}_4$ , about 73% of residual lignin was found to be removed from the pulp. This fact may indicate that the major part of the residual lignin is entrapped in the carbohydrate matrix of pulp.

2001-P05

白色腐朽菌によるケナフおよびシラカバパルプの漂白特性の比較

大前陽子、大谷慶人、鮫島一彦

高知大学農学部

Bleaching effects of kenaf and shirakaba pulps by white rot fungi.

Yoko Ohmae, Yoshito Ohtani, Kazuhiko Sameshima

Faculty of Agriculture, Kochi University

Abstract: Soda-Anthraquinone (AQ) and kraft pulps from kenaf bark, core, or shirakaba were bio-bleached by four white rot fungi, two of them were obtained from the fields and the others were *Phanerochaete chrysosporium* and *Pleurotus ostreatus*. Bleachabilities, such as brightness, kappa number, viscosity of the pulps were investigated in connection with laccase, manganese peroxidase, and lignin peroxidase activities of each fungus. Bleachability of kenaf core pulp was similar to that of shirakaba pulp, but far from that of kenaf bark pulp. Relationship between bleachability and enzymatic activity was quite dependent upon not only the fungi but also the pulps.

2001-P06

蒸煮・爆砕処理を用いた建築廃材中のリグニンの挙動

前田めぐみ<sup>\*1</sup>、樋口暁浩<sup>\*1</sup>、佐藤雅俊<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学アジア生物資源環境研究センター

Characterization in lignin in waste boards during steam-explosion treatment.

Megumi Maeda<sup>\*1</sup>, Akihiro Higuchi<sup>\*1</sup>, Masatoshi Sato<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup> Asia Natural Environmental Science Center, the University of Tokyo

Abstract: It was tried to produce binderless board from waste woody materials used in construction using steam explosion procedure. Properties of lignin treated with steam explosion process under various conditions were investigated by chemical analyses and scanning electron microscopy. Hemicellulose was decomposed at higher pressure of steam explosion, and significant amounts of lignin was dissolved in exhaust liquor of steam explosion. S/V ratio of alkaline nitrobenzene oxidation products of lignin in steam explosion pulps was almost constant under conditions used in this study. Mechanical strength of binderless board from steam exploded pulp was also discussed.

2001-P07

酸加水分解リグニンより機能性物質調製の試み(その2)

田村敬史、安田征市

名古屋大学大学院生命農学研究科

Preparation of functional materials from gymnosperm acid hydrolysis lignin. (2).

Takashi Tamura, Seiichi Yasuda

Graduate School of Bioagricultural Sciences, Nagoya University,

Abstract: The chemical conversion of sulfuric acid lignin (Klason lignin) (SAL) as an acid hydrolysis lignin into functional materials was investigated. SAL has lower reactivity owing mainly to the high rate of condensed structures and then was phenolized (P-SAL) for its activation. In order to prepare surface-active agents having monosaccharide and carboxyhydroxymethyl (-CH(OH)COOH) group from P-SAL, phenolized lignin model compounds were treated with xylose in 72% sulfuric acid and glyoxylic acid in alkaline media. The yields of a C-xyloside and products with carboxyhydroxymethyl group were <5% and 75% respectively. The preparation of a surface-active agent with carboxy- hydroxymethyl group from P-SAL is attempted.

2001-P08

PEG・バイサルファイト法により液化したスギ樹皮由来ポリウレタンフィルムの調製

芦谷竜矢<sup>\*1</sup>、上野智子<sup>\*2</sup>、栗本康司<sup>\*3</sup>、坂井克己<sup>\*1</sup>

<sup>\*1</sup> 九州大学大学院生物資源環境科学研究科、<sup>\*2</sup> 福岡女子大学人間環境学科、<sup>\*3</sup> 秋田県立大学木材

## 高度加工研究所

Polyurethane film prepared from liquefied sugi bark by PEG-bisulfite method.

Tatsuya Ashitani<sup>\*1</sup>, Tomoko Ueno<sup>\*2</sup>, Yasushi Kurimoto<sup>\*3</sup>, Kokki Sakai<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Fukuoka Women's University, Institute of Wood Technology, <sup>\*3</sup> Akita Prefectural University

Abstract: Sugi (*Cryptomeria japonica* D. Don) bark was liquefied using PEG-400 and sodium bisulfite at 250°C. Polyurethane (PU) films were prepared by a solution casting technique after co-polymerization of the obtained liquefied bark and polymeric methylene diphenylene diisocyanate (PMDI) in dichloromethane. Thermal and mechanical properties of the PU films were investigated by thermo gravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA) and mechanical measurements. Tensile strengths of the PU films prepared from liquefied sugi bark were 0.2–70 MPa at [NCO]/[OH] ratio = 0.25–1.25. It was suggested from results of DMTA and TGA that components in liquefied bark acted as cross linking agents.

## 2001-P09

木材及び腐朽材によるクロム(III)および銅(II)の吸着

オスカー・ビコベンス<sup>\*1\*2</sup>、ヤニス・グラビティス<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

ラトビア国立木材科学研究所、東京大学アジア生物資源環境研究センター

Sorption of chromium(III) and copper(II) on wood and biologically decayed wood.

Oskars Bikovens<sup>\*1\*2</sup>, Janis Gravitis<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

<sup>\*1</sup>Latvian State Institute of Wood Chemistry, <sup>\*2</sup>Asian Natural Environmental Science Center, the University of Tokyo

## 2001-P10

リグニンペルオキシダーゼの電気化学的解析

親泊政二三<sup>\*1</sup>、割石博之<sup>\*2</sup>、田中浩雄<sup>\*2</sup>、篠原寛明<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科, <sup>\*2</sup>九州大学大学院農学研究院, <sup>\*3</sup>岡山大学工学部

Electrochemical analysis of lignin peroxidase.

Masafumi Oyadomari<sup>\*1</sup>, Hiroyuki Wariishi<sup>\*2</sup>, Hiroo Tanaka<sup>\*2</sup>, Hiroaki Shinohara<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Bioresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Faculty of Agriculture, Kyushu University, <sup>\*3</sup>Faculty of Engineering, Okayama University

Abstract: The redox potential of lignin peroxidase (LiP) was measured by a cyclic voltammetry technique. The pyrolytic graphite electrode coated with LiP-embedded tributylmethyl phosphonium chloride membrane was utilized. Quasi-reversible electron transfer between LiP and the electrode surface was observed. The redox potential between ferric and ferrous LiP exhibited pH-dependency, indicating that the reductive half-reaction of the LiP occurred as; ferric LiP + 1e<sup>-</sup> + H<sup>+</sup> → ferrous LiP.

## 2001-P11

*Phanerochaete crassa* WD1694 菌株由来のマンガンペルオキシターゼの精製

高野麻理子、中村雅哉、関谷 敦、山口宗義、西田篤実

森林総合研究所

Purification of manganese peroxidase from *Phanerochaete crassa* WD1694

Mariko Takano, Masaya Nakamura, Atsushi Sekiya, Muneyoshi Yamaguti, Atsumi Nishida  
Forestry and Forest Products Research Institute,

Abstract: Four manganese peroxidase isozymes were purified from the culture fluid of *Phanerochaete crassa* WD1694. The culture filtrate was subjected to DEAE-Sepharose chromatography and DEAE-Toyopearl FPLC, and eluted as a single peak of manganese peroxidase

activity. The sample showed a single band at a molecular weight of approximately 50,000 on SDS-PAGE. The same sample was separated as four bands which had the pI value of 4.50, 4.52, 4.62, and 4.65 on isoelectric focusing, and all four bands were stained by manganese peroxidase active staining. These results showed that *Phanerochaete crassa* WD1694 produced four manganese peroxidase isozymes which have same molecular weight and different pI values described above.

2001-P12

選択的白色腐朽菌 *Celiporiopsis subvermispora* の菌体外フリーラジカル反応 -NDAによる鉄酸化還元 の阻害と電荷移動錯体形成

榎 牧子<sup>\*1\*2</sup>、本田与一<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>、桑原正章<sup>\*1</sup>

<sup>\*1</sup> 京都大学木質科学研究所、<sup>\*2</sup> 理化学研究所

Extracellular free radical reactions of selective white-rot fungus, *Celiporiopsis subvermispora*.

- Inhibition effects on iron redox reactions and formation of charge transfer complexes.

Makiko Enoki, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: A selective white-rot fungus, *Celiporiopsis subvermispora* is able to decompose lignin without intensive damage of cellulose accompanied by lipid peroxidation. Recently we reported production of three novel lipid-related itaconic acid derivatives by this fungus. Among of them, 1-nonadecene-2,3-dicarboxylic acid (NDA) was analyzed in this report. Electron transfer reactions of Fe(II) and Fe(III) were inhibited by NDA. NDA formed charge transfer complexes with a quinoid compound originating from phenolic compounds in aqueous solutions. These phenomena suggest that NDA stabilizes Fe(II) and Fe(III) and interacts with oxidation products from phenolic compounds during wood decay by *C. subvermispora*.

2001-P13

白色腐朽菌による土壤中ダイオキシン類の処理の試み -土壤成分の分解への影響について-  
好光正豪<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>、坂井克己<sup>\*1</sup>、東房健一<sup>\*2</sup>

<sup>\*1</sup> 九州大学大学院生物資源環境科学研究科、<sup>\*2</sup> 財団法人九州環境管理協会

Attempt to treat dioxins in soils by white rot fungi. -Influence of soil components on degradation of dioxins.

Masahide Yoshimitsu<sup>\*1</sup>, Ryuichiro Kondo<sup>\*1</sup>, Kokki Sakai<sup>\*1</sup>, Kenichi Tobo<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup> Kyushu Environmental Evaluation Association

Abstract: We demonstrated that polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/DFs) in toluene extracts of the soil were degraded by a white rot fungus *Celiporia* sp. MZ-340. Degradation of a mixture of PCDDs/DFs extracted from the soil by the white rot fungus was examined in a low-nitrogen Kirk medium. The toxic equivalence quantity (TEQ) of the extracts of the soil reduced from 19.0 to 12.4 ng-TEQ/flask, and that of the soil extracts, from which polar organic compounds had been removed by silica gel, reduced from 10.0 to 2.4 ng-TEQ/flask by the treatment for 10 days with the white rot fungus.

2001-P14

白色腐朽菌の有する ferrereductase システムを用いた *in vitro* 系での二酸化マンガン還元  
伊藤敬訓、平井浩文、西田友昭

静岡大学農学部

*In vitro* reduction of manganese dioxide by ferrereductase system in white-rot fungi.

Takanori Itoh, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: *In vitro* reduction of manganese dioxide by ferrireductase system in white-rot fungi was investigated. The reduction of manganese dioxide by Fe(II)-iron binding compound complex, which occurs at extracellular region of the fungi, was dependent on pH, and Fe(II)-iron binding compound complex was a good electron donor for the reduction of manganese dioxide compared with Fe(II) itself. Fe(III)-iron binding compound complex was the best substrate for NADPH-dependent ferrireductase than other ferric chelate. These results suggest that ferrireductase system, including NADPH-dependent ferrireductase and Fe(III)-iron binding compound, is involved in the reduction of manganese dioxide by white-rot fungi.

2001-P15

熱分解におけるリグニン中の各結合様式の反応性

堀越 直、河本晴雄、坂 志朗

京都大学大学院エネルギー科学研究科

Reactivity of lignin substructures in pyrolysis of lignin。

Sunao Horigoshi, Haruo Kawamoto, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: Reactivity of lignin in pyrolysis was studied at 400°C focusing on depolymerization, polymerization, carbonization and gasification reactions by using  $\alpha$ -O-4,  $\beta$ -O-4,  $\beta$ -1 and biphenyl types of dimeric lignin model compounds. As a result, the following results were obtained. ① Reactivity for depolymerization varies significantly depending on the model compound structure:  $\alpha$ -O-4, phenolic  $\beta$ -O-4 > non-phenolic  $\beta$ -O-4, non-phenolic  $\beta$ -1 > phenolic  $\beta$ -1, biphenyl types of model compounds. ② Carbonization occurs from almost structures via very reactive intermediate without leaving polymerization products soluble in THF. ③ Gasification is not important at 400°C.

2001-P16

フェノール性  $\beta$ -O-4 型構造の熱分解開裂における  $\alpha$ -及び  $\gamma$ -位の水酸基の役割

河本晴雄、堀越 直、坂 志朗

京都大学大学院エネルギー科学研究科

Haruo Kawamoto, Sunao Horigoshi, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: Role of C  $\alpha$ - and C  $\gamma$ -hydroxyl groups on pyrolytic cleavage of phenolic  $\beta$ -O-4 type of structure was investigated by using a series of dimeric lignin model compounds with regiospecifically deoxygenated structures or regiospecifically methylated structures. As a result, it is revealed that hydrogen bonding between these hydroxyl groups plays an important role in  $\beta$ -ether cleavage, and that this effect is only effective in phenolic structure. These results indicate that conformation of the phenolic  $\beta$ -O-4 type of structure is important in the mechanism of the  $\beta$ -ether cleavage.

2001-P17

エレクトロポレーションによるヒラタケの形質転換

馬上 学、本田与一、渡辺隆司、桑原正章

京都大学木質科学研究所

Genetic transformation of *Pleurotus ostreatus* using electroporation.

Manabu Moue, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: *Pleurotus ostreatus* is one of the white rot basidiomycetes researched to utilize for biobleaching, bioremediation and catalysis of difficult chemical transformation. In order to elucidate the degrading mechanism of lignin by *P. ostreatus*, it is important to introduce genetic engineering techniques which permit us molecular genetic analysis, such as overexpression of ligninolytic enzymes. In our laboratory, drug resistant marker gene *Cbx<sup>R</sup>* and transformation system have been developed in this fungus. However, many genetic manipulations, such as gene targeting and functional cloning, are not available if the transformation efficiency is low. We examined transformation of *P. ostreatus* by electroporation aiming at high transformation efficiency.

2001-P18

担子菌のプロテオームディフアレンシャルディスプレイ解析 —培地成分の発現タンパク質への影響—

中村朋史\*<sup>1</sup>、一瀬博文\*<sup>1</sup>、割石博之\*<sup>2</sup>、田中浩雄\*<sup>2</sup>

\*<sup>1</sup>九州大学大学院生物資源環境科学研究科、\*<sup>2</sup>九州大学大学院農学研究院

Proteome differential display analysis of basidiomycetes.

Tomofumi Nakamura, Hirofumi Ichinose, Hiroyuki Wariishi, Hiroo Tanaka

Faculty of Agriculture, Kyushu University

Abstract: The white-rot basidiomycete, *Coriolus versicolor*, metabolizes a series of sulfur-containing heterocyclic compounds found in fossil fuels as impurities. In our previous study, certain thiophene and sulfide compounds were degraded by *C. versicolor* more effectively under sulfur-limiting culture conditions, suggesting that the fungus utilizes sulfur compounds as a sulfur source for growth. To better understand a metabolic system for sulfur compounds and to search for proteins related to the desulfurization, proteome differential display analysis was performed.

2001-P19

ラッカーゼ/1-HBT 系による  $\beta$ -O-4 型リグニンモデル化合物の新規  $\beta$ -エーテル開裂反応について

岩月正人、中川 誠、稲垣真澄、浜辺鮎佳、河合真吾、大橋英雄

岐阜大学農学部

New  $\beta$ -ether cleavage reaction of  $\beta$ -O-4 lignin model compounds by laccase/1-HBT system.

Masato Iwatsuki, Makoto Nakagawa, Masumi Inagaki, Ayuka Hamabe, Shingo Kawai, Hideo Ohashi  
Faculty of Agriculture, Gifu University

Abstract: We have studied that the degradation mechanism of non-phenolic  $\beta$ -O-4 lignin model compounds by laccase/1-HBT system. In the previous work, we proposed new mechanisms for the formation of C $\alpha$ -C $\beta$  cleavage product via benzylic radical. In this study, we further investigated the incorporation experiments of <sup>18</sup>O from <sup>18</sup>O<sub>2</sub> into the degradation products of substrate (1) and (2) catalyzed by laccase/1-HBT system respectively. The results suggest that a novel  $\beta$ -ether cleavage reaction is caused by laccase/1-HBT system.

2001-P20

植物細胞壁成分の安定炭素同位体比に関する研究

上平雄也、谷川一樹、福島和彦、安田征市

名古屋大学大学院生命農学研究科

Stable carbon isotope ratios of some plant cell wall components.

Yuya Kamihira, Kazuki Tanigawa, Kazuhiko Fukushima, Seiichi Yasuda

Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: Stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of some plant cell wall components were

determined by an isotope ratio mass spectrometer (IRMS). The carbon of sugarcane (C<sub>4</sub> plant) was isotopically heavier than that of pine and poplar (C<sub>3</sub> Plants) significantly, and the carbon of the Klason lignins from all the species were about 2.6–3.7 ‰ lighter than that of the α-celluloses. These results showed the same tendency as the previous reports<sup>1) 2)</sup>. Although δ<sup>13</sup>C of components of each tissue in sugarcane were also determined, the reproducibility was not enough. Further precise measurements are needed to make differences between the tissues clear.

2001-P21

コニフェリルアルコールの脱水素重合中に生成するシリングル核

斉藤香織<sup>\*1</sup>、安田征市<sup>\*1</sup>、小名俊博<sup>\*2</sup>、福島和彦<sup>\*1</sup>

名古屋大学大学院生命農学研究科、<sup>2</sup>王子製紙(株)森林資源研

Syringyl units generated during the polymerization of coniferyl alcohol

Kaori Saito<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Toshihiro Ona<sup>\*2</sup> and Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: Syringyl (S) and *p*-hydroxyphenyl (H) units were detected in addition to guaiacyl (G) unit in thioacidolysis products obtained from the DHP prepared from only coniferyl alcohol using a peroxidase-H<sub>2</sub>O<sub>2</sub> System. To determine the DHP at the dimer level, we analyzed thioacidolysis products of the DHP and detected dimers of G-G, S-G, S-S and H-G types.

2001-P22

カプール (*Dryobalanops* spp.) 心材の抗う蝕活性成分の検索

三原理江、光永 徹

三重大学生物資源学部

Anti-dental caries active compounds of kapur (*Dryobalanops* spp.) heart wood extracts.

Rie Mihara, Tohru Mitsunaga

Faculty of Bioresources, Mie University

Abstract: The inhibitory effects of 22 species of wood extracts on the glucosyltransferase (GTase) activity were investigated. Kapur (*Dryobalanops* spp.) heart wood extracts showed inhibited GTase activity more effectively than any other species. The results obtained by the Folin-Denis method for the determination of total phenol contents, vanillin-HCl method to determine flavanol contents and protein adsorption by using BSA suggested that the active fractions contained hydrolyzable tannin like component. The main components which inhibit GTase activity in kapur were probably ellagitannins, because a large amount of ellagic acid was released by acid hydrolysis. Furthermore, these components exhibited antioxidative activity in a rabbit erythrocyte membrane ghost system.

2001-P23

分子軌道計算を用いたポリフェノールの反応性の解析 —フラボノイド類の付加縮合反応速度と分子軌道計算値との相関性—

渡辺泰高、光永 徹

三重大学生物資源学部

Reactivities of polyphenols with formaldehyde by Molecular Orbital Computation. —Correlation additional condensation rates of flavanoids and the parameters calculated by molecular orbital method.

Yasutaka Watanabe, Tohru Mitsunaga

Faculty of Bioresources, Mie University

Abstract: Molecular Orbital Computation for flavonoids, (+)-catechin and taxifolin, has been used to study the relationship between the calculated electrostatic charges at the carbons existed Highest Occupied Molecular Orbital (HOMO) and the reaction rate of hydroxymethylation with formaldehyde. Electrostatic charges (q) of several kinds of flavonoids were calculated by semi-empirical methods at the AM1 and PM3 and *ab initio* methods at RHF/3-21G level of theory. The rate (k) of flavonoids consumption were determined by HPLC. When q were plotted against logarithm of k in these flavonoids, phenol, resorcinol and phloroglucinol, high correlation ( $R^2=0.92$ ) was obtained.

2001-P24

マタイレジノールの5位水酸化過程に関する考察

大須賀優夫、鈴木視番、木原智仁、榎本慎一、河合真吾、大橋英雄、小山博之、原徹夫  
岐阜大学農学部

5-Hydroxylation of matairesinol in syringyl lignan biosynthesis.

Masao Osuka, Mitsuru Suzuki, Tomonori Kihara, Shin-ichi Enomoto, Shingo Kawai, Hideo Ohasi, Hiroyuki Koyama, Tetsuo Hara

Faculty of Agriculture, Gifu University

Abstract: We have studied on the biosynthesis of syringyl lignans in *Thuja* species. In the previous work, we suggested that matairesinol is the possible intermediate on the biosynthetic pathway of syringyl lignans. In this study, we report the feeding experiment of [7, 7-<sup>2</sup>H<sub>2</sub>, 3'-OC<sup>2</sup>H<sub>3</sub>]matairesinol into *T. occidentalis* young shoot. The results indicated for the first time that matairesinol was converted into thujaplicatin. Last of all, we show a preliminary experiment for the detection of matairesinol 5-hydroxylase gene.

2001-110

ペルオキシダーゼ遺伝子を抑制した形質転換ポプラの化学的・組織化学的解析

李並紅、太田祥弘、梶田真也、諸星紀幸

東京農工大学大学院 BASE

Characterization of transgenic aspens inhibited by a peroxidase gene.

Yahong Li, Nobuyuki Nishikubo, Shinya Kajita, Noriyuki Morohoshi

Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology

Abstract: To study the down-regulation of specific peroxidase involved in lignin biosynthesis and its correlation with lignification, an anionic peroxidase gene, prxA3a was transferred into its original host, hybrid aspen *P. kitakamiensis* (*P. sieboldii* X *P. gradidentata*) under the control of the original promoter of prxA3a. Twelve transformed lines were regenerated and confirmed by PCR and Southern blotting. Enzyme assay showed that both total peroxidase activity and prxA3a specific activity were decreased in most transgenic lines as compared to control plant. In addition, difference in lignin content and structure was observed between transformants and control aspen. Furthermore, histochemical analysis revealed that suppressed lignification in the secondary xylem was the result of down-regulated peroxidase expression. These results indicated that it was achievable to develop genetically improved woody plant.

2001-111

担子菌カワラタケの環境汚染物質分解酵素遺伝子 (*mnp, lac*) を導入した植物の分子育種と持続的環境修復に関する研究(2)

池田成一郎\*<sup>1</sup>、園木和典\*<sup>1</sup>、飯村洋介\*<sup>2</sup>、早川敏夫\*<sup>3</sup>、金原和秀\*<sup>3</sup>、梶田真也\*<sup>1</sup>、片山義博\*<sup>1</sup>

\*1 東京農工大学大学院 BASE、\*2 産業技術総合研究所、\*3 JR 総合技術研究所

Studies on molecular breeding of plants with ability of MnP, Lac derived from *Coliorus versicolor* degrade environmental pollutants and continuous remediation.

Seiichiro Ikeda\*1, Tomonori Sonoki\*1, Yosuke Iimura\*2, Toshio Hayakawa\*3, Kazuhide Kinbara\*3, Shinya Kajita\*1, Yoshihiro Katayama\*1

\*1 Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, \*2 National Institute of Advanced Industrial Science and Technology, \*3 Railway Technical Research Institute

Abstract: Remediation methods for environmental pollutants such as physical & chemical treatment and bioremediation have been experimentally tested. However, these methods have some problems; these are impractical in view of cost efficiency of hazardous chemicals accumulated at low levels in the environment or becomes labored as the area of contamination expands. Meanwhile, plant can be grown independently taking nourishment from the sun, water, and inorganic ions, and can be cultivated extensively by controlling seeds. Because of this, plants have attracted attention as a method for long-lasting environmental decontamination. And, we have attempted to degrading hazardous chemicals directly using transgenic plants into which Mn-Peroxidase gene and Laccase gene for degrading hazardous chemicals derived from *Coliorus versicolor* is transferred. If a plant capable of exerting the effect of these enzyme could be prepared, it would be very useful for degrading and removing hazardous chemicals in the environment.

2001-112

微生物の物質変換機能の導入による、植物のフェニルプロパノイド合成系の制御

補永文子\*1、梶田真也\*1、園木和典\*1、上杉幹子\*1、政井英司\*2、原田恭\*2、福田雅夫\*2、諸星紀幸\*1、片山義博\*1

\*1 東京農工大学大学院 BASE、\*2 長岡技術科学大学

Manipulation of phenylpropanoid-biosynthetic pathway by genetic engineering with bacterial genes. Fumiko Honaga\*1, Shinya Kajita\*1, Tomonori Sonoki\*1, Mikiko Uesugi\*1, Eiji Masai\*2, Kyo Harada\*2, Masao Fukuda\*2, Noriyuki Morohoshi\*1, Yoshihiro Katayama\*1

\*1 Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, \*2 Nagaoka University of Technology

Abstract: Hydroxycinnamoyl-CoA esters are intermediates of phenylpropanoid biosynthetic pathway and can be precursors of many secondary metabolic compounds such as flavonoids, stilbenes and lignin. A bacterial gene *FerB* isolated from *Sphingomonas paucimobilis* SYK-6 encodes feruloyl-CoA hydratase/lyase. This enzyme can catalyze the reaction step for conversion from hydroxycinnamoyl-CoAs to corresponding hydroxybenzaldehydes. We tried to express this gene in tobacco and hybrid aspen plants by genetic engineering in aim to biosynthesize beneficial phenolic compounds in vivo. The transgenic plants showed activities to produce hydroxybenzaldehydes.

2001-113

ペルオキシダーゼアイソザイムの基質認識とシリングルリグニン生合成の役割

佐々木慎弥\*1、堤 祐司\*1、西田友昭\*1、光永 徹\*2

\*1 静岡大学農学部、\*2 三重大学生物資源学部

Substrate utilization toward monolignols of peroxidase isoenzymes and their involvement in syringyl lignin biosynthesis.

Shinya Sasaki, Yuji Tsutsumi, Tomoaki Nishida, Thoru Mitsunaga

Faculty of Agriculture, Shizuoka University, Faculty of Bioresource, Mie University

Abstract: A peroxidase, SyPO, isolated from the cell wall of poplar (*Populus alba* L.) callus

culture is capable to utilize sinapyl alcohol (Salc) as substrate most effectively in plant isoperoxidases. SyPO polymerized sinapyl alcohol-oligomer (Salc-oligomer) and sinapyl alcohol, producing a polymer of greater molecular weight. In contrast, horseradish peroxidase (HRP), which is specific to coniferyl alcohol (Calc), produced sinapyl alcohol dimers, rather than catalyzing polymerization. Adding coniferyl alcohol as a radical mediator in the HRP-mediated reaction did not result in Salc-oligomer polymerization.

2001-114

シナップ酸に活性を有する 4-coumarate:coenzyme A ligase の検索

浜田勝義\*<sup>1</sup>、堤 祐司\*<sup>1</sup>、西田友昭\*<sup>1</sup>、山内一慶\*<sup>2</sup>、福島和彦\*<sup>2</sup>

\*<sup>1</sup> 静岡大学農学部、\*<sup>2</sup> 名古屋大学大学院生命農学研究科

Screening of 4-coumarate: coenzyme A ligase utilizing sinapic acid as substrate.

Katsuyoshi Hamada, Yuji Tsutsumi, Tomoaki Nishida, Kazuchika Yamauchi, Kazuhiko Fukushima  
Faculty of Agriculture Shizuoka University, Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: The conversion of sinapic acid to sinapoyl CoA was confirmed by an enzyme assay using <sup>14</sup>C-labeled sinapic acid and crude enzyme preparation from *Robinia pseudoacacia* L.. This and previous results indicate that *R. pseudoacacia* has a biosynthetic pathway for sinapyl alcohol via sinapic acid. Fractionation of the crude enzyme using a Mono Q column resulted into the resolution of two 4CL isoforms. The molecular weight of the one major 4CL fraction was estimated to be ca. 64kD by SDS-PAGE followed by the treatment with 4CL-specific antiserum. This partially purified 4CL showed high activity with *p*-coumaric acid but very low with sinapic acid and ferulic acid. Isolation of the 4CL isozyme active against sinapic acid in *R. pseudoacacia* is ongoing.

2001-115

特別講演

茶の香気生成機構の研究から植物グリコシダーゼ研究の新展開へ

坂田完三

京都大学化学研究所

Invited Lecture: New research developments of plant glycosidases from studies on molecular basis of aroma formation during tea manufacturing.

Kanzo Sakata

Institute for Chemical Research, Kyoto University,

Abstract: We have clarified the molecular mechanism of floral tea aroma formation during tea manufacturing. Floral aroma such as geraniol, linalool, etc. are present mainly as  $\beta$ -primeveroside (6-*O*- $\beta$ -D-xylopyranosyl- $\beta$ -D-glucopyranosides in fresh tea leaves), which are hydrolyzed by a disaccharide specific glycosidase,  $\beta$ -primeverosidase, to aglycons (aroma compounds) and primeverose. The glycosidase shows a very high substrate specificity to  $\beta$ -primeverosides. Gene cloning of the glycosidase shows very high homology in its amino acid alignment to that of amygdalin hydrolase (57 %). We also have succeeded in synthesis of new type of glycosidase inhibitors (glycosyl amidines), which can be easily synthesized from each sugar without protecting hydroxy groups. Each glycosyl amidine shows very high selective and competitive inhibitory activity against its corresponding glycosyl hydrolase. A successful application for affinity chromatography is shown.

2001-116

特別講演

リグノセルロースの利用 -現状と将来

畠山兵衛

福井工業大学工学部

Invited Lecture: Utilization of lignocellulosics. —Present and future.

Hyo Hatakeyama

Faculty of Engineering, Fukui University of Technology

Abstract: This paper reviews liquid crystals, high performance polymers and environmentally compatible polymers that have been derived from saccharides and phenolic compounds. Liquid crystals were synthesized from 4-hydroxyphenyl, guaiacyl and syringyl derivatives which are obtainable from lignin. Polymers such as polyurethanes containing saccharide and lignin structures were also synthesized. Polycaprolactone derivatives were synthesized from lignin, cellulose and cellulose acetate. Thermal and mechanical properties of the above saccharide- and lignin-derivatives were studied by differential scanning calorimetry, thermogravimetry, thermogravimetric infrared spectroscopy (TG-FTIR) and mechanical measurements.

2001-201

*Anthriscus sylvestris* におけるシリングル型リグナン生合成経路について

榑原紀和、鈴木史朗、梅澤俊明、島田幹夫

京都大学木質科学研究所

Syringyl type lignan biosynthesis in *Anthriscus sylvestris*.

Norikazu Sakakibara, Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Feeding experiments with *Anthriscus sylvestris* have indicated that thujaplicatin, 5-methylthujaplicatin, 4, 5-dimethylthujaplicatin are good precursors of the syringyl type lignan yatein. Furthermore, *Anthriscus sylvestris* cell-free extracts catalyzed O-methylation of several lignans including thujaplicatin and 5-methylthujaplicatin.

2001-202

熱帯産イネ科飼料植物の消化性と細胞壁化学構造

樋口暁浩<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学アジア生物資源環境研究センター

Structural feature of indigestible wall components of tropical forage grasses.

Akihiro Higuchi<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup> Asia Natural Environmental Science Center, the University of Tokyo

Abstract: Setaria grass (*Setaria sphacelata* (Schmach.) Stapf & Hubbard ex M.B. Moss) and Guinea grass (*Panicum maximum* Jacq.) as tropical forage grass were investigated for the relationship between cell wall structure and their digestibilities. *In vitro* cell wall digestibility (IVCWD) was highly correlated with hydroxycinnamic acid content, especially indigested hydroxycinnamic acid content. This result suggests that indigestible cell wall contain high amount of covalent association between lignin and wall polysaccharides (LCC) through hydroxycinnamic acids. Generally, parenchyma cell in grass stems was easily digested. However, Setaria and Guinea grasses have indigestible parenchyma.

2001-203

カカオ (*Theobroma cacao* L.) 種皮の導管及び非導管組織中のポリフェノールの差異

Byung-Yeoup Chung<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学アジア生物資源環境研究センター

Differences in accumulated polyphenolic compounds between vascular bundles and non-vascular bundles of Cacao (*Theobroma cacao* L.) hull.

Byung-Yeoup Chung<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Asian Natural Environmental Science Center, the University of Tokyo

2001-204

ラット尿中に存在する DHP 由来のファイトエストロジェン

長野和種<sup>\*1</sup>、福島和彦<sup>\*1</sup>、安田征市<sup>\*1</sup>、堀尾文彦<sup>\*1</sup>、Augustin Scalbert<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>INRA-Clermont-Ferrand

Phytoestrogens found in the urine of a rat after oral administration of DHP

Kazutane Nagano<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Fumihiko Horio<sup>\*1</sup>, Augustin Scarbert<sup>\*</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>INRA, Saint-Genes-Champanelle, France

Abstract: Two groups of hormone-like diphenolic phytoestrogens, lignans and isoflavonoids, are exist in human body fluids, and have gained increasing interest because of their possible cancer protective properties. The phytoestrogenic lignans are called mammalian lignans. The two major mammalian lignans, enterodiol and enterolactone, are thought to be the products of colonic bacterial metabolism of the plant precursors secoisolariciresinol and matairesinol. However little is known about, the biotransformation of these compounds. And the possibility that lignin in the dietary fiber might be converted into mammalian lignans has been considered. In order to clarify whether lignin is biotransformed to mammalian lignans, lignin model compound, DHP prepared by endwise polymerization of coniferyl alcohol was administrated to the female Wistar rat and the urine was analyzed by GC-MS. Enterodiol and enterolactone were detected, which were not detected in the control urine. This is sufficient to show the possibility that DHP could be converted into mammalian lignans.

2001-205

無機系粒子分散型ポリウレタン系ジオコンポジットの機械的性質

馬淵将人、畠山兵衛

福井工業大学工学部

Mechanical properties of geocomposites of the polyurethane system containing lignin.

Masato Mabuchi, Hyoe Hatakeyama

Fukui University of Technology

Abstract: Polyurethane (PU) geocomposites were prepared from a mixture of lignin, polyethylene glycol (PEG) (Mw=ca.200) and silicic sand. The content of lignin in PEG was changed from 0 to 90%. Mechanical properties of the above PU geocomposites were investigated by mechanical measurements. In the kraft lignin (KL)-PEG200-polyphenyl polyethylene polyisocyanate (MDI) system and in the lignosulfonate (LS)-PEG200-MDI system, the permeation distance of PU into silicic sand increased with increasing lignin contents. However, a maximum stress of the PU geocomposites decreased with increasing lignin contents.

2001-206

リグノスルホン酸含有硬質ポリウレタンフォームの調製と物性

浅野育洋<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>大妻女大学家政学部

Preparation and Properties of Lignosulfonate-based Rigid Polyurethane Foams

Y. Asano<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui University of Technology, <sup>\*2</sup>Otsuma Women's University

Abstract: Rigid polyurethane (PU) foams were prepared from lignosulfonate (LS) dissolved in diethylene glycol (DEG), triethylene glycol (TEG) or polyethylene glycol (Mw=200:PEG200) by the reaction with polyphenyl polymethylene polyisocyanate (MDI). Thermal and mechanical properties of the above polyurethanes (PU's) were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), and compression tests. Glass transition temperatures ( $T_g$ 's) of the PU's from the LS-PEG200-MDI system increased slightly with increasing LS content. However,  $T_g$ 's of the PU's from the LS-DEG-MDI system did not show obvious change with increasing LS content.

2001-207

リグニンを原料とするエステル系エポキシ樹脂の合成と熱的性質

廣瀬重雄<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>

<sup>\*1</sup>産業技術総合研究所、<sup>\*2</sup>福井工業大学工学部

Synthesis and thermal properties of ester-epoxy resins from lignin.

Shigeo Hirose<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Research Institute of Materials and Chemical Process, AIST, <sup>\*2</sup> Fukui University of Technology

Abstract: Alcoholysis lignin (AL) was dissolved in ethylene glycol and the obtained mixture was reacted with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (AL-polyacid, ALPA). Ethylene glycol-polyacid (EGPA) was also prepared from ethylene glycol. The obtained mixture of ester carboxylic acid derivatives was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form ester-epoxy resins. The curing reaction was analyzed by Ozawa's method using differential scanning calorimetry (DSC). The activation energy (E) of curing reaction in the initial step was found to be ca. 83 kJ/mol. The molar ratios of epoxy groups to carboxylic acid groups ([EPOjN]/[AA] ratios, mol/mol) were varied from 0.8 to 1.3. The contents of ALPA in the mixture of ALPA and EGPA (ALPA content) were also varied from 0 to 100 %. Thermal properties of epoxy resins were studied by DSC and thermogravimetry (TG). Glass transition temperatures ( $T_g$ 's) of epoxy resins showed a maximum value of  $-11.5^\circ\text{C}$  when [EPOXY]/[AA] ratio was 1.1.  $T_g$ 's increased with increasing ALPA contents suggesting that lignin acts as a hard segment in epoxy resin networks. Thermal degradation temperatures ( $T_d$ 's) of epoxy resins slightly decreased with increasing ALPA contents.

2001-208

アルカリ性酸素処理に伴うリグニンの赤外吸収スペクトルの変化

矢田 実、角田靖典、新谷博幸、飯塚堯介

東京大学大学院農学生命科学研究科

The changes in infrared spectra of lignin by alkaline oxygen treatment.

Minoru Yada, Yasunori Tsunoda, Hiroyuki Shintani, Gyosuke Meshitsuka

Graduated School of Agricultural and Life Science, The University of Tokyo

Abstract: Various oxidizing agents were applied for bleaching sequence of kraft pulp. Oxygen delignification under alkaline condition which is employed by many plants is important process for pulp bleaching. Structural changes of lignin during oxygen delignification stage are, however, not clarified yet in detail. In this study, softwood and hardwood kraft lignins were treated with alkaline oxygen (1M NaOH, 0.3MPa, 70°C) for 0.5-8.5 hours, and the reaction solutions were analyzed by IR spectroscopy with ATR (Attenuated Total Reflection) methods. The changes in spectra depending on reaction time indicated that aromatic rings with high reactivities to oxygen were almost cleaved until 2.5 hours of reaction, while increase of absorbance due to carboxyl group continued to 8.5

hours of reaction. Spectral changes were observed when pH of the reaction solution of softwood kraft lignin treated for 3.0 hours was increased from 9.4 to 12.2, which should be caused by the difference of degree of dissociation of phenolic hydroxyl groups.

2001-209

酸素漂白過程におけるフェノール類の酸化反応速度

横山朝哉、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Model studies on kinetics of phenol oxidation during oxygen bleaching.

Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Several phenolic compounds were subjected to oxygen-alkali treatment, and their degradations were analyzed in detail by applying a novel formula. This formula was established by two considerations. One was that the degradation of phenolic compounds should be expressed by the sum of two reactions; one of which is caused by molecular oxygen and the other by active oxygen species. The other consideration was that the degradation of phenolic compounds should be written by a pseudo-first-order reaction in which the rate constant  $k_{obs}(t)$  is dependent on reaction time. By arrangements,  $k_{obs}(t)$  was shown as a hyperbola. The contribution of active oxygen species to the degradation of phenolic compounds is visualized by illustrating  $k_{obs}(t)$ . The higher the temperature is, the more active oxygen species contribute to the degradation of phenolic compounds. The extrapolation of  $k_{obs}(t)$  to the beginning of the reaction gave an initial pseudo-first-order reaction rate constant  $k_{obs}((initial))$ . The reaction between phenolic compounds and molecular oxygen without any influence of active oxygen species can be elucidated by using  $k_{obs}((initial))$ . As expected,  $k_{obs}((initial))$  is dependent on functional groups, which indicates that their electronic effect on the aromatic  $\pi$  electron system provides the reaction rate of phenolic compounds with molecular oxygen.

2001-210

非塩素系漂白過程における  $\alpha$ -カルボニル型リグニン構造の挙動 II. 定量法の確立とそのパルプ残存リグニンへの適用

友田生織、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Formation and degradation of  $\alpha$ -carbonyl structure in lignin during chlorine free bleaching. II.

Method to estimate the  $\alpha$ -carbonyl content in lignin remaining in pulp.

Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka

Graduated School of Agricultural and Life Science, the University of Tokyo

Abstract: When guaiacylglycerol- $\beta$ -guaiacyl ether carrying deuterium at  $\alpha$ -methin position (GG $\alpha$ -D) was subjected to nitrobenzene oxidation under the usual reaction condition, the retention of deuterium in the formyl group of the reaction product (vanillin) was quite low because of the D-H exchange during the reaction. The D-H exchange could be suppressed by employing LiOH or Ba(OH)<sub>2</sub> as an alkali during nitrobenzene oxidation. This finding was applied to the semi-quantitative analytical method of lignin  $\alpha$ -carbonyl structure, which consists of successive NaBD<sub>4</sub> reduction of  $\alpha$ -carbonyl structure and nitrobenzene oxidation. Experiments using  $\alpha$ -carbonyl enriched MWL (DDQ treated MWIJ) and its H<sub>2</sub>O<sub>2</sub> treatment product revealed that the increase and the decrease of  $\alpha$ -carbonyl structure in lignin could be successfully analyzed by this method.

2001-211

酸処理・過酸化水素漂白を用いるクラフトパルプの無塩素漂白

大井 洋、池田 努

筑波大学農林工学系

Non-chlorine bleaching of kraft pulp using acid and hydrogen peroxide.

Hiroshi Ohi, Tsutomu Ikeda

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Chlorine dioxide is most popular chemical to convert the bleaching from chlorine system to ECF system. But usually over three times chlorine dioxide need to get the same result that of chlorine system. We discussed about decreasing chlorine dioxide during ECF and non-chlorine bleaching using acid, ozone and hydrogen peroxide. Kappa number 9.4 LKOP contained hexeneuronic acid that was equivalent to kappa number 2.3. After acid treatment and ozone bleaching kappa number decreased to 2.9. But about 26% hexeneuronic acid that was equivalent to kappa number 0.6 still existed in pulp.

2001-212

On-line Kappa number determination in sulfite pulping by visible spectroscopic measurements on spent Liquor.

Yimin Xie, Wenhao Shen, Huanbin Liu

South China University of Technology

Abstract: This paper presents a method of on-line measurement of Kappa number with visible spectroscopy during batch sulfite cooking. It was discovered that the absorption of the spent liquor from Masson's pine in 460-580nm wave range resulted mainly from lignin-sulfonate with high molecular weight ( $MW > 30KD$ ) and that Kappa number maintained a linear relationship with the absorbency of the spent liquor within the wave range. Mathematical models of on-line Kappa number determination with visible light of 460-580nm wavelength were developed by chemometrics for batch sulfite cooking. These models had high learning and prediction precision. Their relative errors were less than 1.5 Kappa number.

2001-213

HBS パルプ化 - 溶媒の安定性とパルプの漂白性

佐野嘉柘、オリギル、梶本純子

北海道大学大学院農学研究科

HBS pulping- sabilization of solvents and bleachability of HBS pulp.

Yoshihiro Sano, Aorigele and Junko Kajimoto

Graduate School of Agriculture, Hokkaido University

Abstract: We has reported in the earlier work of this series that not only hardwood and nonwood, but softwood can be pulped at elevated temperatures and low pressure by HBS pulping process using low-volatile solvents (HBS) with the boiling pint of about 200°C. One HBS introduced into pulp process has to be recovered quantitatively from spent liquors to be used repeatedly as pulping solvents, so the stability of HBS to heat was investigated. Also, in order to prepare complete-bleached pulp for paper-grade, functional cellulose and biopolymers, the bleachability of HBS pulps was studied. The results showed that the pulps were easily bleached by ECF sequence and TI of each pulp was improved significantly by bleaching.

2001-214

HBS パルプ化 - リグニンの理化学的性質

長岡秀明、佐野嘉柘

北海道大学大学院農学研究科

HBS pulping. –Physical and chemical properties of lignin.

Hideaki Nagaoka, Yoshihiro Sano.

Graduate School of Agriculture, Hokkaido University

Abstract: HBS pulping of birch wood with PG in a rotating autoclave was carried out. Spent liquors were separated into lignin and RPG. RPG consisted of low molecular lignin products, sugars and modified sugar products in addition to PG as a main material. The results on the yields of pulp, pulp residual lignin (KL) and lignin showed that PG and RPG were good pulping solvents corresponding to butanediols (BDOL) and RBDOL, though RPG and RBDOL were better solvents than PG and BDOL. Lignins prepared by HBS pulping with RPG in a rotating autoclave have lower molecular weight, a lower amount of methoxyl groups and a higher amount of phenolic hydroxyl groups than those with PG.

2001–215

酢酸パルプの機能化(2) –パルプ化・漂白および誘導体化を酢酸中で行うシステムの構築–

佐藤大典、辻 洋路、浦木康光、岸本崇生、佐野嘉柘

北海道大学大学院農学研究科

Functionalization of acetic acid pulp. (2). –Construction of the successive system from pulping to derivatization performed in acetic acid.

Hironori Sato, Hiromichi Tsuji, Yasumitsu Uraki, Takao Kishimoto, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: To explore the further application of acetic acid pulp (AP) in addition to the use as chemical pulp, we investigated the production system of cellulose acetate (CA) from wood by the successive treatment of acetic acid pulping, TCF bleaching and acetylation, which were performed in acetic acid. AP with Kappa number 30 and ISO brightness 16 was bleached by ozone (Z) to Z-AP with 1.9 and 48, respectively, and then by the following peracetic acid (Pa) to Z-Pa-AP with 0.6 and 66. The resulting bleached AP could be derivatized to CA with degree of substitution of 2.54 and high solubility in acetone by the conventional acetylation.

2001–216

メソ多孔体へ固定化したマンガンペルオキシダーゼによるバイオパルプ漂白システム

梶野 勉、杉山英彦、浅見 修、高橋治雄

株式会社豊田中央研究所

New pulp biobleaching system involving manganese peroxidase immobilized in a silica support with controlled pore sizes.

Tsutomu Kajino, Hidehiko Sugiyama, Osamu Asami, Haruo Takahashi

Toyota Central R & D Laboratories, Inc.

Abstract: Attempts have been made to use manganese peroxidase (MnP) for chlorine-free pulp biobleaching, but they have not been commercially viable because of the enzyme's low stability. We developed a new pulp biobleaching method involving mesoporous material-immobilized manganese peroxidase from *Phanerochaete chrysosporium*. MnP immobilized in FSM, a folded-sheet mesoporous material whose pore size is nearly the same as the diameter of the enzyme, had the highest thermal stability and tolerance to H<sub>2</sub>O<sub>2</sub>. We constructed a thermally discontinuous two-stage reactor system, in which the enzyme (39°C) and pulp-bleaching (70°C) reactions were performed separately. After seven cycles of MnP-treatment and alkaline extraction, the brightness of the pulp increased to about 85% within 6h.

2001-217

マンガンペルオキシダーゼを用いたアゾ系反応性染料の脱色

原園幸一<sup>\*1</sup>、渡辺吉雄<sup>\*2</sup>、深津武馬<sup>\*1</sup>

<sup>\*1</sup>産業技術総合研究所、<sup>\*2</sup>メルシヤン(株)生資研究所

Decolorization of azo reactive dye by manganese peroxidase system.

Koichi Harazono<sup>\*1</sup>, Yoshio Watanabe<sup>\*2</sup>, Takema Fukatsu<sup>\*1</sup>

<sup>\*1</sup>National Institute of Advanced Industrial Science and Technology (AIST), <sup>\*2</sup>Bioresource Laboratories, Mercian Corporation

Abstract: We investigated the decolorization of azo reactive dye, Reactive Red 120 by white rot fungus *Phanerochaete sordida* YK-624 and its enzyme. The dye (200 mg/l) was decolorized 90.6% by *P. sordida* YK-624 in a medium containing 3% malt extract for 7 days. Manganese peroxidase (MnP) activity was detected during decolorization by the fungus. By methylation with H<sub>2</sub>SO<sub>4</sub> and methanol, linoleic acid methyl ester was also detected from the mycelium. The dye was treated with MnP purified from *P. sordida* YK-624. The dye was decolorized by MnP system in the presence of Mn<sup>2+</sup> and Tween 80. These results suggest that *P. sordida* YK-624 and MnP have potential applications for the cleanup of textile mill effluents.

2001-218

Production and purification of laccase from white rot fungus *Lentites* sp.NP21.

Chartchai Khanongnuch<sup>\*1</sup>, Nittaya Wanphrut<sup>\*1</sup>, Saisamorn Lumyong<sup>\*1</sup>, Yoichi Honda<sup>\*2</sup>, Masaaki Kuwahara<sup>\*2</sup>, Takashi Watanabe<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agro-industry, Chiang Mai University, <sup>\*2</sup>Wood Research Institute, Kyoto University

Abstract: The laccase was produced by the thermotolerant wood rotting fungus isolated from tropical rain forest in northern Thailand, *Lentites* sp. NP21, on solid state fermentation containing the rubber wood chips as a nutrient source. The laccase production was 2.94 units/gram substrate. Addition of 4% (w/v) peptone solution increased the enzyme production yield up to 5.69 units/gram substrate and addition of 150 μM of CuSO<sub>4</sub> increased the enzyme produced to 9.43 units/gram substrate. The laccase was purified to the homogeneity using the DEAE-cellulose column chromatography, ultrafiltration and gel filtration on Sephadex G-100 column. The enzyme was purified 893 folds with 49.8% of recovery yield. The optimal pH of enzyme was found at pH 4.0 and the maximum stability, after incubation for 24 hours at various pH, was found from pH 3.5-5.0. The enzyme showed the thermal stability up to 45°C and decreased continuously at the higher temperature. The half-life of heat inactivation at 55°C and 60°C were 130 and 70 min, respectively. The enzyme was inactivated completely with 1 mM Hg<sup>2+</sup> ion. Further research on characterization of the purified laccase is in progress.

2001-219

白色腐朽菌 *Phanerochaete sordida* YK-624 株の産生するペルオキシダーゼによるリグニンモデル化合物の分解

杉浦むつみ、平井浩文、西田友昭

静岡大学農学部

Degradation of lignin model compound by peroxidase produced by white-rot fungus *Phanerochaete sordida* YK-624.

Mutsumi Sugiura, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: The peroxidase which involves in the degradation of nonphenolic β-O-4 lignin model

compound by white-rot fungus *Phanerochaete sordida* YK-624 was purified to homogeneity by Mono Q and Superdex 75 chromatographies. The peroxidase was monomeric heme protein, and the molecular weight was about 50 kDa. The study of degradation of nonphenolic  $\beta$ -O-4 lignin model compound by the peroxidase showed that the C $\alpha$ -C $\beta$  cleavage dominantly occurs, and that very small amount of degradation products, which are originated from  $\alpha$ -oxidation,  $\beta$ -O-4 bond cleavage and B-ring cleavage, are detected. These oxidative degradation of nonphenolic model were obtained by lignin peroxidase (LiP) from *P. chrysosporium*, however, more effective degradation was observed with the peroxidase of *P. sordida* YK-624 compared with the LiP.

2001-220

非フェノール性リグニン  $\beta$ -aryl ether 結合の特異的開裂活性を持つ糸状菌の新規細胞外分泌酵素の検出とその分解機能の解析

大塚祐一郎<sup>\*1</sup>、園木和典<sup>\*1</sup>、中村雅哉<sup>\*2</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

東京農工大学大学院 BASE、森林総合研究所

Detection and isolation of new fungus that cleave the  $\beta$ -aryl ether linkage of high molecular lignin by using the high sensitive assay system.

Yuichiro Otsuka<sup>\*1</sup>, Tomonori Sonoki<sup>\*1</sup>, Masaya Nakamura<sup>\*2</sup>, Shinya Kawai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Forestry and Forest Products Research Institute

Abstract: Cleavage of the arylglycerol- $\beta$ -aryl ether linkage is the most important process in the biological degradation of lignin. The bacterial  $\beta$ -etherase was already described and was tightly associated with the cellular membrane. This function is not able to cleave  $\beta$ -aryl ether linkage in the high molecule lignin, because this enzyme does not secret to extracellular space. In our previous study, the fungal  $\beta$ -aryl ether cleavage enzyme was also described and required the *p*-hydroxyl group and Ca alcohol structure. In this study, we tried the search of the fungi that cleave the  $\beta$ -aryl ether linkage of non-phenolic structure by extracellular function. We succeeded to isolation the fungus, 2T6-6-strain that has  $\beta$ -aryl ether cleavage function for non-phenolic lignin model compounds.

2001-221

耐塩性白色腐朽菌に関する研究(IV)耐塩性白色腐朽菌 MG-60 株による MnP 産生の海塩添加による促進効果について

李 シン、近藤隆一郎、坂井克己

九州大学大学院生物資源環境科学研究科

Study on hypersaline-tolerant white-rot-fungi. (IV). A study on the stimulation of sea salts on MnP production by the salt-tolerant white rot fungus *Phlebia* sp. MG-60.

Xin Li, Ryuichiro Kondo, Kokki Sakai.

Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: A white rot marine isolate, *Phlebia* sp. MG-60, secreted manganese peroxidase (MnP) under different sea salt incubation conditions, and its MnP production was strongly enhanced by the added sea salts into incubation media. In this paper, we demonstrate how and why sea salts enhanced the MnP production by *Phlebia* sp. MG-60, and the results pointed out that the combination of NaCl and Ca<sup>2+</sup> enhanced MnP production as strongly as sea salts.

2001-222

選択的白色腐朽菌 *Ceriporiopsis subvermispora* の菌体外フリーラジカル反応 -NDA による水酸化ラジカル生成反応の抑制

寺西紘子、榎 牧子、本田与一、渡辺隆司、桑原正章  
京都大学木質科学研究所

Extracellular free radical reactions of selective white-rot fungus, *Ceriporiopsis subvermispora*.  
—Suppression of hydroxyl radical generation by NDA.

Hiroko Teranishi, Makiko Enoki, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara  
Wood Research Institute, Kyoto University

Abstract: A selective lignin-degrading fungus, *Ceriporiopsis subvermispora* is able to decompose lignin without morphological changes of wood cell walls. Since lignolytic enzymes are too big to penetrate inside of plant cell walls, this fungus decomposes lignin at a site far from enzymes using low molecular mass metabolites. In the wood decaying process, it is expected that the fungus suppresses hydroxyl radical generation to prevent depolymerization of cellulose. In this paper, we report that hydroxyl radical generation by Fenton reaction is suppressed by a novel metabolite of *C. subvermispora*, 1-nonadecene-2, 3-dicarboxylic acid (NDA).

2001-223

ラッカーゼ-メディエーター系によるポリエチレンとナイロンの分解  
藤澤幹仁、平井浩文、西田友昭  
静岡大学農学部

Degradation of polyethylene and nylon in laccase-mediator system.

Mikihito Fujisawa, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: We investigated whether the laccase-mediator system (LMS) with 1-hydroxybenzo-triazole (HBT) as a mediator could degrade high-molecular-weight polyethylene and nylon-66 membranes. The LMS markedly reduced the elongation and tensile strength of these membranes. After 3 days of treatment with the LMS, the Mw of polyethylene decreased from 242,000 to 28,300, and that of nylon-66 Mw from 79,300 to 14,700. The LMS also decreased the polydispersity (Mw/Mn) of polyethylene and nylon-66. Furthermore, these reductions in elongation, tensile strength, and molecular weight were accompanied by morphological disintegration of the polyethylene and nylon-66 membranes. These results strongly suggest that the LMS with HBT can effectively degrade polyethylene and nylon-66.

2001-224

クラフトパルプ ECF 漂白排水中のダイオキシン類発生レベル  
中俣恵一\*1、大井 洋\*2

\*1 北越製紙株式会社、\*2 筑波大学農林工学系

Dioxins level of kraft pulp ECF bleaching mill sewers.

Keiichi Nakamata, Hiroshi Ohi

Hokuetsu Paper Mills, Ltd., Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: In accordance with the new legislation on dioxin abatement put into effect in Japan in January 2000, kraft and sulfite pulp bleaching mills with chlorine and chlorinated compounds are specified as dioxin generation sources, and since then such pulp mills are subject to restriction of this code. With this code, the concentration of dioxins and coplanar PCBs are restricted below 1 pg-TEQ<sup>WHO1998</sup>/L for the river water and below 10pg-TEQ/L for the effluents from the mills. Under the circumstances above, the Hokuetsu Paper Niigata mill converted in April 2000 its conventional bleaching line with the annual production of 200,000 ADMT into an ECF process following the new ECF bleaching line with the annual production of 400,000 ADMT started up in 1998.

2001-225

ダイオキシン分解微生物の新規アツセイ基質によるスクリーニング

中村雅哉<sup>\*1</sup>、菱山正次郎<sup>\*1</sup>、大塚祐一郎<sup>\*2</sup>、小林 崇<sup>\*2</sup>、片山義博<sup>\*2</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 東京農工大学大学院 BASE

Screening of dioxin degrading microorganisms by new assay substrate.

Masaya Nakamura<sup>\*1</sup>, Shojiro Hishiyama<sup>\*1</sup>, Yuichiro Otsuka<sup>\*1</sup>, Takashi Kobayashi<sup>\*2</sup>, Yoshihiro Katayama<sup>\*2</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Graduate School Bio-application and System Engineering, Tokyo University of Agriculture and Technology

Abstract: A new method to facilitate rapid and sensitive screening of dioxin degrading microorganisms was developed. The dioxin-like substrates were synthesized with the conjugation of chlorobenzene and fluorescence substrates. Microorganisms including fungi and bacteria are cultivated in liquid culture containing these dioxin-like substrates. Fluorescence based on the cleavage of the dioxin ring of the dioxin-like substrates was measured. The method is especially useful for screening for powerful dioxin degrading strains in natural environments. It eliminates the need for special equipments and laborious analysis which are used for the radiolabeled dioxin. In this study, the new assay method has been used to screen our stock fungi.

2001-226

数種のダイオキシン分解菌を用いた PCB 分解の試み

三好進祐、木村圭助、伊藤和貴、橋 燦郎

愛媛大学農学部

Biodegradation of polychlorinated biphenyls by some microorganisms having ability for degradation of dioxins.

Shinsuke Miyoshi, Keisuke Kimura, Kazutaka Ito, Sanrou Tachibana

Faculty of Agriculture, Ehime University

Abstract: To obtain the basic information for purification of polychlorinated biphenyl (PCBs) by bioremediation, microbial degradation of PCB was conducted. Microbial degradation of two kinds of PCBs, 4-chlorobiphenyl (4CB) and 3,3',4,4'-tetrachlorobiphenyl (TCB) was conducted by the three microorganisms, two white-rot fungi (PL1 and 267) and a bacteria screened from the nature, respectively, in a liquid medium. The two fungi degraded about 90% and 70% of 4CB and TCB, respectively, for 30 days. On the contrary, the bacteria degraded about 20% of TCB were degraded by manganese peroxidase (MnP) and mediator complex system for 24 hours.

2001-227

白色腐朽菌 *Phlebia lindtneri* による dibenzo-*p*-dioxin および dibenzofuran の分解

森 智夫、近藤隆一郎

九州大学大学院生物資源環境科学研究科

Degradation of dibenzo-*p*-dioxin and dibenzofuran by the white-rot fungus, *Phlebia lindtneri*.

Toshio Mori, Ryuichiro Kondo

Faculty of Agriculture, Kyushu University

Abstract: Dibenzo-*p*-dioxin (DD) and dibenzofuran (DF) was rapidly degraded in lignolytic cultures of the white-rot fungus *Phlebia lindtneri*. Although DF was oxidized to 2- and other position hydroxylated dibenzofuran, the amounts of these metabolites were too little (< 1 %). 2-hydroxy-dibenzofuran (2-OH-DF) was rapidly decreased over 50 times than DD and DF. Significant inhibition of DD and DF degradation was observed in incubation with the cytochrome P-450 inhibitor 1-amino-benzotriazole. In this fact, we concluded that DD and DF were oxidized to hydroxy derivatives by the

cytochrome P450, and hydroxy derivatives will be degraded by the further oxidation by the extracellular laccase and /or peroxidase.

## 第 47 回 (2002.10.31-11.01)アクロス福岡国際会議場

2002-101

単離過程におけるリグニン構造の変化とその要因について

藤本 文、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Stereo preferential degradation of  $\beta$ -O-4 structure during the process of MWL isolation.

Aya Fujimoto, Yuji Matstmoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Beech (*Fagus crenata* Blume) wood meal was milled for 40 to 120 hr with/without toluene by vibratory ball mill to prepare the milled woods, from which the MWLs were isolated by Björkman's method. The derived milled wood and MWL samples were subjected to the ozonation to investigate the changes in E/T ratio and the content of  $\beta$ -O-4 structure. As the milling effect proceeds, both the E/T ratio and  $\beta$ -O-4 content of the milled wood decreased suggesting that the *erythro*  $\beta$ -O-4 structures is more frequently degraded than the *threo* one during the milling. This indicates that the stereo preferential degradation of lignin proceeds during milling. On the other hand, E/T ratio of MWL increased with the progress of milling but was always lower than that of milled wood from which MWL was extracted. MWL seems to be extracted easily from a region with low E/T ratio and, with the progress of milling, lignins in regions with higher E/T ratio gradually become extractable.

2002-102

MWL 抽出残渣から得た水溶性多糖類に含まれるリグニンの構造

相見 光、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Structure of small lignin fragment retained in water soluble polysaccharide extracted from MWL isolation residue.

Hikaru Aimi, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Water soluble polysaccharide (WS) was extracted from finely divided softwood residues after extraction of MWL. WS contains only 5.3% of lignin. In a gel filtration curve of WS, lignin was found together with sugars at higher molecular weight part. After treatment of WS with carbohydrate degrading enzyme, the apparent molecular weight of both lignin and sugars decreased significantly. Contrary to this, mild alkaline treatment of WS resulted in the significant decrease of the apparent molecular weight of lignin while that of sugars were almost unchanged. These results may indicate that lignin in WS is present as small fragments attached to polysaccharide chain.

2002-103

MWL 抽出残渣への TIZ 法適用の試み

廣澤修一、高野俊幸、中坪文明

京都大学大学院農学研究科

Attempts to application of TIZ degradation method to wood meal after extraction of MWL.

Shuichi Hirose, Toshiyuki Takano, Fumiaki Nakatsubo

Graduate School of Agriculture, Kyoto University

Abstract: Tosylation of wood meal after extraction of MWL (WMEM) was investigated for TIZ degradation analysis. The degree of tosylation was evaluated by FT-IR. The WMEM was tosylated under conventional TsCl / Pyridine condition, but only small amount of Tosyl group was introduced into the WMEM. Then, the WMEM was divided into three fractions, Cellulose-Lignin fraction (CL), Hemicellulose-Lignin fraction (HCL), Insoluble-Lignin fraction (IL). Each fraction was highly tosylated under appropriate reaction conditions. Thus, TIZ degradation method may be applied to elucidate total lignin structure in wood.

2002-104

リグニンの  $\beta$ -O-4 結合の生成に対するコンピュータシミュレーション  
重松幹二、小林孝行、田口大安、棚橋光彦  
岐阜大学農学部

Computer simulation on the formation of  $\beta$ -O-4 linkage of lignin.

Mikiji Shigematsu, Takayuki Kobayashi, Hiroyasu Taguchi, Mitsuhiko Tanahashi  
Faculty of Agriculture, Gifu University

Abstract: Dehydrogenative polymerization of monolignols was computer-simulated with semi-empirical molecular orbital calculation, MOPAC2002. The reactivity was predicted by activation enthalpy at the transition state with the assumption of a kinetic control. In radical coupling stage, it was predicted that the production ratio of  $\beta$ -O-4 coupling was low compared with those of  $\beta$ - $\beta$ ,  $\beta$ -5 and 5-5 couplings, however, it was increased in non-polar solvent. In the reaction of water to  $\alpha$ -carbon of  $\beta$ -O-4 quinonemethide, it was predicted that *threo* form was predominant. However, the reactivity depended on the charge of hydroxyl group and the molecular size of nucleophile.

2002-105

熱分解-TMS 化によるリグニンの分析: けい皮アルコール末端基分析への応用  
黒田健一、中川明子  
筑波大学農林工学系

Pyrolysis-trimethylsilylation of lignin: a sensitive and easy method for analysis of cinnamyl alcohol-end groups.

Ken-ichi Kuroda, Akiko Nakagawa-izumi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Pyrolysis in the presence of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), pyrolysis-trimethylsilylation, was proposed as a new method for analysis of cinnamyl alcohol-end groups in lignin. It preferentially provided large levels of trimethylsilyl (TMS) derivatized cinnamyl alcohols such as coniferyl alcohol diTMS ether (**1**). This method was sensitive to the formed cinnamyl alcohols compared to the conventional pyrolysis and pyrolysis-methylation methods. Pyrolysis-trimethylsilylation of a diazomethane-methylated Japanese cedar (*Cryptomeria japonica*) wood gave two coniferyl alcohol TMS ethers, **1** in 1.3% yield stemming from coniferyl alcohol-end groups and **3** (OMe instead of the phenolic TMS ether of **1**) stemming from the guaiacylglycerol moieties involved in  $\beta$ -O-4 subunits. The results indicated that pyrolysis-trimethylsilylation conveniently provides information on cinnamyl alcohol-end groups when applied to diazomethane-methylated lignins.

2002-106

電子スピン共鳴法によるリグニンの活性酸素消去機能の評価  
藤加珠子、野田博行  
生物ラジカル研究所

Evaluation of the active oxygen scavenging activity of lignin using an electron spin resonance method.

Kazuko Toh, Hiroyuki Noda

Institute of Life Support Technology

Abstract: The superoxide scavenging activity of water solution of lignin extracted from *Quercus acutissima* (KLW) and rice bran (RLW) was evaluated by employing an electron spin resonance combined with the superoxide dismutase addition method. It was found that both samples had superoxide scavenging activity (LLW = 600Unit/g, RLW = 1000Unit/g) with small inhibition rate for superoxide generation in hypoxanthin-xanthine oxidase system (less than 26%).

2002-107

湖沼堆積物のリグニン由来物質

上平雄也<sup>\*1\*2</sup>、福島和彦<sup>\*1</sup>、安田征市<sup>\*1</sup>、寺井久慈<sup>\*3</sup>、大田啓一<sup>\*4</sup>

<sup>\*1</sup> 名大院生命農、<sup>\*2</sup> 永大産業(株)、<sup>\*3</sup> 中部大応用生物、<sup>\*4</sup> 名大地球水循環研究センター

Lignin-derived matters in surface sediments of Japanese lakes

Yuya Kamihira<sup>\*1\*2</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Hisashi Tera<sup>\*3</sup> and Keiichi Ohta<sup>\*4</sup>

<sup>\*1</sup> Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup> Eidai Co., Ltd., <sup>\*3</sup> The college of Bioscience and Biotechnology, Chubu University, <sup>\*4</sup> Hydrospheric Atmospheric Research Center, Nagoya University

Abstract: Lignin derived matters were detected by degradative methods chemically from the surface sediments of three kinds of lake, Biwa, Seto-Taisho and Fukami, located in Japan. Monomers of lignin fragments obtained by CuO oxidation and thioacidolysis were quantified by GC. Dimers obtained by desulphuration of thioacidolysis products were analyzed by GC-MS. In all samples, biphenyl (5-5') structures were dominant among the dimeric compounds derived from lignin.

2002-108

維管束および木繊維における多糖-リグニン結合の定性的・定量的考察

勝亦京子、廣川朋子、飯山賢治

東京大学アジア生物資源環境研究センター

Covalent associations between lignin and polysaccharides in vascular bundle and fiber of plant.

Kyoko S. Katsumata, Tomoko Hirokawa, Kenji Iiyama

Asian Natural Environmental Science Center, the University of Tokyo

Abstract: In this study, structural evidences of each type of cell wall were discussed on the view-point of covalent associations between lignin and polysaccharides, which were evaluated qualitatively and quantitatively with carboxymethylation followed by water extraction for vascular bundle, fiber and compound middle lamella separated from some plants. Chemical composition of vascular bundles and fibers, and secondary walls and compound middle lamella of plants and structural feature of Björknian lignin isolated from their walls were also investigated. Role of covalent associations between lignin and polysaccharides in different types of cell walls was discussed for subsistence and effective utilization of plants on the basis of these results.

2002-109

ペルオキシダーゼ/H<sub>2</sub>O<sub>2</sub>によるモノリグノール類酸化速度に対する3,5位置換基の影響

小林孝行<sup>\*1</sup>、田口大安<sup>\*2</sup>、重松幹二<sup>\*2</sup>、棚橋光彦<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学大学院連合農学研究科、<sup>\*2</sup> 岐阜大学農学部

The effect of 3,5-substituents on oxidation rates of monolignols by peroxidase/H<sub>2</sub>O<sub>2</sub> as oxidant.

Takayuki Kobayashi\*<sup>1</sup> Hiroyasu Taguchi\*<sup>2</sup>, Mikiji Shigematsu\*<sup>2</sup>, Mitsuhiro Tanahashi\*<sup>2</sup>

\*<sup>1</sup>The United Graduate School of Agricultural Science, Gifu University, \*<sup>2</sup>Faculty of Agriculture, Gifu University

Abstract: It is thought that one-electron oxidation of Monolignols is mainly catalyzed by peroxidase/H<sub>2</sub>O<sub>2</sub> in lignification in the cell wall. To elucidate the process of lignification in the all wall, it is important to clarify the mechanism of one-oxidation of monolignol by peroxidase/H<sub>2</sub>O<sub>2</sub>. In this study, to investigate the difference of the reactivity of monolignols in terms of 3,5-substituents, the order listed as to oxidation rates of monolignols and 3,5-substituted monolignols with Horseradish Peroxidase (HRP) /H<sub>2</sub>O<sub>2</sub> as oxidant and the order listed as to oxidation potential of them, which were measured with cyclic voltammetry, were compared.

2002-110

白色腐朽菌 *Phanerochaete sordida* YK-624 株の産生するペルオキシダーゼについて(II)

平井浩文、森田英弘、杉浦むつみ、西田友昭

静岡大学農学部

Peroxidases produced by white-rot fungus *Phanerochaete sordida* YK-624 (II).

Hirofumi Hirai, Hidehiko Morita, Mutsumi Sugiura, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: The inhibitor for peroxidases produced by *Phanerochaete sordida* YK-624 was investigated. The inhibitor, of which the molecular weight was less than 10 kDa, was purified by gel permeation chromatography. The inhibitor inhibited the oxidation of verahyl alcohol (VA) by YK-PO1, YK-PO2 and lignin peroxidase, although the inhibitor did not affect on the reactions of manganese peroxidase and horseradish peroxidase (HRP). In the spectral analysis, compound I of YK-PO2 changed to the native state of YK-PO2 by the addition of the inhibitor, although compound I of HRP did to compound II. On the other hand, little change of compound I of YK-PO2 to native state was observed by the addition of the inhibitor. The inhibitor inhibited VA oxidation by YK-PO1 in an uncompetitive manner.

2002-111

リグニンペルオキシダーゼの酸化反応機構:電気化学的特性からの考察

親泊政二三\*<sup>1</sup>、篠原寛明\*<sup>2</sup>、割石博之\*<sup>3</sup>、田中浩雄\*<sup>3</sup>

\*<sup>1</sup>九州大学大学院生物資源環境科学研究科, \*<sup>2</sup>岡山大学工学部、\*<sup>3</sup>九州大学大学院農学研究院)

Redox mechanism of lignin peroxidase: Electrochemical characterization.

Masafumi Oyadomari\*<sup>1</sup>, Hiroaki Shinohara\*<sup>2</sup>, Hiroyuki Wariishi\*<sup>3</sup>, Hiroo Tanaka\*<sup>3</sup>

\*<sup>1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, \*<sup>2</sup>Faculty of Engineering, Okayama University, \*<sup>3</sup>Faculty of Agriculture, Kyushu University,

Abstract: Electrochemical analysis of lignin peroxidase (LiP) was performed using a pyrolytic graphite electrode coated with peroxidase-embedded tributylmethyl phosphonium chloride membrane. The formal redox potential for the ferric/ferrous couples of LiP was found to be -126 mV (vs. SHE), which was comparable with that of manganese peroxidase and horseradish peroxidase p*K*<sub>a</sub> values for the distal His in peroxidases were calculated using the Nernst equation, to be 5.8 for LiP, 4.7 for MnP, and 3.8 for HRP. A high p*K*<sub>a</sub> value of the distal His might be crucial for LiP compound II to uptake a proton from the solvent. Therefore, LiP is able to complete its catalytic cycle during the oxidation non-proton-donating substrates with a low pH optimum.

2002-112

白色腐朽菌 *Pleurotus ostreatus* により生産される MnP アイソザイムの発現調節について

上辻久敏<sup>\*1</sup>、本田与一<sup>\*1</sup>、波辺隆司<sup>\*1</sup>、桑原正章<sup>\*2</sup>

<sup>\*1</sup> 京都大学木質科学研究所, <sup>\*2</sup> 秋田県立大学木材高度加工研究所

The analysis of expression on the production of manganese peroxidase by white-rot fungi *Pleurotus ostreatus*.

Hisatoshi Kamitsuji, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara  
Wood Research Institute, Kyoto University, Akita Prefectural University

Abstract: Manganese peroxidase (MnP) was secreted by *Pleurotus ostreatus* in liquid stationary culture. Two different MnP isozymes were produced in glucose/Yeast-extract medium (GY) and peptone/glucose/yeast-extract medium (PGY). The isoelectric points of MnP produced in GY medium (MnP-GY) and PGY medium (MnP-PGY) were found to be 3.70 and 3.95, respectively. The molecular masses of both isozymes were 42 kDa. N-terminal amino acid sequences of MnP-PGY was found to be identical to that of MnP 3. It was also similar to that of MnP which was produced in the sawdust culture. To better understand a MnP isozyme production system for medium content, RT-PCR analysis was performed.

2002-113

カワラタケの遺伝子導入系の確立

仁田由美<sup>\*1\*2</sup>、(森総研)宮崎安将<sup>\*3</sup>、中村雅哉<sup>\*3</sup>、飯村洋介<sup>\*4</sup>、  
宍戸和夫<sup>\*5</sup>、(農工大院 BASE)梶田真也<sup>\*2</sup>、諸星紀幸<sup>\*2</sup>

<sup>\*1</sup> 株式会社コシダテック、<sup>\*2</sup> 農工大院 BASE、<sup>\*3</sup> 森林総合研究所、<sup>\*4</sup> 産業技術総合研究所、<sup>\*5</sup> 東京工業大学生命工学科

Development of transformation system in *Coriolus versicolor*.

Yumi Nitta<sup>\*1\*2</sup>, Yasumasa Miyazaki<sup>\*3</sup>, Masaya Nakamura<sup>\*3</sup>, Yosuke Iimura<sup>\*4</sup>, Kazui Shishido<sup>\*5</sup>, Shinya Kajita<sup>\*2</sup>, Noriyuki morohoshi<sup>\*2</sup>

<sup>\*1</sup>Koshida Co Ltd., <sup>\*2</sup>Graduate school of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Forestry and Forest Products Research Institute, <sup>\*4</sup>National Institute of Advanced Industrial Science and Technology, <sup>\*5</sup>Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology

Abstract: Since white rot fungi have a system for the degradation of lignin and various types of persistent organic pollutants (POPs), it has been proposed that these fungi are useful for bioremediation and bioconversion of them. A white-rot basidiomycete, *Coriolus versicolor*, secretes laccase and the enzyme contributes to degrade lignin and POPs. In this study, we tried to establish the transformation system in order to over-produce gene of enzyme such as laccase in *C. versicolor*. We constructed pT7GPDHPT vector containing promoter of glyceraldehydes-3-phosphate dehydrogenase (gpd) gene from *C. versicolor* with hygromycin B resistance gene as marker gene. This plasmid vector was integrated into genome of *C. versicolor* and resultant transformations could be selected on medium including hygromycin B.

2002-114

メソ多孔体による酵素の超安定化と無塩素パルプ漂白への応用

杉山英彦, 梶野勉, 高橋治雄

株式会社豊田中央研究所

Enzyme stabilization in mesoporous material and its application for TCF pulp bleaching.

Hidehiko Sugiyama, Tsutomu Kajino, Haruo Takahashi

Toyota Central R & D Laboratories, Inc.

Abstract: Enzymes were adsorbed on the silica mesoporous materials and their stabilities were studied. Both the surface character and size matching between pore sizes and the molecular

diameters of enzyme were important in achieving a high stability. Manganese peroxidase (MnP) immobilized in mesoporous material, whose pore size just matched the diameter of the enzyme, showed the best stability and high H<sub>2</sub>O<sub>2</sub> tolerance. We constructed a thermally discontinuous two stage reactor system (TSRS), in which the enzyme and pulp bleaching reactions were separately performed. After treatment of pulp with TSRS, the brightness of pulp increased to about 85% within 6hr.

2002-115

特別講演:

非水媒体中における酸化還元酵素の機能発現とその応用

後藤雅宏

九州大学大学院工学研究院、科技団さがけ 21

Invited Lecture: Catalytic activation of peroxidase in nonaqueous media and its novel application.

Masahiro Goto

Department of Applied Chemistry, Kyushu University

Abstract: Activation of peroxidase in an organic solvent by reversed micelle or surfactant coating method was investigated. Lyophilized LIP from an optimized aqueous solution exhibited no enzymatic activity in any organic solvents examined in his study; however, LIP was catalytically active by being entrapped in the AOT reversed micellar solution. LIP activity in the reversed micelle was enhanced by optimizing either preparation or operation conditions such as water and pH in water pools of the reversed micelle, and the reaction temperature. The degradation reaction of several environmental pollutants was attempted using LP hosted in the reversed micelle.

2002-116

特別講演:

リグニンの加溶媒分解 –ホモリシス、クレゾリシス、アルドソリシス、アセトソリシス

佐野嘉拓

北海道大学大学院農学研究科

Invited Lecture: Solvolysis of lignin. – Homolysis, cresolysis, acetosolysis and aldolysis.

Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: Depolymerization and solubilization of lignin by solvolysis are of primary importance for industrial processes of wood proceeded by heating at different pH such as pulping processes as well as for fundamental lignin chemistry. We have been studying the mild hydrolysis of lignin with 50% aqueous dioxane at 180°C for 20 min for the chemical structure of lignin, and solvent pulping processes, solvolysis pulping with 50% aqueous cresol, atmospheric AcOH pulping with a small amount of mineral acid and HBS pulping with aqueous high-boiling alcoholic solvent for the fractionation of lignocelluloses. Also the reaction mechanisms for their processes have been studied using lignin model compounds. This paper reviews the reaction mechanisms of lignin by solvolysis processes in hot neutral, weakly acidic and weakly alkaline solutions.

2002-201

酸加水分解リグニンの陰イオン交換樹脂への変換

松下泰幸、安田征市

名古屋大学大学院生命農学研究科

Preparation of anion-exchange resins from acid hydrolysis lignin

Yasuyuki Matsushita and Seiichi Yasuda

Graduate School of Bioagricultural Sciences, Nagoya University. Nagoya

Abstract: One of the key points in developing saccharification process is to find effective ways to utilize acid lignin. The authors investigated the chemical conversion into anion-exchange resins of phenolized acid lignin (P-SAL), prepared from acid lignin by phenolation with sulfuric acid catalyst, by two methods. The restricted resinification of P-SAL followed by Mannich reaction to yield a weakly basic anion-exchange resin with 2.4 meq/g ion exchange capacity. Another method is the reaction of resinified P-SAL with glycidyltrimethylammonium chloride to yield a strongly basic anion-exchange resin with 2.1 meq/g ion exchange capacity.

2002-202

リグニン系ポリウレタン複合材料の力学物性に及ぼす充填材形状の影響

船橋正弘<sup>\*1</sup>、廣瀬重雄<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup>産業技術総合研究所、<sup>\*2</sup>大妻女大学家政学部、<sup>\*3</sup>福井工業大学工学部

Effect of filter shape on mechanical properties of lignin-based polyurethane composites.

Masahiro Funabashi<sup>\*1</sup>, Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>National Institute of Advanced Industrial Science and Technology, <sup>\*2</sup>Otsu Women's University, <sup>\*3</sup>Fukui University of Technology

Abstract: Polyurethane (PU) composites were prepared using a lignin polyol (KLP, a mixture of kraft lignin and polyethylene glycol, Mw=200) diphenylmethane diisocyanate (MDI) and fillers. Wood meal and coffee grounds were used as fillers. The mixture of KLP and fillers was reacted with MDI by adding an adequate amount of acetone as a solvent. Mechanical properties of composite samples were determined by compression tests. Master curves of the relationships between the specific values of mechanical properties and the apparent volume ratio, determined as the ratio of the apparent volume of filters to the reciprocal values of the apparent density of the samples, were obtained.

2002-203

リグノスルホン酸ソーダのナノレベル構造と熱的性質

畠山兵衛<sup>\*1</sup>、角野浩崇<sup>\*1</sup>、善定和博<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>大妻女大学家政学部

Nanoscale morphology and thermal properties of sodium lignosulfonate.

Hyoe Hatakeyama<sup>\*1</sup>, T. Sumino<sup>\*1</sup>, Kazuhiro Zenjyo<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui University of Technology, <sup>\*2</sup>Otsu Women's University

Abstract: Sodium lignosulfonate (NaLS) has been examined using differential scanning calorimetry (DSC) and tapping mode atomic force microscopy (AFM). NaLS from aqueous solutions was deposited onto freshly cleaved mica surfaces and then air-dried. AFM images of NaLS showed clear network structure at the concentration of 10 pg/ml. DSC was carried out at the scanning rate of 10°C/min from -150°C to 200°C. Glass transition was observed for a dry sample. However, glass transition, cold crystallization and melting of water were observed for wet samples.

2002-204

非塩素系漂白過程における $\alpha$ -カルボニル型リグニン構造の挙動(III): パルプ残存リグニン中の $\alpha$ -カルボニル型リグニン構造の挙動

友田生織、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Formation and degradation of  $\alpha$ -carbonyl structure in lignin during chlorine free bleaching. (III).

Formation and degradation of  $\alpha$ -carbonyl structure in lignin remaining in pulp.

Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: We have already proposed a new method to evaluate the content of  $\alpha$ -carbonyl structure in residual lignin without isolating the lignin from the pulp. In this report, we applied this method to MWL and soft wood oxygen-bleached kraft pulp (NOKP), and the changes in the content of  $\alpha$ -carbonyl structure during alkali and alkali hydrogen peroxide treatment were evaluated. In MWL experiment, hydrogen peroxide treatment under pH13 was very effective to reduce the  $\alpha$ -carbonyl content, but pH10 was not as effective as pH13. The results of hydrogen peroxide treatment of NOKP suggested that hydrogen peroxide bleaching is a process in which the formation and degradation of  $\alpha$ -carbonyl structure take place at the same time.

2002-205

広葉樹クラフトパルプのオゾン・過酸化水素を用いる無塩素漂白

池田 努、大井 洋

筑波大学農林工学系

Non-chlorine bleaching of hardwood kraft pulp with ozone and hydrogen peroxide.

Tsutomu Ikeda, Hiroshi Ohi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Acid treatment was developed for non-chlorine bleaching with ozone and hydrogen peroxide.

Medium consistency ozone bleaching of hard wood oxygen delignified kraft pulp required higher ozone charge than high consistency ozone bleaching did to bleach at a given brightness. Although, high consistency ozone bleaching could not keep a viscosity at an acceptable level, medium consistency ozone bleaching could keep it. Hexeneuronic acid could be removed by both acid treatment and ozone bleaching. Then, a bleaching sequence with acid treatment and ozone bleaching could decrease the ozone charge and improve bleaching selectivity.

2002-206

酸性条件下におけるリグニンの反応機構: アシドリシス条件下におけるリグニン構造の変質に関する分析

坂口智一、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Reaction mechanism of lignin under acidic conditions. Analysis of structural modification of lignin during acidolysis.

Tomokazu sakaguchi, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Acidolysis by the use of hydrochloric acid has been widely applied to the analysis of chemical structure of lignin (analytical acidolysis), and to the isolation of lignin (preparative acidolysis). Compared with analytical acidolysis, preparative acidolysis employs milder condition. It is considered that preparative acidolysis gives less chemical changes of lignin than analytical acidolysis. In this work, wood meal and milled wood lignin (MWL) were treated under several acidolysis conditions and structural modification caused by acid treatment was quantitatively analyzed by ozonation method. Not only the solubilized part but also the solid part (precipitates for MWL and residual lignin for wood meal) were analyzed.

2002-207

Kinetic and mechanism of the degradation of non-phenolic lignin model compounds under aerobic polyoxometalate (POM) bleaching conditions.

Tomoya Yokoyama<sup>\*1</sup>, John F. Kadla<sup>\*1</sup>, Hou-min Chang<sup>\*1</sup>, Ira A. Weinstock<sup>\*2</sup>, Richard S. Reiner<sup>\*2</sup>  
<sup>\*1</sup> Department of Wood and Paper Science, North Carolina State University, <sup>\*2</sup> USDA Forest Service, Forest Products Laboratory

Abstract: A non-phenolic lignin model compound, **1**, **2** and **4**, was reacted with polyoxometalate (POM) under anaerobic bleaching conditions, and the kinetic and mechanism were investigated. A syringyl type, **1**, was degraded slower than a guaiacyl type, **2**, although the activation energy of **1** is a little lower than **2**. Instead, the frequency factor of **1** is considerably smaller than **2**, suggesting that steric factor controls the rate of the reaction between POM and model compound, and dominates over electronic property of its aromatic ring. The significance of steric factor was confirmed by the reaction using **4** that has an ethoxyl group instead of a methoxyl group. The degradation of **4** was slower than **1**, giving a lower activation energy and a much smaller frequency factor. A kinetic isotope effect was observed when the  $\alpha$ -deuterated compound of **1** and **2** was subjected to the reaction. It is suggested that the rate-determining step of the reaction between POM and non-phenolic models is the abstraction of the benzylic hydrogen. Further kinetic and mechanism will be discussed in the presentation.

2002-208

Structural characteristics of lignin in humified materials.

Oskars Bikovens<sup>\*1\*2</sup>, Janis Gravitis<sup>\*2</sup>, Kenji Iiyama<sup>\*1</sup>

<sup>\*1</sup>Asian Natural Environmental Science Center, the University of Tokyo, <sup>\*2</sup>Latvian State Institute of Wood Chemistry

Abstract: The behavior of lignocellulosic material during humification was investigated using grass compost. Lignin of grass compost prepared by the Björkman's method suggested that lignin macromolecules were modified even after short time composting. Soluble fraction of composted grasses gave the same products with lignin by alkaline nitrobenzene oxidation and by ozonation, and also by methoxyl group determination. These results suggested that some portion of lignin macromolecules were biologically modified to be dissolved in water by introduction of hydrophilic groups such as carboxyl groups, which could play same role as soil humic matters.

2002-209

$\beta$ -O-4 型側鎖の立体構造を規定する要因の解明 --樹種間における  $\beta$ -O-4 型側鎖立体構造の分布--

秋山拓也<sup>\*1</sup>、松本雄二<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、Deded S. Nawawi<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup>Bogor Agricultural University

Distribution of diastereomeric forms of  $\beta$ -O-4 structures among different wood species.

Takuya Akiyama<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>, Deded S Nawawi<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Dept. of Forest Products Technology, Bogor Agricultural University

Abstract: The *erythro/thero* ratios of  $\beta$ -O-4 structures were investigated by the ozonation analysis for about 20 species including both softwood and hardwood. The *erythro/threo* ratio exhibited wide variation among species, about 1.0 for softwood and 1.5-3.5 for hardwood. The correlation between *erythro/thero* ratios of  $\beta$ -O-4 structures and the methoxyl group contents were clearly observed among the species. It was confirmed that there is the relationship between the *erythro/thero* ratio and syringyl/guaiacyl ratio among different species, suggesting that the aromatic ring type is one of the factors which control the formation of diastereomeric forms of  $\beta$ -O-4 structures during lignin biosynthesis.

2002-210

熱帯モンスーン気候と温帯における樹木主要成分の生分解過程の定量的・定性的考察

小野 芳<sup>\*1</sup>、目黒あい<sup>\*2</sup>、Maria F. A. Navera<sup>\*3</sup>、武内和彦<sup>\*1</sup>、飯山賢治<sup>\*4</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学大学院新領域、<sup>\*3</sup> フィリピン大学、<sup>\*4</sup> 東京大学アジア生物資源環境研究センター

Qualitative and quantitative discussions for biodegradation of wood components in the tropical monsoon area and in the temperate area.

Kaori Ono<sup>\*1</sup>, Ai Meguro<sup>\*2</sup>, Maria F. A. Navera<sup>\*3</sup>, Kazuhiko Takeuchi<sup>\*1</sup>, Kenji Iiyama<sup>\*4</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup> Graduate School of Frontier Sciences, the University of Tokyo, <sup>\*3</sup> University of the Philippines, <sup>\*4</sup> Asian Natural Environmental Science Center, the University of Tokyo

Abstract: Urban green spaces should be promoted in tropical monsoon area such as in the Philippines, where their effects on mitigation of urban climate would be expected to be greater than those in temperate area. Huge amounts of plant residues produced under high plant productivity should be utilized as resources. This study discusses the process of biodegradation of plant remains into soil organic matter for their utilization. Quantitative and qualitative analyses were carried out to discuss changes in biomass weight, lignin weight (Klason lignin and acid soluble lignin), aromatic composition of lignin and neutral sugar composition of major urban trees in the Philippines during biodegradation. The results were compared with those carried out in Japan.

2002-211

落葉のマルチング過程におけるリグニン量の変化

金 貞福<sup>\*1</sup>、渡辺達三<sup>\*2</sup>、飯山賢治<sup>\*3</sup>、秋山拓也<sup>\*1</sup>、松本雄二<sup>\*1</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 東京大学大学院新領域、<sup>\*3</sup> 東京大学アジア生物資源環境研究センター

Changes in lignin content of leaf litters during mulching.

ZhenFu Jin<sup>\*1</sup>, Satomi Watanabe<sup>\*2</sup>, Kenji Iiyama<sup>\*3</sup>, Takuya Akiyama<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Agriculture and Life Science, the University of Tokyo, <sup>\*2</sup> Asian Natural Environmental Science Center, the University of Tokyo, <sup>\*3</sup> Graduate School of Frontier Science, the University of Tokyo,

Abstract: Alkaline nitrobenzene oxidation procedure, ozonation method and methoxyl content determination have been applied to the decomposing leaf litters during mulching to investigate the properties of lignin and to approximately estimate lignin content as assumed lignin content during mulching. Assumed lignin content based on methoxyl content of Klason residue was much lower (3.9 to 10.0%) than that of Klason residue (37.1 to 46.7%). Absolute amount of assumed lignin somewhat decreased during mulching, while the structure of lignin remaining in leaf litters after mulching was not quite different from its original structure.

2002-212

ケイヒ酸／モノリグノール経路のメタボローム解析に用いる重水素標識モノリグノールの合成

榊原紀和、梅澤俊明、島田幹夫

京都大学木質科学研究所

Syntheses of deuterium-labelled monolignols for metabolome analysis of the cinnamate/monolignol pathway.

Norikazu Sakakibara, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: In the postgenomic era, much attention has been focused on the overall

understanding of the metabolism of the cinnamate/monolignol pathway in relation to lignin, lignan and norlignan biosynthesis. Recently, transcriptome and proteome analysis of the pathway has been reported. On the other hand, metabolome analysis has not been yet applied to the pathway, because of the lack of an appropriate methodology. Herein, we have synthesized deuterium-labelled monolignols, which can be used for internal standards of stable isotope dilution method-guided metabolome analysis of the cinnamate/monolignol pathway.

2002-213

新生木部におけるリグニン前駆物質配糖体の挙動

辻 幸子、安田征市、福島和彦

名古屋大学大学院生命農学研究科

On the behaviors of glucosides of lignin precursors in the differentiating xylem

Yukiko Tsuji, Seiichi Yasuda and Kazuhiko Fukushima

Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: To clarify the mechanism of storage and supply of monolignol in the metabolism of lignin, the roles and behaviors of coniferin and coniferyl aldehyde glucoside in lignin biosynthesis were examined by tracer experiments using labeled precursors. The microautoradiography showed coniferyl aldehyde glucoside was incorporated into lignin with almost similar pattern to the case of coniferin. The results of lignin chemical analysis, DFRC/GC-MS ensured that coniferyl aldehyde glucoside was metabolized as monolignol precursor. Coniferin might be incorporated into lignin through the complex pathway with oxidative step that is independent of coniferin/ $\beta$ -glucosidase system.

2002-214

イネをモデルとした植物細胞壁形成過程に関する研究(1)ーイネ科植物細胞壁成分の生合成制御に関する研究ー

間瀬浩平<sup>\*1</sup>、佐藤かな<sup>\*1</sup>、中野仁美<sup>\*1</sup>、西窪伸之<sup>\*1</sup>、北野英己<sup>\*2</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院生物システム応用科学研究所、<sup>\*2</sup>名古屋大学大学院生命農学研究科

Studies on genetic regulation of cell wall formation in rice plant. (1). –The research on biosynthesis control of cell wall component in the Gramineae plant.

Kohei Mase<sup>\*1</sup>, Kanna Sato<sup>\*1</sup>, Yoshimi Nakano<sup>\*1</sup>, Nobuyuki Nishikubo<sup>\*1</sup>, Hidemi Kitano<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Graduate school of Bioagricultural Sciences, Nagoya University

Abstract: It is obvious that genes involved in lignin biosynthesis have to be coordinately regulated in response to developmental and environmental cues. So, we think that the elucidation of regulation mechanisms of such genes is effective for the acquisition of useful characteristics such as environmental adaptation and blocking of the ingress of pathogens and increase in the biomass resource. The rice plant in which genome analysis advances is very useful in order to understand these regulation mechanisms using the genetic and molecularbiological technique. In this study, as a part of program characterizing the biosynthetic regulation of plant cell wall component, we examined the polysaccharide-linked hydroxycinnamoyl esters biosynthetic pathway and its molecular mechanism of genetic regulation in rice plant using rice one gene recessive mutant.

2002-215

イネをモデルとした植物細胞壁形成過程に関する研究(2)ーイネ細胞壁成分の生合成制御遺伝子のマップベースクローニングと新しい2次壁形成異常を持つイネの解析ー

佐藤かな\*<sup>1</sup>、間瀬浩平\*<sup>1</sup>、北野英己\*<sup>2</sup>、梶田真也\*<sup>1</sup>、片山義博\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学大学院生物システム応用科学研究所、\*<sup>2</sup> 名古屋大学大学院生命農学研究科

Studies on genetic regulation of cell wall formation in rice plant. (2). —Map based cloning of biosynthesis control gene of cell wall component and analysis of novel secondary cell wall mutant. Kanna Sato, Kohei Mase, Hidemi Kitano, Shinya Kajita, Yoshihiro Katayama

Graduate School of Bio-Applications and System Engineering, Tokyo University of Agriculture and Technology, Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: The plant cell walls are composed of a complex mixture of phenolic component, carbohydrates and proteins. To date, the structure and biosynthesis of major cell wall components, lignin and cellulose have been clarified, but the co-ordinate regulations of individual steps in end biosynthetic pathway and different pathways through cell wall establishment remain unclear. To understand these co-ordinate regulations, we perform map based cloning of *d50* gene which induces abnormal parenchyma cell walls in Fukei71 as shown in previous presentation. In addition, using histochemical and chemical methods, we analyze a novel rice mutant of alterations in the thick secondary cell wall formation.

2002-216

白色腐朽菌のバイオレメディエーション環境下でのモニタリング

須原弘登\*<sup>1</sup>、大黒千映子\*<sup>1</sup>、近藤隆一郎\*<sup>2</sup>

\*<sup>1</sup> 九州大学大学院生物資源環境科学研究科、\*<sup>2</sup> 九州大学大学院農学研究院

Monitoring of white-rot fungus during bioremediation.

Hiroto Suhara, Chieko Daikoku, Ryuichiro Kondo

Faculty of Agriculture, Kyushu University

Abstract: Bioremediation is a low-cost treatment alternative for the cleanup of dioxin-contaminated environment, when pollution spread broad-ranging. An interesting fungus was isolated from white rotten wood of a broadleaf tree from Kyushu island, in Japan, named strain MZ-340. This isolate has ability to degrade dioxin. We have tried to use this strain for bioremediation of dioxin-contaminated environment *on site*. Hence, we have to develop a PCR-based assay to detect strain MZ-340 reliably on bioremediation site. We successfully monitored the strain MZ-340 *on site*. The relationship between the population of the fungus and the effect of bioremediation by this fungus will be discussed.

2002-217

ペルオキシダーゼ及び遷移金属反応を開始系とするリピッドペルオキシデーションによる加硫・未加硫イソプレンゴムの分解

佐藤 伸\*<sup>1</sup>、本田与一\*<sup>1</sup>、渡辺隆司\*<sup>1</sup>、桑原正章\*<sup>2</sup>

\*<sup>1</sup> 京都大学木質科学研究所、\*<sup>2</sup> 秋田県立大学木材高度加工研究所

Degradation of vulcanized and non-vulcanized isoprene rubbers by lipid peroxidation initiated with peroxidases and transition metals.

Shin Sato\*<sup>1</sup>, Yoichi Honda\*<sup>1</sup>, Takashi Watanabe\*<sup>1</sup>, Masaaki Kuwahara\*<sup>2</sup>

\*<sup>1</sup> Wood Research Institute, Kyoto University, \*<sup>2</sup> Institute of Wood Technology, Akita Prefectural University

Abstract: Degradation of vulcanized and non-vulcanized synthetic polyisoprene (IR) by lipid peroxidation initiated with peroxidases and transition metals was analyzed by CHCl<sub>3</sub>-extraction, gel permeation chromatography, and double-shot pyrolysis GC-MS (DS-Py-GCMS). Non-vulcanized IR was depolymerized intensively by the free radicals from unsaturated fatty acids produced by manganese peroxidase (MnP), Mn(III) chelate, and the Fenton reagent (FR). Partial

depolymerization was observed in lipid peroxidation with horseradish peroxidase (HRP) and laccase/mediator. Distinct degradation was not observed in the reactions with lipoxygenase (LOX). In these reaction systems, the depolymerization of polyisoprene depended on the presence of peroxidizable lipids. Degradation of vulcanized IR sheets was observed in the lipid peroxidation initiated by FR. Reactions by MnP and Mn(III) chelate in sodium oxalate buffer also degraded the rubbers. The reaction system by FR degraded the vulcanized rubber sheet intensively as 80 % of the rubber component was solubilized with CHCl<sub>3</sub>. By the DS-Py-GCMS analysis of CHCl<sub>3</sub> extracts, low molecular mass fragments, isoprene, 1,4-dimethyl-4-vinylcyclohexene, 1-methyl-5-(1-methyl-ethenyl)-cyclohexene and limonene were identified. These results indicate that control of free radical chain reactions of lipids by enzymes and transition metals is a key to degrade the recalcitrant vulcanized rubber products.

2002-218

リグニン分解酵素による Irgarol の分解

小川直人\*<sup>1</sup>、平井浩文\*<sup>1</sup>、西田友昭\*<sup>1</sup>、岡村秀雄\*<sup>2</sup>

\*<sup>1</sup> 静岡大学農学部、\*<sup>2</sup> 神戸商船大学

Degradation of Irgarol by ligninolytic enzymes.

Naoto Ogawa, Hideo Okamura, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University, Kobe University of Mercantile Marine

Abstract: 2-Methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine (Irgarol 1051), which is a newly developed herbicidal additive for use in copper-based antifouling paints, was treated with partially purified MnP and laccase. The HPLC data showed that Irgarol 1051 disappears by 36–37% after a 24-h treatment with both enzymes and two peaks suspected the transformation products of Irgarol 1051 are newly formed by the treatment. One of the transformation products was identified to be 2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine (M1) by comparing its retention time and mass spectrum with those of an authentic compound using GC-MS. This suggests that *N*-dealkylation occurs at the cyclopropylamino group of Irgarol 1051 resulting in metabolite M1. Toxicities of Irgarol 1051 and M1 were evaluated by the growth inhibition tests using alga (*Selenastrum capricornutum*) and duckweeds (*Lemna gibba* and *L. minor*). M1 showed the toxicity about 10 times lower than that of Irgarol 1051 for all the aquatic plant species tested, indicating that the treatment with ligninolytic enzyme is effective in detoxification of Irgarol 1051.

2002-219

木材腐朽担子菌による Polychlorinated Naphthalenes の分解

北野史朗\*<sup>1</sup>、森 智夫\*<sup>1</sup>、近藤隆一郎\*<sup>2</sup>

\*<sup>1</sup> 九州大学大学院生物資源環境科学研究科、\*<sup>2</sup> 九州大学大学院農学研究院

Degradation of polychlorinated naphthalenes by wood decaying fungi.

Shirou Kitano\*<sup>1</sup>, Toshio Mori\*<sup>1</sup>, Ryuichiro Kondo\*<sup>2</sup>

\*<sup>1</sup> Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, \*<sup>2</sup> Graduate School of Agriculture, Kyushu University

Abstract: The transformation of polychlorinated naphthalenes (PCNs) has been studied using six strains of wood decaying fungi. In one of these strains, *Phlebia lindtneri* GB-1027 degraded 2-chloronaphthalene (2CN) immediately. The initial metabolites were detected by gas chromatography-mass spectrometry. The hydroxylation of substrates was initially observed during degradation of 2CN. Significant inhibition of degradation of 2CN was observed in incubation with cytochrome P-450 monooxygenase inhibitors, 1-aminobenzotriazole and piperonyl butoxide. These experiments with cytochrome P-450 monooxygenase inhibitors, and formation of the mono-

hydroxylated metabolites suggested that *P. lindtneri* initially degraded 2CN by monooxygenases oxidation system.

2002-220

白色腐朽菌 *Phlebia lindtneri* による塩素化 dibenzo-*p*-dioxin および dibenzofuran の酸化  
森 智夫、近藤隆一郎

九州大学大学院生物資源環境科学研究科

Oxidation of chlorinated dibenzo-*p*-dioxin and dibenzofuran by white-rot fungus; *Phlebia lindtneri*.  
Toshio Mori, Ryuichiro Kondo

Graduate School of Bioresources and Bioenvironmental Sciences, Kyushu University

Abstract: The actions of white-rot fungus on two chlorinated aromatic compounds, known to be persistent environmental contaminants, were studied. Two both-ring chlorinated dioxin-models, 2,7-dichlorodibenzo-*p*-dioxin (2,7-diCDD) and 2,8-dichlorodibenzofuran (2,8-diCDF), were metabolized by white-rot fungus *Phlebia lindtneri*. 2,7-DiCDD was disappeared linearly in the culture of *P. lindtneri*; after a 20 day incubation period, only 45 % remained in the culture. One of metabolites each produced by *P. lindtneri* from a 5-day incubated culture with 2,7-diCDD or 2,8-diCDF was identified by gas chromatography-mass spectrometry. *P. lindtneri* was shown to metabolize 2,7-diCDD and 2,8-diCDF to a hydroxy-diCDD and a hydroxy diCDF, respectively.

2002-P01

微生物相互作用による白色腐朽菌の酵素生産

原園幸一<sup>\*1</sup>、渡辺吉雄<sup>\*2</sup>、中村和憲<sup>\*1</sup>

<sup>\*1</sup> 産業技術総合研究所、<sup>\*2</sup>メルシヤン生資研

Induction of ligninolytic enzyme production in white-rot fungi by antagonistic microorganisms.

Koichi Harazono<sup>\*1</sup>, Yoshio Watanabe<sup>\*2</sup>, Kazunori Nakamura<sup>\*1</sup>

<sup>\*1</sup>National Institute of Advanced Industrial Science and Technology (AIST), <sup>\*2</sup>Bioresource Laboratories, Mercian Corporation

Abstract: We investigated enzyme production in white-rot fungi by antagonistic microorganisms. Fungi often produce the phenoloxidase enzyme laccase during interactions with other organisms. By pairings of white-rot fungi *Trametes versicolor* or *Lentinus edodes*, and antagonistic organism *Trichoderma longibrachiatum* on malt extract agar, laccase activity was mainly detected on the region in contact with both fungi. On the other hand, manganese peroxidase (MnP) activity was detected on the region in contact with *T. longibrachiatum* in the case of white-rot fungus *Phanerochaete sordida*.

2002-P02

白色腐朽菌 *Phanerochaete sordida* YK-624 株の産生するペルオキシダーゼについて(III)

杉浦むつみ、森田英弘、平井浩文、西田友昭

静岡大学農学部

Peroxidases produced by white-rot fungus *Phanerochaete sordida* YK-624 (III)

Mutsumi Sugiura, Hidehiro Morita, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: The characteristics of two peroxidase isozymes (YK-PO1, YK-PO2), produced by *Phanerochaete sordida* YK-624 were investigated. The substrate specificities of lignin peroxidase from *P. chrysosporium* (Pc-LiP), YK-PO1, and YK-PO2 for monomeric lignin model compounds were not differ. On the other hand, dimeric  $\beta$ -O-4 lignin model compound was more efficiently consumed by YK-PO1 and YK-PO2 than by Pc-LiP. Moreover, YK-PO1 had a higher specificity for sinapyl

alcohol oligomer than did YK-PO2 and Pc-LiP, though the specific activity of veratryl alcohol (VA) oxidation was the lowest with YK-PO1. YK-PO1 showed high tolerance to hydrogen peroxide compared with YK-PO2 and Pc-LiP. It is thought that low reactivity of YK-PO1 with hydrogen peroxide affects on VA oxidation by YK-PO1.

2002-P03

非フェノール性  $\beta$ -O-4 型リグニンモデル化合物の酸化電位とラッカーゼ/1-HBT 系による酸化力との相関

岩月正人、山本明日香、中川 誠、稲垣真澄、重松幹二、河合真吾、大橋英雄

岐阜大学農学部

The correlation between the oxidation potentials of non-phenolic  $\beta$ -O-4 lignin model compounds and the oxidation abilities of laccase/1-HBT system.

Masato Iwatsuki, Asuka Yamamoto, Makoto Nakagawa, Masumi Inagaki, Mikiji Shigematsu, Shingo Kawai, Hideo Ohashi.

Faculty of Agriculture, Gifu University

Abstract: We have studied on the degradation of non-phenolic  $\beta$ -O-4 lignin model compounds by laccase/1-HBT system. In this Study, we investigated the oxidation potentials and HOMO energies of non-phenolic  $\beta$ -O-4 lignin model compounds (1)-(7). These results suggest that the oxidation ability of laccase/1-HBT system correlates with their oxidation potentials and HOMO energies.

2002-P04

スジチヤダイゴケ (*Cyathus stercoreus*) による非フェノール性リグニンモデル化合物の分解とリグニン分解酵素

稲垣真澄、大畑直人、河合真吾、大橋英雄

岐阜大学農学部

Degradation of non-phenolic lignin model compound by *Cyathus stercoreus* and its lignin degrading enzymes.

Masumi Inagaki, Naoto Ohata, Shingo Kawai, Hideo Ohashi

Faculty of Agriculture, Gifu University

Abstract: The white rot fungus *Cyathus stercoreus* degraded a non-phenolic  $\beta$ -O-4 lignin model compound, 1,3-dihydroxy-2-(2,6-dimethoxyphenoxy)-1-(4-ethoxy-3-methoxyphenyl) propane [I], in Tien and Kirk medium. The fungus catalyzed the  $\beta$ -ether cleavage and the aromatic ring cleavage of substrate I. Furthermore, the enzyme activities of extracellular fluid of *C. stercoreus* were investigated.

2002-P05

白色腐朽菌によるダイオキシン汚染土壌のバイオレメディエーションにおける土壌成分の影響  
城村真衣\*<sup>1</sup>、近藤隆一郎\*<sup>2</sup>

\*<sup>1</sup>九州大学大学院生物資源環境科学研究科、\*<sup>2</sup>九州大学大学院農学研究院

Effect of soil components on bioremediation of dioxin-polluted soil by white-rot fungi.

Mai Jomura, Ryuichiro Kondo

Faculty of Agriculture, Kyushu University

Abstract: A white-rot fungus, *Ceriporia* sp. MZ-340 is able to degrade polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. However, dioxins in soils are hardly degraded by the fungus. In order to clarify inhibitory effect of soil components on the degradation of dioxins by the fungus, glass beads and soil were used as carriers for dioxins. As model compounds for dioxins,

2,7-dichlorodibenzo-*p*-dioxin (DCDD) or octachlorodibenzo-*p*-dioxin (OCDD) were added to the glass beads or soil, and treated with the fungus. Although both DCDD and OCDD added on glass beads were degraded extensively, the degradation of both DCDD and OCDD added on soil was inhibited completely. Furthermore, toluene extracts of soil was suggested to affect inhibitory on the degradation of DCDD.

2002-P06

Polychlorinated Biphenyls (PCBs)の酵素による分解の試み

三好進祐、伊藤和貴、橘 燦郎

愛媛大学農学部

Biodegradation of polychlorinated biphenyl by enzymes from fungus having ability for degradation of dioxins.

Shinsuke Miyoshi, Kazutaka Ito, Sanrou Tachibana

Faculty of Agriculture, Ehime University

Abstract: To obtain the basic information for purification of polychlorinated biphenyls (PCBs) by bioremediation, degradation of PCBs by crude enzymes from fungus PL1 having ability for degradation of dioxins was tried in this research. Two kind of PCBs, 4-Chlorobiphenyl (4CB) and 3,3',4,4'-Tetrachlorobiphenyl (TCB) were used as substrates. About 74% and 13% of 4CB and TCB were degraded by the crude enzymes from fungus PL1 in a liquid medium for 24 hours, respectively. And furthermore, about 33% and 26% of 4CB and TCB in a soils were degraded by the crude enzymes from fungus PL1 for 30 days, respectively. From the results obtained here, it was found that PCBs could be degraded by crude enzymes from fungus having ability for degradation of dioxins.

2002-P07

白色腐朽菌ミノタケが分泌する新規リグニンペルオキシダーゼの触媒特性

三木佑太<sup>\*1</sup>、割石博之<sup>\*2</sup>、田中浩雄<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院

Characterization of novel lignin peroxidase from the white-rot basidiomycete *Trametes cervina*.

Yuta Miki, Hiroyuki Wariishi, Hiroo Tanaka.

Faculty of Agriculture, Kyushu University

Abstract: Among several white-rot basidiomycetes examined, *Trametes cervina* was found to show relatively higher lignin peroxidase (LiP) activity in the extracellular medium. Utilizing DEAE Sepharose FF, Sephadex G-100, and Mono Q, LiP from *T. cervina* (TcLiP) was purified. TcLiP was obtained as a major band with Mr of 37 kDa but with a minor band on SDS-PAGE analysis. Further study revealed that the minor band was derived from a contamination of MnP. However, the contamination was minimal; thus, steady-state kinetic and spectroscopic analyses could be achieved. Electron absorption spectrum of TcLiP shows a typical characteristics for a hexa-coordinate high spin ferric iron state of the heme.

2002-P08

担子菌の示す細胞応答機構の解析: 外因性有機化合物が引き起こす種々の応答反応

一瀬博文<sup>\*1\*3</sup>、栗原宏征<sup>\*1\*4</sup>、平塚宜博<sup>\*1</sup>、志水元亨<sup>\*1</sup>、中村朋史<sup>\*1\*5</sup>、三浦大典<sup>\*1</sup>、湯田直樹<sup>\*1</sup>、割石博之<sup>\*2</sup>、田中浩雄<sup>\*2</sup>

九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院、<sup>\*3</sup>九州大学大学院工学研究院、<sup>\*4</sup>東京大学大学院工学研究科、<sup>\*5</sup>財務省印刷局

Fungal cellular responses against exogenous chemicals.

Hirofumi Ichinose<sup>\*1\*3</sup>, Hiroyuki Kurihara<sup>\*1\*4</sup>, Nobuhiro Hiratsuka<sup>\*1</sup>, Motoyuki Shimizu<sup>\*1</sup>, Tomofumi

Nakamura<sup>\*1\*5</sup>, Daisuke Miura<sup>\*1</sup>, Naoki Yuda<sup>\*1</sup>, Hiroyuki Wariishi<sup>\*2</sup>, Hiroo Tanaka<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Graduate School of Agriculture, Kyushu University, <sup>\*3</sup>Graduate School of Engineering, Kyushu University, <sup>\*4</sup>Graduate School of Engineering, Tokyo University, <sup>\*5</sup>Printing Bureau, Ministry of Finance

Abstract: Extracellular ligninolytic enzymes are thought to be involved in the initial attack on polymeric lignin and aromatic pollutants via the one-electron oxidation mechanism, resulting in the formation of a variety of aromatic and quinoid fragments which are further metabolized intracellularly. Therefore, basidiomycetes seem to have highly regulated and specific intracellular metabolic systems for each fragment. However, a fungal cellular response mechanism against chemical compounds has not been well studied. In this study, the fungal responses occurred against the addition of a wide variety of chemicals to fungal cells were analyzed using transcriptomic, proteomic, and metabolomic techniques.

2002-P09

8-O-4' 型シリングルネオリグナンのジアステレマーの立体化学とトチュウにおけるそれらの生合成  
ラウリット ナタヤ, 片山健至、石川貴美子, 栗田陽輔, 鈴木利貞  
香川大学農学部

Stereochemistry of 8-O-4' syringyl neolignans and their biosynthesis in *Eucommia ulmoides*.

Nattaya Lourith, Takeshi Katayama, Kimiko Ishikawa, Yousuke Kurita, Toshisada Suzuki  
Faculty of Agriculture, Kagawa University

Abstract: 8-O-4' type neolignans, syringylglycerol-8-O-4'-(sinapyl alcohol) ether (SGSE) and guaiacylglycerol-8-O-4'-(sinapyl alcohol) ether (GGSE) were synthesized. Their *erythro* and *threo* isomers were separated and identified by means of NMR. To understand their biosynthesis in *Eucommia ulmoides*, feeding experiments of a labeled precursor, [8-<sup>14</sup>C]sinapyl alcohol, to excised shoots were undertaken. It was found that the radioactivity was incorporated into SGSE (and its glucoside) in the stems and the leaves, and that the present incorporation into *erythro* isomer was more than that into *threo* isomer.

2002-P10

クラフトパルプの漂白過程で生成する高分子成分の生分解挙動  
幸田圭一

北海道大学大学院農学研究科

Biodegradation of high-molecular-weight compounds produced by kraft pulp bleaching process.  
Keiichi Koda

Graduate School of Agriculture, Hokkaido University

Biodegradation behavior of high molecular portion of kraft pulp bleach effluent containing substantial amount of organochlorine was investigated. Chlorine-based bleach liquor containing microorganisms was subjected to dialysis cultivation to trace low-molecular-weight degradation products (MW<1000), some of which may cause environmental impact. A few degradation products were successively detected as intermediary metabolites by HPLC equipped with UV detector (270nm). It was observed that about 50 % of organically bound chlorine in the fraction was removed during the incubation period of three months.

2002-P11

ケナフ靱皮の中間温度での蒸解  
吉永新司、鮫島一彦  
高知大学農学部

Pulping of kenaf bast fiber at moderate temperature.

Faculty of Agriculture, Kochi University

Abstract: It was already shown that it is possible to make a high viscosity kenaf bast pulp by normal pressure soda pulping although the residual lignin is still at high level. To realize a commercial pulping to make high viscosity (strength) pulp, it is needed to reduce the lignin content and the load of bleaching even if some reduction of viscosity occur. A moderate temperature pulping was examined here to reduce the residual lignin content of unbleached pulp. At 140°C, the pretreatment of ammonium oxalate was not effective to the delignification, but viscosity was kept comparatively at high level. The addition of anthraquinone and the extension of keeping time at 140°C was proved to be effective. The viscosity was 62 cp and the Kappa number was 39.

2002-P12

シラカンバ常圧酢酸パルプの無塩素漂白(2)

辻 洋路、岸本崇生、浦木康光、佐野嘉拓

北海道大学大学院農学研究科

Non-chlorine bleaching of atmospheric acetic acid pulp from *Betula platyphylla var. japonica* Hara. (2).

Hiromichi Tsuji, Takao Kishimoto, Yasumitsu Uraki, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: Atmospheric acetic acid pulp from Japanese white birch wood was treated with non-chlorine bleaching agents such as oxygen (O), ozone (Z) and chlorine dioxide (D). In the previous investigation we showed that the pulp was fully bleached with multi-stage bleaching in DEDED or ZZZEpD sequence. In order to decrease the amount of ozone or chlorine dioxide, oxygen bleaching was performed in this investigation. Deacetylation of the pulp prior to oxygen bleaching was essential. Bleachability of the pulp was improved by EO treatments, and brightness reached 86–87% ISO in EOZED sequence. However, paper strength of the pulp was inferior to that in DEDED or ZZZEpD sequence. Further investigations were necessary to optimize oxygen bleaching stage.

2002-P13

HBS パルプ化におけるリグニンの構造変化 –NMRによる解析(2)–

植木飛鳥、岸本崇生、佐野嘉拓

北海道大学大学院農学研究科

Structural changes in lignin during HBS pulping. –NMR Analysis. (2).

Asuka Ueki, Takao Kishimoto, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: Structural changes in lignin during HBS pulping were investigated by quantitative <sup>13</sup>C-NMR and HMQC spectra. The content of phenolic hydroxyl groups in MWL increased significantly, which may be attributed to hydrolysis of  $\alpha$ -O-4 bonds and homolytic cleavage of phenolic  $\beta$ -aryl ether. The decrease in the content of  $\beta$ -O-4 structures and introduction of 1,4-butanediol into  $\alpha$ -position of  $\beta$ -O-4 moiety were confirmed. The  $\beta$ -5 and  $\beta$ - $\beta$  substructures were relatively resistant to HBS pulping conditions, but  $\beta$ -1 may not. The signals corresponding to Hibbert's ketones were not observed, which suggests that acidolysis is not important degradation pathway in HBS pulping.

2002-P14

アルカリ性酸素脱リグニン段排液リグニンの土壌改良剤としての性状

王 東香、勝亦京子、飯塚堯介

東京大学大学院農学生命科学研究科

Characterization of lignin fragments in alkaline-oxygen stage waste liquor as soil conditioning agent.

Dongxiang Wang, Kyoko Katsumata, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

2002-P15

酸可溶性リグニンのクロロホルム可溶成分

宮脇 慈、松下泰幸、安田征市

名古屋大学大学院生命農学研究科

Chloroform soluble components of acid soluble lignin

Shigeru Miyawaki, Yasuyuki Matsushita and Seiichi Yasuda

Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: To elucidate the formation and chemical structures of chloroform soluble materials in acid soluble lignin (ASL), lignin model compounds of arylglycero1- $\beta$ -aryl ethers with guaiacyl (I) and syringyl (II) nuclei were treated by the Klason procedure. Model compound I gave only insoluble polymerized condensation product, while II gave insoluble polymerized product and chloroform soluble low molecular weight products, which were dissolved in 3% sulfuric acid.

2002-P16

リグニンと新聞古紙を原料とする成形活性炭ボードの作成

根本純司、浦木康光、佐野嘉拓

北海道大学大学院農学研究科

Preparation of activated carbon boards from a mixture of lignin and waste newspaper.

Junji Nemoto, Yasumitsu Uraki, Yohihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: Activated carbon boards (ACB) were prepared from mixture of hardwood acetic acid lignin (HAL) and waste newspaper. The mixture was molded to precursory boards by thermal press, and then converted to ACB by carbonization and steam activation. The ACB prepared from the precursory boards with 20% HAL molded under the conditions of 130°C and 6 MPa showed the most excellent adsorption properties and flexural strength among the ACB tested. The adsorption ability and flexural strength of ACB were deteriorated with the increase in the board thickness. The laminated ACB with 3 layers showed better adsorption property than that of mono layer ACB with the corresponding thickness.

2002-P17

リグニンの構造および反応研究のための  $^{13}\text{C}$ -標識 NMR 示差スペクトル分析法

寺島典二

名古屋大学名誉教授

Carbon 13-NMR spectrometry measuring difference between spectra of  $^{13}\text{C}$ -enriched and unenriched lignins. -An effective tool for analysis of structure and reactions.

Noritsugu Terashima

Professor emeritus, Nagoya University

Abstract: Lignin is a structurally heterogeneous polymer formed by an irreversible random polymerization of several kinds of monolignol radicals. Therefore, it is impossible to degrade lignin quantitatively into monomeric or oligomeric units, and degradation loses information on heterogeneity. Accordingly, destructive analyses can provide limited information on the chemical structure of lignin macromolecule. Nondestructive analyses by  $^{13}\text{C}$ -NMR difference spectrometry

between spectra of specifically  $^{13}\text{C}$ -enriched lignin and unenriched lignin can provide definite information not only on the structure of lignin macromolecule but also on the structural change during various reactions that is hardly obtained by any other conventional destructive analyses. Information on the structural heterogeneity can also be obtained by combination of this technique with pulse labeling and anatomical separation techniques.

## 第 48 回 (2003.10.30-30) 福井工業大学芦原学舎

2003-101

TOF-SIMS によるリグニン構造の解析

斉藤香織<sup>\*1</sup>、高森ひとみ<sup>\*2</sup>、岸本崇生<sup>\*2</sup>、安田征市<sup>\*1</sup>、福島和彦<sup>\*1</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>北海道大学大学院農学研究科

Analysis of lignin structures by TOF-SIMS

Kaori Saito<sup>\*1</sup>, Hitomi Takamori<sup>\*2</sup>, Takao Kishimoto<sup>\*2</sup>, Seiichi Yasuda<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>Graduate School of Agriculture, Hokkaido University

Abstract: Lignin model compounds were investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS) to study the relationship between the chemical structure and the secondary ion spectra. The formation mechanism of two prominent fragment ions ( $m/z$  137 and 151), each of which has a CG-CI Structure With a guaiacyl nuclei, was deduced by using deuterium labeling of specific positions of coniferyl alcohol. We also examined 8-O-4', 8-1', 5-5', 8-5' and 8-8' types of dimers, showing dominant  $\text{C}_6\text{-C}_1$  ions originated from specific inter-unit bonds in lignin.

2003-102

近赤外分光計測による植物葉リグニンの定量

高橋俊守<sup>\*1</sup>、安岡善文<sup>\*1</sup>、飯山賢治<sup>\*2</sup>

<sup>\*1</sup>東京大学生産技術研究所、<sup>\*2</sup>東京大学アジア生物資源環境研究センター

Estimation of lignin content in fallen leaves using near-infra-red spectroscopy.

Toshimori Takahashi<sup>\*1</sup>, Yoshifumi Yasuoka<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

<sup>\*1</sup>Institute of Industrial Science, the University of Tokyo, <sup>\*2</sup>Asia Natural Environmental Science Center, the University of Tokyo

Abstract: It is important to develop the measuring method of organic matter in conjunction with carbon circulation or global warming. Near-infra-red (NIR) spectroscopy may be an effective method to estimate contents of organic matter such as lignin. Lignin contents of fallen leaves were determined using various analytical procedures. In laboratory, NIR spectra were recorded for each sample of leaves on ground. The correlation coefficient between NIR spectra and lignin content varied with analytical procedures used to determine lignin content and plant species. The combination of plant species and analytical method should be considered to develop a suitable regression model using NIR spectroscopy.

2003-103

光による熱帯産材の変色とそれらのスペクトルの特徴

岸野正典<sup>\*1</sup>、中野隆人<sup>\*2</sup>

<sup>\*1</sup>北海道立林産試験場、<sup>\*2</sup>島根大学総合理工学部

Photo-induced color changes of some tropical woods and their spectral features.

Masanori Kishino<sup>\*1</sup>, Takato Nakano<sup>\*2</sup>

\*<sup>1</sup>Hokkaido Forest Products Research Institute, \*<sup>2</sup> Interdisciplinary Faculty of Science and Engineering, Shimane University

Abstract: Although for bangkirai (*Shorea* spp.), jahhra (*Eucalyptus marginata*) and robusta (*E. robusta*), both  $\Delta a^*$  (shifty to red) and  $\Delta b^*$  (yellowing) decreased with increased exposure time up to 600 h, for auri (*Acacia auriculiformis*), cumaru (*Amnuranana acreana*), ipe-high (*Tabebuia* spp. with relative high specific gravity), ipe-low (with relative low specific gravity), keruing (*Dipterocarpus* spp.),  $\Delta b^*$  increased with exposure up to 50 h, and decreased above 50 h. Further information on the correlation between the above color changes and their spectral features such as diffuse reflectance Fourier transform infrared (DRIFT) and ultraviolet-visible (UV-Vis.) spectra are given at the presentation.

2003-104

マカンバ MWL 抽出残渣から得た水溶性多糖類に含まれるリグニンの構造

相見 光、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Structure of small lignin fragment retained in water soluble polysaccharide extracted from birch MWL isolation residue.

Hikaru Aimi, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: To investigate the structural feature of lignin existing nearby the lignin-carbohydrate linkages, water soluble fraction with low lignin content was prepared from the residual Birch wood meal after the extraction of MWL. Gel filtration behavior before and after treatment with polysaccharide degrading enzyme revealed that this fraction was composed of relatively high molecular weight polysaccharide to which small lignin fragments were linked. Structural analysis of lignin in this fraction revealed that it is rich in syringyl nuclei with non-condensed type structures and have different character in condensed type one.

2003-105

アシドリシス条件下におけるリグニン構造の変質に関する分析(2)

坂口智一、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Analysis of structural modification of lignin during acidolysis. (2).

Tomokazu Sakaguchi, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: In the last lignin symposium, we reported that about 25% of  $\beta$ -O-4 structure was lost under preparative acidolysis condition (0.1M HCl in dioxane-water, reflux for 2h), and that  $\alpha$ -condensed structure was not detected even under 5% sulfuric acid treatment by ozonation analysis. In this work, Hibbert's ketone type side-chain structure of acidolysis MWL was quantitatively analysed by NaBH<sub>4</sub> reduction followed by ozonation. In this result, it was indicated that about 45% of  $\beta$ -O-4 structure was lost during analytical acidolysis (0.2M HCl, reflux for 4h) and about 40% of lost  $\beta$ -O-4 structure was converted into C6-C3 type Hibbert's ketone structure. However, C6-C3 type Hibbert's ketone structure was not detected when H<sub>2</sub>SO<sub>4</sub> was used as catalyst.

2003-106

花卉道管部におけるトラケアリー・エレメントの形成とリグニンの化学構造

勝亦京子\*<sup>1</sup>、飯山賢治\*<sup>1</sup>、江前敏晴\*<sup>2</sup>

\*<sup>1</sup> 東京大学アジア生物資源環境研究センター、\*<sup>2</sup> 東京大学大学院農学生命科学研究科  
Genesis of tracheary element and chemical structure of lignin at vessel of flower petal.  
Kyoko S. Katsumata\*<sup>1</sup>, Kenji Iiyama\*<sup>1</sup>, Toshiharu Enomae\*<sup>2</sup>

\*<sup>1</sup>Asian Natural Environmental Science Center, the University of Tokyo, \*<sup>2</sup>Graduate School of  
Agricultural and Life Sciences, the University of Tokyo

Abstract: It is hardly recognized the presence of lignin in flower pedals. But flower pedals have to be supplied water through vessels, which may be quite different from "normal vessels" in other tissues of plant. Vessels of flower pedals are characterized by quick formation and significantly short life span. The vessels would be excellent specimens to investigate the formation of secondary walls in plants. Morphology of vessels of flower pedals of 14 popular species were observed by light and scanning electron microscopies, and found tracheary element structures from all of specimens. In addition, chemical composition of secondary walls of camellia (*Camellia reticulata* Lindl.) was analyzed and structural feature of Björkman lignin isolated from camellia was investigated. Lignin was significantly rich in p-hydroxyphenyl nuclei and condensed structure, which could characterize as initial stage of lignin biosynthesis.

2003-107

樹木の防御反応としてのリグニン生合成について

堀啓映子\*<sup>1</sup>、谷田貝光克\*<sup>1</sup>、山田利博\*<sup>2</sup>

\*<sup>1</sup> 東京大学大学院農学生命科学研究科、\*<sup>2</sup> 東京大学大学院農学生命科学研究科附属演習林

Lignin biosynthesis for defense responses against fungus.

Keko Hori\*<sup>1</sup>, Mitsuyoshi Yatagai\*<sup>1</sup>, Toshihiro Yamada\*<sup>2</sup>

\*<sup>1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, \*<sup>2</sup>Experimental Station at Tanashi, University Forests, the University of Tokyo

Abstract: Mass mortality of oaks is caused by the infection of a fungus *Raffaelea quercivora*, vectored by ambrosia beetle *Platypus quercivorus*. Reaction zone barrier (RZB) was observed near the discolored part in the infected wood. Lignin content of RZB was higher than the other part, and S/V ratio was lower. Guaiacyl type and condensed type lignin was synthesized for the defense response against fungus in the reaction zone barrier.

2003-108

イネをモデルとした植物細胞壁形成過程に関する研究(3)ーイネ科植物細胞壁成分の生合成制御に関する研究ー

中野仁美\*<sup>1</sup>、間瀬浩平\*<sup>1</sup>、佐藤かんな\*<sup>1</sup>、北野英己\*<sup>2</sup>、梶田真也\*<sup>1</sup>、片山義博\*<sup>1</sup>

\*<sup>1</sup> 東京農工大学大学院生物システム応用科学研究科、\*<sup>2</sup> 名古屋大学大学院生命農学研究科

Studies for genetic regulation of cell wall formation in rice plant. (3).- The research on biosynthesis control of cell wall component in the Gramineae plant.

Yoshimi Nakano\*<sup>1</sup>, Kohei Mase\*<sup>1</sup>, Kanna Sato\*<sup>1</sup>, Hidemi Kitano\*<sup>2</sup>, Shinya Kajita\*<sup>1</sup>, Yoshihiro Katayama\*<sup>1</sup>

\*<sup>1</sup>Graduate School of Bio-Applications and System Engineering, Tokyo University of Agriculture and Technology, \*<sup>2</sup>Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: The series of genes involved in the biosynthesis of lignin and polysaccharide-linked hydroxycinnamoyl esters, which compose plant cell walls, have to be coordinately regulated in order to respond and adapt to environmental stresses during plant growth process. The rice plant that genome analysis make advance is very useful in understanding these regulation mechanisms using the genetic and molecular biological technique. In this study, as a part of program characterizing the biosynthetic regulation of plant cell wall component, we examined the polysaccharide-linked hydroxycinnamoyl esters biosynthetic pathway and its molecular mechanism of genetic regulation in

rice plant with rice one gene recessive mutant.

2003-109

ラッカーゼ反応系における 1-Hydroxybenzotriazole の役割

柴田浩志<sup>\*1</sup>、平井浩文<sup>\*1</sup>、西田友昭<sup>\*1</sup>、大西正健<sup>\*2</sup>

<sup>\*1</sup> 静岡大学農学部, <sup>\*2</sup> 京都府立大学大学院農学研究科

The role of 1-hydroxybenzotriazole in laccase reaction system.

Hiroshi Shibata<sup>\*1</sup>, Hirofumi Hirai<sup>\*1</sup>, Tomoaki Inita<sup>\*1</sup>, Masatake Ohnishi<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture Shizuoka University, <sup>\*2</sup>Graduate School of Agriculture, The Prefecture University of Kyoto

Abstract: We investigated the role of 1-hydroxybenzotriazole (HBT) in laccase (Lac) reaction system. No metabolites which were produced from a non-phenolic  $\beta$ -O-4 lignin model compound in Lac/HBT system was detected in artificial HBT radical system, although the artificial HBT radical degraded the model compound. In the kinetics studies, HBT was not a competitive inhibitor for Lac, and the inhibition pattern was changed by the addition of HBT. On the other hand, HBT was an uncompetitive inhibitor for horseradish peroxidase (HRP). Moreover, ferrocyanochrome c was competitively oxidized by Lac/HBT system. These results suggest that HBT might be involved in the formation of ES complex, but not a radical mediator.

2003-110

ポプラ分化中木部におけるラッカーゼの局在

竹内美由紀、高部圭司、藤田 稔

京都大学大学院農学研究科

Localization of laccase in differentiating xylem of poplar.

Miyuki Takeuchi, Keiji Takabe, Minoru Fujita

Graduate School of Agriculture, Kyoto University

Abstract: Laccases and peroxidases are thought to be the candidates for dehydrogenative polymerization of monolignols, however their differences have not been clarified. We have, therefore, investigated the localization of these two enzymes in poplar trees using immunocytochemistry to reveal the possible difference between laccases and peroxidases in their localization and perhaps the role in lignification. For immunolabeling of laccase, antibodies were raised against the peptides synthesized according to the amino acid sequences of laccase. The labeling of laccase was observed in the cell walls of secondary wall forming fibers and vessels, especially in compound middle lamella and in outer layer of secondary wall. In parenchyma cells, intensive labeling was seen in the innermost layer of cell wall.

2003-111

リグニン生合成の抑制による飼料消化性の向上

久保賢太郎、川合伸也

東京農工大学農学部

Down regulation of cinnamoyl-CoA reductase(CCR) induces increase of cell wall digestibility in rice (*Oryza sativa*).

Kentaro Kubo, Shinya Kawai

Faculty of Agriculture, Tokyo University of Agriculture & Technology

Abstract: Cinnamoyl-CoA reductase(CCR) is the first enzyme to the lignin-specific biosynthesis. Inverted repeats constructs of the DNA encoding CCR of *Oryza sativa* have been introduced into rice plants. Some CCR down-regulated plants displayed phenotype like *Brownn*

*midrib* mutants. Histochemical analysis was performed on the transformants. The internodes from them, in contrast to wild type, indicated weaker red staining when treated with phloroglucinol-HCl. This suggested reduction in aldehydes and/or lignin contents. Little difference was detected between wild type and transformants with the Mäule reagent.

2003-112

超高感度蛍光アツセイシステムにより見出されたリグニンの  $\beta$ -aryl ether 結合を特異的に切断する糸状菌の分解機能とその多様性

大塚祐一郎<sup>\*1</sup>、中村雅哉<sup>\*2</sup>、菱山正二郎<sup>\*2</sup>、梶田信也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 森林総合研究所

Detection, characterization and its diversity of new fungus that cleave the  $\beta$ -aryl ether linkage of high molecular lignin by using the high sensitive assay system.

Yuichiro Otsuka<sup>\*1</sup>, Masaya Nakamura<sup>\*2</sup>, Shoujiro Hishiyama<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Forestry and Forest Products Research Institute

Abstract: Cleavage of the arylglycerol- $\beta$ -aryl ether linkage is the most important process in the biological degradation of lignin. The bacterial  $\beta$ -etherase was already described and was tightly associated with the cellular membrane. This function is not able to cleave  $\beta$ -aryl ether linkage in the high molecule lignin, because this enzyme does not secret to extracellular space. In this time, we aimed to detect and isolate of the fungi catalyzing cleavage of  $\beta$ -aryl ether linkage of high molecular lignin in the soil fungi. We screened and isolated the several fungi, named 2BW-1, f5053, 2T6-6, FA1 and FC5 by using GOU, GOUbz and DHP-GOU as the high sensitive assay system. Resulting

analysis of 18srDNA, we determined that these fungi belong to Ascomycetes and it suggest that various fungi affect to degrade the phenolic compounds of plant involving lignin in nature.

2003-113

リグナン生合成の系統分類的多様性

梅澤俊明

京都大学木質科学研究所

Phylogenetic aspects of lignan biosynthesis.

Toshiaki Umezawa

Wood Research Institute, Kyoto University

Abstract: The chemical structures of lignans vary substantially in basic carbon frameworks, as do their oxidation levels and substitution patterns. In this review, the phylogenetic distribution of plants producing 66 typical lignans with a variety of chemical structures are listed based on a data base search. The distribution is correlated with the possible biosynthetic pathways of the lignans and discussed from evolutionary aspects.

2003-114

アベマキ及びイチヨウ外樹皮におけるスベリン芳香族部分の予想前駆体と外樹皮のメタノリシス分解生成物の比較

鈴木利貞、滝野修平、泉 大輔、片山健至

香川大学農学部

Predicted precursors of the aromatic domain of suberin and methanolysis products of two kinds of outer bark: comparison between *Quercus variabilis* and *Ginkgo biloba*.

Toshisada Suzuki, Shuhei Takino, Daisuke Izumi, Takeshi Katayama

Faculty of Agriculture, Kagawa University

Abstract: *p*-Hydroxycinnamic acid esters, as predicted precursors of the aromatic domain of suberin, in two kinds of bark of *Quercus variabilis* and *Ginkgo biloba* were analyzed. The esters were specifically present in both of the outer bark. Dehydrogenative polymerizations of butyl ferulate and butyl caffeate were carried out as a model system. The polymerization of butyl ferulate gave dimers of  $\beta$ -O-4',  $\beta$ -5', dihydronaphthalene, naphthalene and  $\beta$ - $\beta$ ' symmetry types. The polymerization of butyl caffeate afforded dimers of  $\beta$ -6' and dihydronaphtharene types. Extractive free powders obtained from the two kinds of bark were treated by methanolysis. Feruloyloxy fatty acid esters and methyl ferulate were isolated from both of the decomposition products.

2003-115

特別講演:

樹木心材成分の生理活性と生成

坂井克己

九州大学大学院生物資源環境科学研究科

Invited Lecture: Bioactivity and production of heartwood components.

Kokki Sakai

Faculty of Agriculture, Kyushu University

Abstract: Here I review our works on anti-tyrosinase activity of the *Artocarpus incisus* heartwood and steroid 5 $\alpha$ -reductase inhibitory of resveratrol oligomers isolated from *Shorea* spp. heartwood. Contribution of the 2,4-dihydroxyphenyl structure to the anti-tyrosinase activity is noted. Dehydrogenative polymerization of resveratrol yielded 5 $\alpha$ -reductase inhibitory oligomers. In addition, I deal with our studies on hinokitiol ( $\beta$ -thujaplicin), a heartwood constituent of Cupressaceae species exhibiting a variety of bioactivities. Its production by *Cupressus lusitanica* cell cultures, signal transduction after elicitation, and biosynthetic pathway has been studied.

2003-116

特別講演:

自然に学ぶ高分子合成の現状

蒲池幹治

福井工業大学工学部

Invited Lecture: Development in nature-inspired polymer synthesis.

Mikiharu Kamachi

Fukui University of Technology

Abstract: Molecular design in polymer synthesis has been inspired by fine functions of natural polymers. Remarkable advance has been made in artificial control of molecular weight in chain-growth polymerization, preparation a helical polymers, application of enzymes to polymer synthesis, and matrix polymerization due to supra molecules. In this lecture, living radical polymerization, asymmetric polymerization, enzymatic polymerization, and preparation of tubular polymer from cyclodextrin are mentioned.

2003-201

®-O-4 結合からなる規則性人工リグニンポリマーの化学合成

岸本崇生、浦木康光、生方 信

北海道大学大学院農学研究科

Synthetic lignin polymer composed of  $\beta$ -O-4 structure.

Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: The  $\beta$ -O-4 structure is one of the most important substructures in lignin. In this investigation, highly regulated synthetic lignin polymers composed of  $\beta$ -O-4 structure were prepared from simple aromatic compounds as starting materials by a solution polymerization method. Acetophenone derivatives were brominated and polymerized in the presence of  $K_2CO_3$ . The polymer was converted to synthetic lignin polymer composed of  $\beta$ -O-4 structure. The polymer was soluble in usual lignin solvents such as 1,4-dioxane and DMSO. Molecular weight of acetate derivatives of the polymer was determined by GPC analysis.

2003-202

$\beta$ -O-4 型リグニンオリゴマーの簡便な合成法の検討

片平 類、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Facile synthetic method for  $\beta$ -O-4 type lignin oligomers.

Rui Katahira, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Graduate School of Agriculture, Kyoto University

Abstract: A novel synthetic method for obtaining lignin oligomers that are composed of only the  $\beta$ -O-4 structure was investigated. This method consists of two reaction steps: the continuous nucleophilic addition oligomerization of butoxycarbonylmethyl vanillin (**1**) and subsequent reduction of the oligomeric  $\beta$ -hydroxyl ester. In the first step, the oligomeric  $\beta$ -hydroxyl ester (**2**) was obtained in 90% yield; the repeating units of these oligomers were joined exclusively by  $\beta$ -O-4 linkages. The number-average degree of polymerization of **2** was calculated to be about 7.2 ( $M_w/M_n=1.36$ ). In the second step, the oligomeric  $\beta$ -hydroxyl ester (**2**) was treated with  $LiAlH_4$  to give product **3** in 73% yield. On the basis of NMR, MALDI-TOP-MS, and GPC analysis of the acetate of **3**, it was indicated that compound **3** is an oligomeric lignin related compound containing only  $\beta$ -O-4 interunit linkage.

2003-203

熱帯泥炭湿地環境中有機物の性状と土壌有機物形成過程

金 貞福、勝亦京子、飯山賢治

東京大学アジア生物資源環境研究センター

Zhenfu JIN, S. Kyoko Katsumata, Kenji Iiyama

Asian Natural Environmental Science Center, the University of Tokyo

Abstract: A series of structural features of the three main humic fractions, namely humic acid, fulvic acid and humin from different depths of peat profile in Narathiwat Province, southern Thailand were isolated and analyzed. Humin and humic acid contained similar amount of total carbon and nitrogen in acid insoluble fractions of humin and humic acid. Ash free acid insoluble fractions in humin ranged from 76.4% to 86.2% of original peat samples and there was no significant difference among different peat profiles. Contents of methoxyl groups and total yield of alkaline nitrobenzene oxidation products were significantly lower than those of fresh wood specimens. Those values increased with depth of sampling and the amount of water extractives, the content of acid soluble lignin and the ratio of acid to aldehyde of alkaline nitrobenzene oxidation products showed the same trend.

2003-204

ケナフ茎芯加溶媒分解物から繊維強化型ポリウレタン

執行 薫\*<sup>1</sup>、堀 成人\*<sup>1</sup>、竹村彰夫\*<sup>1</sup>、小野拓邦\*<sup>1</sup>、飯山賢治\*<sup>2</sup>

\*<sup>1</sup> 東京大学大学院農学生命科学研究科、\*<sup>2</sup> 東京大学アジア生物資源環境研究センター

Fiber reinforced polyurethane film prepared from solvolysis product of Kenaf (*Hibiscus cannabinus* L.) core.

Kaoru Shigyo\*<sup>1</sup>, Naruhito Hori\*<sup>1</sup>, Akio Takemura\*<sup>1</sup>, Hirokuni Ono\*<sup>1</sup>, Kenji Iiyama\*<sup>2</sup>

\*<sup>1</sup>Graduated School of Agricultural and Life Sciences, the University of Tokyo, \*<sup>2</sup>Asian Natural Environmental Science Center, the University of Tokyo

Abstract: Solvolysis of Kenaf (*Hibiscus cannabinus* L.) core with polyethylene glycol (PEG) is studied to acquire plant-biomass-derived polyols from which polyurethane products are prepared. Conventional study to obtain alternative oil resources from the biomass has focused on the solubilization as much as possible. In this work, the solvolysis is carried out to the extent of that the cellulose fiber remains in the solvolyzed crude. Polyurethane products prepared from this crude would be reinforced with the residual fiber. This report deals with 1) optimization of solvolysis condition suited to the above idea, 2) mechanical properties of the polyurethane films prepared from the solvolyzed.

2003-205

Development of Effective Utilization of Rice Waste-byproducts

Maxima E. Flavier\*<sup>1\*2</sup>, Kyoko S. Katsumata\*<sup>1</sup>, Kenji Iiyama\*<sup>1</sup>

\*<sup>1</sup> 東京大学アジア生物資源環境研究センター, \*<sup>2</sup> Institute of Chemistry, University of Philippines.

Development of effective utilization of rice waste-byproducts.

Maxima E. Flavier\*<sup>1\*2</sup>, Kyoko S. Katsumata\*<sup>1</sup>, Kenji Iiyama\*<sup>1</sup>

Asian Natural Environmental Science Center, the University of Tokyo, Institute of Chemistry, University of the Philippines Los Banos

Abstract: This study involved the chemical and structural characterization of 80% aqueous ethanol-extracted samples of rice hull, straw and bran including amylase-treated and roasted bran. Neutral sugar composition, uronic acids, C:N ratio, lignin by acetyl bromide, hydroxycinnamic acids and nitrobenzene oxidation products were determined.

2003-206

リグニン分解のシステム解析を目指した *Phanerochaete chrysosporium* のゲノム解析

割石博之\*<sup>1</sup>、志水元亨\*<sup>2</sup>、平塚宣博\*<sup>2</sup>、湯田直樹\*<sup>2</sup>、松崎芙美子\*<sup>2</sup>、廣瀬宣子\*<sup>2</sup>、野中大輔\*<sup>2</sup>

\*<sup>1</sup> 九州大学大学院農学研究科、\*<sup>2</sup> 九州大学大学院生物資源環境科学研究科

Functional genomic studies on *Phanerochaete chrysosporium* for systematic determination of lignin degradation mechanisms.

Hiroyuki Wariishi, Motoyuki Shimizu, Nobuhiro Hiratsuka, Naoki Yuda, Fumiko Matsuzaki, Noriko Hirose, Daisuke Nonaka

Faculty of Agriculture, Kyushu University

Abstract: To better understand mechanisms involved in fungal ability to degrade lignin and a wide variety of aromatic compounds, systemic analysis on cellular mechanisms is believed to be projected. Functional genomics seems to be a starting point for such studies. In the present study, recent situations for fungal genomic research will be briefly summarized. Furthermore, our recent data on genome annotation of *Phanerochaete chrysosporium* will also be discussed.

2003-207

耐塩性白色腐朽菌 MG-60 株の産生するマンガンペルオキシダーゼの発現特性(2)

大黒千映子\*<sup>1</sup>、須原弘登\*<sup>2</sup>、堤 祐司\*<sup>3</sup>、近藤隆一郎\*<sup>3</sup>

\*<sup>1</sup> 九州大学大学院生物資源環境科学研究科、\*<sup>2</sup> 有明工業高等専門学校、\*<sup>3</sup> 九州大学大学院農学研

## 究院

Characterization and expression of manganese peroxidase produced by halotolerant white-rot fungus *Phlebia* sp. Mg-60. (2),

Chieko Daikoku<sup>\*1</sup>, Hiroto Suhara<sup>\*2</sup>, Yuji Tsutsumi,<sup>\*3</sup> Ryuichiro Kondo<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Ariake National College of Technology, <sup>\*3</sup>Faculty of Agriculture, Kyushu University

Abstract: *Phlebia* sp.MG-60 is a ligninolytic basidiomycete isolated from mangrove stands based on its lignin degradative ability. This fungus can grow and exhibit high lignin degrading ability under the culture condition with high salt concentration. In this study, we investigated the production of manganese peroxidase (MnP) by MG-60. When MG-60 was grown in the medium containing 3% sea salts, it showed higher MnP activity than that in the medium without sea salts. MG-60 produced different MnP isoenzymes under the conditions with or without sea salts, and two partial cDNAs encoding MnP isoenzymes were cloned and sequenced. Investigation of the expression of these MnP mRNA levels under different sea salts conditions is now undergoing.

## 2003-208

白色腐朽菌 *Ceriporiopsis subvermispota* の菌体外代謝物 ceriporic acid B の物理化学的性質  
大橋康典、寺西紘子、渡辺崇人、本田与一、渡辺隆司

京都大学木質科学研究所

Physico-chemical properties of ceriporic acid B, an extracellular product by *Ceriporiopsis subvermispota*.

Yasunori Ohashi, Hiroko Teranishi, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Wood Research Institute, Kyoto University

Abstract: *Ceriporiopsis subvermispota* produces alk(en)yl itaconates (ceriporic acids). In the present study, physico-chemical properties of ceriporic acid B were examined. The acid dissociation constants, pKa<sub>1</sub> and pKa<sub>2</sub> of ceriporic acid B determined in H<sub>2</sub>O/EtOH (1:1, v/v) by pH titration were 4.5 and 8.2, lower than those of itaconic acid (3.6 and 5.0). This result suggests that carboxylic structures were stabilized by a long side chain of ceriporic acid B. Ceriporic acid B strongly inhibited reduction of Fe(III) by L-cysteine. The inhibitory effects were suppressed by chelators such as NTA and EGTA. These results suggest that ceriporic acid B coordinates to Fe(III) and decreases reactivity of Fe(III) with the reductant.

## 2003-209

白色腐朽菌およびその酵素によるポリアクリル酸の分解

桐原朋子、平井浩文、西田友昭

静岡大学農学部

Biodegradation of polyacrylic acid by white rot fungi and ligninolytic enzymes.

Tomoko Kirihara, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: Super absorbent polymer (SAP), which is a crosslinked polymer of polyacrylic acid (PAA), was solubilized by treatments with white rot fungi and ligninolytic enzymes, manganese peroxidase (MnP) and laccase (Lac), and water-soluble PAAs were detected as metabolites. White rot fungi also degraded PAA and the decrease of Mw of PAA was enhanced under LN culture without glucose. Furthermore, the degradation of PAA by MnP and Lac was observed. These results suggest that white rot fungi and ligninolytic enzymes can degrade PAA and have potential applications to decrease environmental levels of water-soluble polymers.

2003-210

白色腐朽菌の産生する酵素による塩素化芳香族化合物の脱塩素について

若月亜希子、平井浩文、西田友昭

静岡大学農学部

Dechlorination of polychlorinated aromatic compounds by enzymes from white-rot fungi

Akiko Wakatsuki, Hirofumi Hirai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: Ligninolytic enzymes from white-rot fungi, manganese peroxidase (MnP), laccase (Lac), and lignin peroxidase (LiP), were used in an attempt to treat methoxychlor (MC), a chemical widely used as a pesticide and an environmental contaminant. MC was converted into methoxychlor olefin (MCO) and 4,4'-dimethoxybenzophenone by MnP or laccase treatment. These results indicate that ligninolytic enzymes from white-rot fungi can catalyze the oxidative dechlorination of MC. The culture fluids from various white-rot fungi decreased 2,4,8-trichlorodibenzofuran (TCDF) by 20-40% after a 24-h treatment. Most of TCDF was dechlorinated and polymerized by the culture fluids. In fact, the dechlorinase was separated with anion-exchange chromatography from the culture fluid inoculated with *P. sordida* YK-624. These results suggest that white-rot fungi secrete hydrolytic dechlorinase, and that the dechlorinase eliminates Cl ion from TCDF and inserts hydroxyl group to TCDF, and that the metabolites which contain hydroxyl group would be oxidized by phenol oxidase, and then polymerized.

2003-211

新規塩素化ダイオキシン分解微生物の分解機能に関する研究(II)

中村雅哉<sup>\*1</sup>、菱山正二郎<sup>\*1</sup>、大塚祐一郎<sup>\*2</sup>、片山義博<sup>\*2</sup>、保科定頼<sup>\*3</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 東京農工大学大学院 BASE、<sup>\*3</sup> 慈恵医科大学

Screening and functional analysis of chlorinated dibenzo-p-dioxin degrading microorganisms by dioxin-like assay substrate.

Masaya Nakamura<sup>\*1</sup>, Shojiro Hishiyama<sup>\*1</sup>, Yuichiro Otsuka<sup>\*2</sup>, Yoshihiro Katayama<sup>\*2</sup>, Sadayori Hoshina<sup>\*3</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, <sup>\*2</sup>Graduate School of Bio-application and System Engineering, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Jikei University School of Medicine

Abstract: We developed a fluorometric assay method for rapid and sensitive evaluation of dioxin degrading capacity by microorganisms. The dioxin-like substrates for fluorometric assay of dioxin degrading microorganisms were synthesized with the conjugation of chlorobenzenes and fluorescence substrate. Cleavage of the ether bridge in these assay substrates would yield the highly fluorescent products. *Bacillus midousuji* SB2B-J2 was isolated from the compost in Osaka by professor Hoshina. The isolated bacterium could degrade chlorinated dibenzo-p-dioxins in the fly ash. The capability of this bacterium for dioxin degradation was analyzed by using the dioxin-like assay substrates biochemically. During incubation of the bacterium with the assay substrates, fluorescence based on the cleavage of the dioxin ring was detected. The activity for the cleavage of the ether bridge in dioxin ring was detected in a membrane fraction of cell free extract from *B. midousuji* SH2B-J2.

2003-212

白色腐朽菌によるダイオキシン汚染土壌の処理

平林徹也<sup>\*1</sup>、迫田江美乃<sup>\*1</sup>、城村真衣<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院

Treatment of polychlorinated dioxin-polluted soil by white-rot fungi.

Tetsuya Hirabayashi<sup>\*1</sup>, Emino Sakoda<sup>\*1</sup>, Mai Jomura<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Graduate School of Agriculture, Kyushu University

Abstract: When dioxin-polluted soil was treated by *Ceriporia lacerate* MZ-340, no decrease of dioxin, contents of octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF), was observed. However, when dioxin-polluted soil pretreated with HCl was treated by the fungus, the decrease of OCDD and OCDF contents was observed. This result indicated that characteristics of soil components (organic and inorganic state) may affect the degradation activity of the fungus. To establish bioremediation technology to treat dioxin-polluted sludge under sea, 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD) was treated by white-rot fungi under hypersaline condition. The halotolerant white-rot fungus, *Phlebia* sp. MG-60 was observed to have an ability to degrade 2,7-DCDD under hypersaline condition.

2003-213

多糖加水分解酵素による MWL 抽出残渣の分解挙動 ～Cellulose-Lignin fraction について～  
吉野寛之、廣澤修一、上高原浩、高野俊幸、中坪文明  
京都大学大学院農学研究科

The behavior of degradation of wood meal after extraction of the MWL by carbohydrate-degrading enzymes. -Analysis of cellulose-lignin fraction.

Hiroyuki Furuno, Shuichi Hirosawa, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo  
Graduate School of Agriculture, Kyoto University

Abstract: Cellulase and xylanase were used to investigate the structure of Cellulose-Lignin fraction (CL), which was extracted from wood meal after extraction of the MWL with LiCl/ DMAc. The peaks in the elution curves of CL from UV detector, which was derived from lignin containing component, was almost corresponding to the peaks in the curves of CL from RI detector, which was due to all components. In the both enzyme treatments, the behaviors of main peaks from UV detector were similar to that of main peaks from RI detector. They indicated that lignin was connected sugar component.

2003-214

リグニンの熱分解機構 -生成物の高分子化について-  
中村健史、河本晴雄、坂 志朗  
京都大学大学院エネルギー科学研究科

Polymerization mechanism of lignin during pyrolysis.

Takeshi Nakamura, Haruo Kawamoto, Shiro Saka  
Graduate School of Energy Science, Kyoto University

Abstract: A series of lignin model compounds were pyrolyzed at 250°C for 2 h to investigate the polymerization mechanism of lignin. Two types of the mechanisms were suggested to be involved in the polymerization; one is via radical intermediates formed by dehydrogenation of phenolic hydroxyl group and C $\alpha$ -hydrogen, and the other is via quinone methide-type intermediates. At 250°C, the latter quinone methide mechanism was dominant and phenolic unit had much higher reactivity than the corresponding non-phenolic one. Furthermore, C $\beta$  in vinylguaiacol was found to have higher reactivity than the aromatic ring in their nucleophilic attack to the quinone methide-type of intermediate.

2003-215

## 熱分解-トリメチルシリル化による広葉樹リグニンの分析

黒田健一、中川明子

筑波大学農林工学系

Analysis of hardwood lignins by pyrolysis-trimethylsilylation.

Ken-ichi Kuroda, Akiko Nakagawa-izumi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Pyrolysis of softwood lignins in the presence of *N,O*-bis(trimethyl-silyl)trifluoroacetamide (pyrolysis-trimethylsilylation, BSTFA/Py) provides coniferyl alcohol and aldehyde trimethylsilyl (TMS) ethers stemming from both terminal phenylglycerol moieties and cinnamyl end-groups. To deep the BSTFA/Py chemistry of lignin, this method was applied to hardwood lignins. The results with syringyl dehydrogenative polymers and a tochinoki milled wood lignin showed that BSTFA/Py provides sinapyl alcohol and aldehyde TMS ethers, with high sensitivity. The yield ratios of sinapyl to coniferyl alcohol TMS ethers (SA/CA) were determined with hardwood type lignins. Most of the lignins showed good correlation between the SA/CA ratios and the yield ratios of syringaldehyde to vanillin (S/V) by nitrobenzene oxidation. Kenaf bast and some hardwood lignins showed rather lower SA/CA ratios than expected from their S/V ratios.

2003-216

## シダおよびコケ植物に存在するリグニンの分析的熱分解法による解析

中川明子<sup>\*1</sup>、松本定<sup>\*2</sup>、樋口正信<sup>\*2</sup>、石井 忠<sup>\*3</sup>、黒田健一<sup>\*1</sup>

<sup>\*1</sup> 筑波大学農林工学系、<sup>\*2</sup> 国立科学博物館、<sup>\*3</sup> 森林総合研究所

Characterization of fern (Pteridophytes) and moss (Bryophytes) *in situ* lignins by analytical pyrolysis.

Akiko Nakagawa-izumi<sup>\*1</sup>, Sadamu Matsumoto<sup>\*2</sup>, Masanobu Higuchi<sup>\*2</sup>, Tadashi Ishii<sup>\*3</sup>, Ken-ichi Kuroda<sup>\*1</sup>

<sup>\*1</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba, <sup>\*2</sup>The National Science Museum, <sup>\*3</sup>Forestry and Forest Products Research Institute

Abstract: Nine ferns and 10 mosses were analyzed by pyrolysis-trimethylsilylation (TMS-Py) and pyrolysis-mass spectrometry (Py-MS). In TMS-Py, coniferyl alcohol derivative (CA) was detected from an ferns samples, and sinapyl alcohol derivative (SA) was detected only from Iwahiba (*Selaginella tamariscina*). Iwahiba, Haiboragoke (*Crepidomanes birmanicum*) and Matsubaran (*Psilotum mudum*) provided the CA peak distinctly. In Py-MS of these ferns, ions derived from lignin were detected. In TMS-Py of mosses, a trace amount of CA was detected from Aohaigoke (*Rhynchostegium riparioides*), Futoryuubigoke (*Hylocomium brevirostre*) and Kumonosugoke (*Pallavicinia longispina*). Oomizugoke provided trace amounts of CA and SA.

2003-217

## 種々のアルカリ条件下でのパルプ処理における過酸化水素の役割

友田生織、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

The role of hydrogen peroxide during pulp treatment under several alkali conditions.

Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Hydrogen peroxide bleaching is important in non-chlorine bleaching. However, there are many unknown parts in the role of hydrogen peroxide during pulp bleaching. We have shown increase of vanillin yield that was produced by nitrobenzene oxidation, after hydrogen peroxide treatment of oxygen bleached kraft pulp. We applied kappa number method to hydrogen peroxide treated pulps and treatment liquors to analyze lignin and other permanganate consuming compounds. The data

show that hydrogen peroxide has at least two different roles. Ionized/non-ionized hydrogen peroxide can remove pulp kappa number. Ionized hydrogen peroxide has another hidden role that is against alkali-promoted creation of permanganate consuming substances.

2003-218

Comparison of different treatment sequences of kenaf bast fiber for high viscosity pulp.

Sherif Keshk<sup>\*1</sup>, Wiwin Suwinarti<sup>\*2</sup>, Kazuhiko Sameshima<sup>\*2</sup>

<sup>\*1</sup>Ain-Shams University, <sup>\*2</sup> Faculty of Agriculture, Kochi University

Abstract: This paper explores the production of high viscosity pulp from kenaf bast by using three different treatment sequences (A, B and C). The chemical compositions (cellulose, hemicellulose and lignin contents) and viscosity from these treatments were determined. Yield and kappa number of sample B are the highest one, while sample A shows the highest viscosity or degree of polymerization rather than those from B and C samples. Furthermore, the pulp extracted from these treatments was investigated by vibration spectroscopy and the structure differences found were validated by X-ray diffractometry. The FT-IR spectra of all pulp samples reveal the same chain conformation but different in mean hydrogen bonding, relative ether linkage and crystallinity index. From X-ray diffractograms of extracted pulp, the crystallinity index percentages for A, B and C samples were 77.0, 73.4 and 75.0 that confirm the FT-IR results.

2003-219

広葉樹材のポリサルファイド・アントラキノン添加等温蒸解の最適方法

横山朝哉<sup>\*1</sup>、大井 洋<sup>\*1</sup>、中俣恵一<sup>\*2</sup>

<sup>\*1</sup> 筑波大学農林工学系、<sup>\*2</sup> 北越製紙株式会社技術開発部

The most suitable method of polysulfide-anthraquinone isothermal cooking of hardwood.

Tomoya Yokoyama<sup>\*1</sup>, Hiroshi Ohi<sup>\*1</sup>, Keiichi Nakamata<sup>\*2</sup>

<sup>\*1</sup>Institute of Agricultural and Forest Engineering, University of Tsukuba, <sup>\*2</sup>Technical and Development Division, Hokuetsu Paper Mills, Ltd.

Abstract: The improvement of pulp yield using a hardwood raw material, *Acacia mearnsii*, was successful in the optimization of isothermal cooking (ITC) parameters. The addition of both polysulfide (PS) and anthraquinone (AQ) gave an about 4.5-5% higher yield at kappa number of about 17. The highest yield was obtained when 70% of total active alkali and 100% of both PS and AQ were added at the beginning, and consecutively, the black liquor was exchanged with fresh white liquor containing the remaining 30% of total active alkali just after cooking temperature reached 135°C. A mill scale trial was conducted to examine the effect of PS and AQ in a practical pulp mill. Pulp samples were collected from a continuous cooking digester not only when the PS-AQ ITC was operating but also when the simple kraft cooking was operating. Kappa number, xylose to glucose ratio, brightness and viscosity of pulps were compared between the PS-AQ ITC and with the simple kraft cooking.

2003-220

クラフトパルプ漂白工場のクロロホルムに関する環境観点からの評価

中俣恵一<sup>\*1</sup>、本永洋一<sup>\*2</sup>、大井 洋<sup>\*3</sup>

<sup>\*1</sup> 北越製紙株式会社技術開発部、<sup>\*2</sup> 北越製紙株式会社新潟工場、<sup>\*3</sup> 筑波大学農林工学系

Evaluation of chloroform formed in processes of a kraft pulp bleaching mill from the environmental aspect.

Keiichi Nakamata<sup>\*1\*2</sup>, Youichi Motoe<sup>\*1\*2</sup>, Hiroshi Ohi<sup>\*3</sup>

<sup>\*1\*2</sup>Hokuetsu Paper Mills, Ltd., <sup>\*3</sup>Institute of Agricultural & Forest Engineering, University of Tsukuba

In the mill scale investigation, it was clarified that the chloroform formation in chlorine bleaching of hardwood oxygen-delignified kraft pulp (LOKP) was approximated 170 g/ pulp ton, approximated 90% of which was discharged to bleaching effluents, and that chloroform in the effluents was un-degradable in the activated sludge treatment. More than 97% of the chloroform was discharged to the air by volatilization. It is suggested that chloroform formation in Japanese LOKP bleaching mills can be decreased to 16–42 t per one year for 8000000 t of pulp production by chlorine dioxide (ECF) bleaching.

2003–221

天然から選抜した白色腐朽菌を用いた数種の環境ホルモンのバイオレメディエーション  
木村圭助、松尾保洋、小堀敦子、鷹見純子、伊藤和貴、橘 燦郎  
愛媛大学農学部

Bioremediation of environmental hormones by white-rot fungi screened from the nature.  
Keisuke Kimura, Yasuhiro Matsuo, Atsuko Kobori, Junko Takami, Kazutaka Ito, Sanrou Tachibana  
Faculty of Agriculture, Ehime University

Abstract: To obtain the basic information for purification of environmental hormones by bioremediation with screened fungi from the nature, degradation of two kinds of environmental hormones by fungus PL1 having ability for degradation of dioxins and with a crude enzyme from the fungus PL1 was tried in this research.  $p,p'$ -DDT and Lindane were used as substrates. About 72% and 64% of  $p,p'$ -DDT and Lindane were degraded by the fungus in a liquid medium for 30 days, respectively. Furthermore, about 75% and 51% of  $p,p'$ -DDT and Lindane were degraded with the crude enzymes from the fungus in a liquid medium for 48 hours, respectively. From the results obtained here, it is suggested that bioremediation of environmental hormones like  $p,p'$ -DDT and Lindane by screened fungi from the nature is possible.

2003–P01

キノコ子実体フェノール性物質に関する研究  
萱 祐絵<sup>\*1</sup>、福島和彦<sup>\*1</sup>、安田征市<sup>\*1</sup>、松井直之<sup>\*2</sup>、平山秀樹<sup>\*3</sup>、重本 桂<sup>\*3</sup>  
<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>日本生薬株式会社

Phenolic constituents in the mushroom fruit bodies.  
Sachie Kaya<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Seiichi Yasuda<sup>\*1</sup>, Naoyuki Matsui<sup>\*2</sup>, Hideki Hirayama<sup>\*3</sup>, Katsura Shigemoto<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya, <sup>\*2</sup>Forestry and Forest Products Research Institute, <sup>\*3</sup>Nihon-Syoyaku Co. Ltd.

Abstract: Thioacidolysis and alkaline nitrobenzene oxidation showed that typical lignin structures were not contained in the mushroom fruit bodies of *Phellinus linteus* and *Agaricus brazei* and the sclerotium of *Inonotus obliquus*. Vanillic and syringic acids were detected in the products of alkaline hydrolysis of *Inonotus obliquus*, but could not be obtained from the other mushrooms. The antioxidant activities of ethanol extracts from mushrooms and sclerotium were measured by the inhibition of lipid peroxidation (ferric thiocyanate) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging methods. The extract of *Phellinus linteus* had high activity as DPPH scavenger. and the extracts except for *Agaricus brazei* had high activities on ferric thiocyanate method.

2003–P02

細胞壁中における高分子リグニン形成過程の電顕観察  
寺島典二<sup>\*1</sup>、栗野達也<sup>\*2</sup>、高部圭司<sup>\*3</sup>  
<sup>\*1</sup>名古屋大学、<sup>\*2</sup>SLU, Sweden、<sup>\*3</sup>京都大学大学院農学研究科

Formation of macromolecular lignin in the cell wall as observed by electron microscope.

Noritsugu Terashima<sup>\*1</sup>, Tatsuya Awano<sup>\*2</sup> and Keiji Takabe<sup>\*3</sup>

<sup>\*1</sup>Professor Emeritus, Nagoya University, <sup>\*2</sup>Umea Plant Science Centre, Dept. of Forest Genetics and Plant Physiology, SLU, Sweden, <sup>\*3</sup>Graduate School of Agriculture, Kyoto University

Abstract: In the lignifying process of xylem cell walls, macromolecular lignin is formed by polymerization of monolignols on the pectic substances, hemicelluloses and cellulose microfibrils that have deposited prior to the start of lignification. Observation of lignifying primary and secondary walls of tracheid of ginkgo by electron microscope gave images that macromolecular lignin or lignin-hemicellulose complexes are formed as modules of similar size surrounding the cellulose microfibrils. This suggests that the starting points of polymerization of lignols are distributed along the cellulose microfibrils at almost regular intervals, 19–26 nm in the outer layer of secondary wall (S1) and 15–18 nm in the middle layer of secondary wall (S2).

2003-P03

*Eucommia ulmoides* Oliv.における 8-O-4' ネオリグナン類の生合成と立体化学:コニフェリルアルコールとシナピルアルコールとの交叉カップリング

ラウリット ナタヤ、片山健至、鈴木利貞

香川大学農学部

Biosynthesis and stereochemistry of 8-O-4' neolignans in *Eucommia ulmoides* Oliv.: cross coupling of coniferyl alcohol and sinapyl alcohol.

Nattaya Lourith, Takeshi Katayama, Toshisada Suzuki

Abstract: Four 8-O-4' neolignans, guaiacylglycerol-8-O-4'-(coniferyl alcohol) ether (GGCE); guaiacylglycerol-8-O-4'-(sinapyl alcohol) ether (GGSE), syringylglycerol-8-O-4'-(sinapyl alcohol) ether (SGSE) and syringylglycerol-8-O-4'-(coniferyl alcohol) ether (SGCE) were synthesized. Their diastereomers were separated and elucidated by means of NMR and C<sub>7</sub>-Hs of *threo* isomers have larger coupling constant than those of *erythro* isomer. To examine their biosynthesis, feeding experiments of *p*-[8-<sup>14</sup>C]hydroxycinnamic acid and a mixture of [8-<sup>14</sup>C]coniferyl alcohol (CA) and [8-<sup>14</sup>C]sinapyl alcohol (SA) into young shoots of *E. ulmoides* were undertaken. The [<sup>14</sup>C]GGCE incorporated from the former precursor was found as aglycone from stems with the *erythro*/*threo* ratio, 1: 1. Its glucosides from the mixed precursors were also found in stems and leaves. Incubation of a mixture of [8-<sup>14</sup>C]CA and [8-<sup>14</sup>C]SA with cell-free extracts from *E. ulmoides* showed the formation of not only [<sup>14</sup>C]GGCE but also [<sup>14</sup>C]GGSE.

2003-P04

白色腐朽菌ミノタケ由来リグニンペルオキシダーゼの反応特性 -*P. chrysosporium* 由来 LiP H8 との特性比較-

三木佑太<sup>\*1</sup>、割石博之<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院

Characterization of lignin peroxidase from the white-rot basidiomycete *Trametes cervina*.

-Comparison with LiPH8 from *Phanerochaete chrysosporium*.

Yuta Miki, Hiroyuki Wariishi

Faculty of Agriculture, Kyushu University

Abstract: A possible site of veratryl alcohol (VA) oxidation in lignin peroxidase of *Trametes cervina* (TcLiP) was investigated. Reactivities of *N*-Bromosuccinimide (NBS) modified TcLiP and LiPH8 of *Phanerochaete chrysosporium* against VA were determined. VA oxidation activity of NBS-LiPH8 decreased with NBS concentration-dependent manner. On the other hand, the activity of TcLiP was not interfered by the NBS modification. Thus, the VA oxidation site of TcLiP is most

likely other amino acid residue than Trp. From 3-D modeling of TcLiP, His170 is the candidate for VA oxidation site.

2003-P05

白色腐朽担子菌による Polychlorinated biphenyls の分解

北野史郎<sup>\*1</sup>、森 智夫<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院

Degradation of polychlorinated biphenyls by white-rot fungi.

Shiro Kitano, Toshio Mori, Ryuichiro Kondo

Graduate School of Agriculture, Kyushu University

Abstract: We have demonstrated that white-rot fungus, *Phlebia lindtneri* has abilities to oxidize many xenobiotic compounds, such as polyaromatic hydrocarbons and dioxins. And, we have screened white-rot fungi for the degradation ability of 4,4'-dichlorobiphenyl (4,4'-DCB). As a result the strain MZ-142 was selected from twenty strains. In this study, the degradation of biphenyl (BPE) and 4,4'-DCB by *Phlebia lindtneri* and the strain MZ-142 was examined and the mechanisms involved in initial hydroxylation were characterized. One of the metabolites, 2-hydroxy-4,4'-dichlorobiphenyl from 4,4'-DCB was identified in the culture of the both fungi during 9-day incubation. When BPE and 4,4'-DCB were treated by the strain MZ-142, the decrease of 4,4'-DCB (50%) was much higher than that of BPE (25%) in the culture of potato dextrose medium. Two kinds of metabolites, 2-hydroxy-4,4'-dichlorobiphenyl and 3-hydroxy-3,4'-dichlorobiphenyl were identified from 4,4'-DCB by the strain MZ-142. The quantity of each products was drastically dependent on the culture medium conditions. Based on these results, the specific pathway for the introduction of hydroxyl group into 4,4'-DCB by the strain MZ-142 was proposed.

2003-P06

<sup>14</sup>C-コニフェリンを用いたヒヤクニチソウ管状要素におけるリグニンの標識

梶田真也<sup>\*1</sup>、辻 幸子<sup>\*2</sup>、福島和彦<sup>\*2</sup>、諸星紀幸<sup>\*1</sup>、片山義博<sup>\*1</sup>、Alain M. Boudet<sup>\*3</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>名古屋大学大学院生命農学研究科、<sup>\*3</sup>UPS-CNRS, France

Radiolabeling of lignin in secondary cell wall of *Zinnia* tracheary elements.

Shinya Kajita<sup>\*1</sup>, Yukiko Tsuji<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*2</sup>, Noriyuki Morohoshi<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Alain M. Boudet<sup>\*3</sup>

<sup>\*1</sup>Graduate school of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*3</sup>UMR CNRS, France

Abstract: In order to identify the protein(s) that play important roles in inhibition and/or proceeding of lignin polymerization in secondary wall, novel experimental system have been constructed with tracheary elements (TEs) of *Zinnia elegans*. In this system, lignin in the secondary wall of the *Zinnia* TEs can be labeled with <sup>14</sup>C that derived from administered coniferin-[beta-<sup>14</sup>C]. The incorporated radioactivity can be estimated after thin layer chromatographic separation of thioacidolysis main monomers that recovered from <sup>14</sup>C-labeled lignin in TEs. This experimental system is useful for quantitative analysis of lignin and lignification with a small amount of cell walls.

2003-P07

キタカミハクヨウ ferulate-5-hydroxylase 遺伝子の解析

中田陽子、村上義彦、川合伸也

東京農工大学農学部

Cloning and characterization of ferulate-5-hydroxylase gene from *Populus kitakamiensis*.

Yoko Nakata, Yoshihiko Murakami, Shinya Kawai

Graduate School of Agriculture, Tokyo University of Agriculture and Technology

Abstract: Ferulate 5-hydroxylase (FA5H) belongs to the family of cytochrome P450-dependent mono-oxygenases. We isolated FA5H cDNA from hybrid aspen, *Populus kitakamiensis*, it was very similar to that of *Populus trichocalpa*. We prepared microsomal fraction from the transformed yeast harboring FA5H expression vector, and measured its FA5H enzyme activity. Further, we constructed expression vector for fused protein of FA5H and NADPH-cytochrome P450 oxidoreductase to increase FA5H activity.

2003-P08

赤色酵母由来 PAL 遺伝子を用いた新規薬剤耐性植物の作出

丸山 亮、織茂良和、赤松智隆、川合伸也

東京農工大学農学部

Molecular breeding of a novel herbicide resistant plant by using phenylalanine ammonia-lyase gene from *Rodotorula rubla*.

Ryo Maruyama, Kazuyoshi Orimo, Tomotaka Akamatsu, Shinya Kawai

Graduate School of Agriculture, Tokyo University of Agriculture and Technology

Abstract: Phenylalanine ammonia-lyase (PAL) is a key enzyme in the secondary metabolism of higher plants. Genes encoding PAL have been identified in yeasts and plants. Amino acid sequences between plant PALs and yeast PALs have low homology and their sensitivity to aminoxy compounds, inhibitors of PAL, are very different. Yeast PALs are less sensitive. We cloned a PAL gene from *Rodotorula rubla* (RRPAL) and constructed expression vector for fused protein in *E. coli*. Further, we introduced the gene into tobacco plants. Heterogeneous expressed fused protein in *E. coli* had PAL activity and RRPAL gene were transcribed in transgenic tobacco plants.

2003-P09

ニセアカシア4CL 遺伝子の単離と機能解析

西口朋子<sup>\*1</sup>、西田友昭<sup>\*2</sup>、堤 祐司<sup>\*3</sup>、近藤隆一郎<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>静岡大学農学部、<sup>\*3</sup>九州大学大学院農学研究院

4-Coumarate : CoA ligase in *Robinia pseudoacacia*: cDNA structures.

Tomoko Nishiguchi<sup>\*1</sup>, Tomoaki Nishida<sup>\*2</sup>, Yuji Tsutsumi<sup>\*3</sup>, Ryuichiro Kondo<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Faculty of Agriculture, Shizuoka University, <sup>\*3</sup> Graduate School of Agriculture, Kyushu University

Abstract: 4-Coumarate CoA ligase (4CL) is a key enzyme in general phenylpropanoid pathway and is believed to catalyze the activation of 4-hydroxy cinnamate analogues, however, studies indicated that most of 4CL isoenzymes are not active for sinapate. On the other hand, we reported that 4CL isoenzyme in *Robinia pseudoacacia* utilized sinapate as substrate. In this study, three 4CL cDNAs were isolated from *R. pseudoacacia* and deduced amino acid sequencess were compared to Gm4CL1 which has a catalytic activity for sinapate. A differential pattern of transcription of each Robinia 4CL gene in various organs was also investigated.

2003-P10

ダイオキシン分解菌から抽出した粗酵素による Polychlorinated Biphenyls (PCB) の分解

松尾保洋、三好進祐、木村圭助、伊藤和貴、橘 燦郎

愛媛大学農学部

Biodegradation of polychlorinated biphenyls with a crude enzyme from fungi having ability for degradation of dioxins.

Yasuhiro Matsuo, Shinsuke Miyoshi, Keisuke Kimura, Kazutaka Ito, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Degradations of 3,3',4,4'-tetrachlorobiphenyl(TCB) with a crude enzyme from fungus PL1 was conducted in this research to obtain basic information for purification of polychlorinated biphenyls by bioremediation with fungi screened from the nature. About 20% of TCB was degraded for 72 hours with an immobilized crude enzyme from fungus PL1 in a liquid medium. Furthermore, about 60% of TCB was degraded for 30 days with the immobilized crude enzyme from the fungus in a soil. From the results obtained here, it is suggested that bioremediation of polychlorinated biphenyls by screened fungi from the nature is possible.

2003-P11

アメリカヤマナラシにおけるシナピルアルコールデヒドロゲナーゼ(SAD)の免疫局在

西原 猛、大室義人、高部圭司、藤田 稔

京都大学大学院農学研究科

Immunolocalization of sinapyl alcohol dehydrogenase (SAD) in *Populus tremuloides*.

Takeshi Nishihara, Yoshihito Omuro, Keiji Takabe, Minoru Fujita

Graduate School of Agriculture, Kyoto University

Abstract: To study biosynthesis of monolignols, it is necessary to know how expression and function of enzymes that are involved in the cinnamic acid pathway are regulated. Sinapyl alcohol dehydrogenase (SAD) has been reported to catalyze the reductive reaction specifically from sinapaldehyde to sinapyl alcohol. We therefore tried to investigate the distribution of SAD in quaking aspen (*Populus tremuloides*) by immunolabeling. The labeling was mainly observed on cytosol of the differentiating xylem cells. It indicates that sinapyl alcohol, which is the last product of monolignol, is synthesized in cytosol.

2003-P12

HBS パルプ化におけるリグニンモデル化合物の反応(2)

高森ひとみ、岸本崇生、浦木康光、生方 信

北海道大学大学院農学研究科

Reaction of lignin model compounds during high-boiling solvent pulping. (2).

Hitomi Takamori, Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: Reaction of  $\beta-\beta$ ,  $\beta-5$  and  $\beta-1$  types of dimeric lignin model compounds were studied in 70wt% aq 1,4-butanediol solution at 180°C to investigate the delignification mechanism under HBS (high-boiling solvent) pulping conditions. Reaction products were separated by TLC, and analyzed by HPLC, GPC and NMR. As a result,  $\beta-\beta$  and  $\beta-5$  type of lignin model compounds was stable, while  $\beta-1$  type is unstable and converted into stilbene. These results are in agreement with those of lignin sample.

2003-P13

HBS パルプ化におけるリグニンの構造変化 -チオアシドリシス及び NMR による解析(2)-

植木飛鳥<sup>\*1</sup>、齊藤香織<sup>\*2</sup>、福島和彦<sup>\*2</sup>、岸本崇生<sup>\*1</sup>、浦木康光<sup>\*1</sup>、生方 信<sup>\*1</sup>

<sup>\*1</sup>北海道大学大学院農学研究科、<sup>\*2</sup>名古屋大学大学院生命農学研究科、

Structural changes in lignin during HBS pulping. -Thioacidolysis and NMR analysis. (2).

Asuka Ueki<sup>\*1</sup>, Kaori Saito<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*2</sup>, Takao Kishimoto<sup>\*1</sup>, Yasumitsu Uraki<sup>\*1</sup>, Makoto Ubukata<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, <sup>\*2</sup>Graduate School of Bioagricultural Science, Nagoya University

Abstract: Structural changes in lignin during high-boiling solvent (HBS) pulping were investigated by thioacidolysis and HMQC spectra. The decrease in the content of  $\beta$ -O-4 structures was confirmed by thioacidolysis. Introduction of 1,4-butanediol into  $\alpha$ -position of  $\beta$ -O-4 moiety was observed by HMQC spectra. The reactivity of syringyl type  $\beta$ -O-4 structure was slightly higher than that of guaiacyl type structure. The higher reactivity of syringyl type was also observed with  $\beta$ -1 structure. The  $\beta$ -1 substructure was unstable under HBS pulping conditions. Formation of stilbene structure was obvious in HMQC spectra.

2003-P14

広葉樹クラフトパルプのキシロース・グルコース比による収率予測(2)

児安 崇、横山朝哉、大井 洋

筑波大学農林工学系

Prediction of pulp yields using xylose/glucose ratios of hardwood kraft pulp (2)

Takashi Koyasu, Tomoya Yokoyama, Hiroshi Ohi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Alkali pulps were acid-hydrolyzed according to TAPPI method T249 cm-85 using 3ml of 72% sulfuric acid for 0.3g of pulp. However, it was shown that the hydrolysis is insufficient. The method was modified by the use of 6ml of 72% sulfuric acid for 0.3g of pulp and the prolonged reaction time; 2.5 hr for the primary hydrolysis. After the modified hydrolysis, the xylose ratios to glucose were obtained by gas chromatography of the alditol acetates and high performance liquid chromatography of the aldoses. Carbohydrates analysis of hardwood alkali pulps was applied to prediction of pulp yields obtained by modified polysulfide-anthraquinone pulping.

2003-P15

直接導入法によるDHPの質量分析

黒田健一、中川明子

筑波大学農林工学系

Mass spectrometry of dehydrogenation polymer of coniferyl alcohol with a direct sample inlet.

Ken-ichi Kuroda and Akiko Nakagawa-jzumi

Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: A 25% tetramethylammonium hydroxide (TMAH) methanolic solution containing a bulk dehydrogenation polymer of coniferyl alcohol (DHP) was introduced into a mass spectrometer with a direct injection probe. Mass analysis employed a rate of 40°C/m, probe temperature 50 to 400°C, and a 70eV ionization voltage. The mass spectrum, time integrated over scans 526-556 (225-235°C), showed a high abundance of the m/z 181 base ion of 1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane (**2**) stemming from guaiacylglycerol moieties involved in  $\beta$ -aryl ether linkages, and a low abundance of the m/z 386 ion, the molecular ion of pinosresinol dimethyl ether (**4**), and the m/z 370 ion, the TMAH thermochemolysis product **3** of dehydrodiconiferyl alcohol, were observed. The mass spectrum, time integrated over scans 602-639 (250-264°C), showed a high abundance of the m/z 181 and 370 ions. The m/z 181 ion was observed ranging scans 180 from 1000 (110-370°C). The 208 m/z molecular ion of coniferyl alcohol dimethyl ether (**1**) was observed in the spectrum integrated over scans 180-660 (110-270°C). The mass spectrum, time integrated over scans 180-1000 (110-370°C), was similar to the 315°C pyrolysis mass spectrum of the DHP. TMAH thermochemolysis-gas chromatography (-mass spectrometry) of the DHP revealed GC(-MS) signals corresponding to **1-4**.

2003-P16

TMSiIによるリグニン  $\beta$ -O-4の開裂機構の検討 - $^{13}\text{C}$ -標識 NMR 示差スペクトル分析法を用いて  
堀啓映子<sup>\*1</sup>、新谷博幸<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、寺島典二<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 名古屋大学

Studies on  $\beta$ -O-4 cleavage by TMSiI treatment: using for  $^{13}\text{C}$ -enriched differential NMR spectroscopy.

Keko Hori<sup>\*1</sup>, Hiroyuki Shintani<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup> Professor emeritus, Nagoya University

Abstract: Trimethylsilyl iodide (TMSiI) is known to cleave  $\beta$ -ether bonds selectively under very mild reaction condition. But side reactions, such as iodination and polymerization, were occurred by long time treatment.  $^{13}\text{C}$ -enriched and unenriched DHPs were synthesized and their differential NMR spectra were measured before and after TMSiI treatment in NMR tube. The differential NMR spectra showed some changes indicating decreased amount of  $\beta$ -O-4, coniferyl alcohol and coniferaldehyde structures and appearance of one signal after TMSiI treatment. However, total peak area was also decreased after TMSiI treatment, probably because of the precipitation of reaction products by water addition for stopping the reaction. Water addition might cause some side reactions.

2003-P17

単離過程におけるリグニン構造の変化とその要因について -磨砕処理の影響-

藤本 文、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Changes of lignin structures during the process of MWL isolation.

Aya Fujimoto, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Milled wood lignin (MWL) is a lignin sample that reflects the characters of protolignin in wood, although it is well recognized that MWL represents only a part of protolignin and it can never be free from structural modification during its isolation procedure. The structures of MWL are featured by such artificial changes and native differences, in addition to general characteristics as lignin. In this paper, we aimed to distinguish the nature of lignin after milling from its original nature by the use of alkaline nitrobenzene oxidation method and determination of methoxyl groups in order to understand the essential characters of MWL and lignin in wood and milled wood. From the results of S/V ratios and the yields of main oxidation products by alkaline nitrobenzene oxidation, it was suggested that the nucleic structural differences in crude MWLs might reflect mainly the native differences in lignin.

2003-P18

アルカリ性酸素脱リグニン段排液リグニンの土壌改良剤としての性状

王東香、勝亦京子、飯塚堯介

東京大学大学院農学生命科学研究科

Characterization of lignin fractions in alkaline-oxygen stage waste liquor as soil conditioning agent.

Dongxang Wang, Kyoko S. Katsumata, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo,

Abstract: In most of the worlds tropical areas where soil is acidic, Al toxicity is a serious problem which limits the productivity of crop plants. The possibility of utilizing lignin fragments from alkaline oxygen delignification stage waste liquor generated from paper mill as soil conditioning agent was studied. Alkaline oxygen delignification stage waste liquor was subjected to Gel Filtration

Chromatography (GFC) and separated into four fractions (F1, F2, F3, and F4). Then, these four fractions were used for plant experiment. The results indicated lignin fragments are capable of alleviating the toxicity of Al, providing improved performance of radish root growth. Each fraction showed different performance on removing the Al toxicity, and so the reason for their different behaviors on Al toxicity was also studied.

2003-P19

スギおよびブナの超臨界水処理により得られるリグニン由来物質の GC-MS 分析

江原克信、高田大士、坂 志朗

京都大学大学院エネルギー科学研究科

Gas chromatographic and mass spectrometric (GC-MS) analysis of lignin-derived products from *Cryptomeria japonica* and *Fagus crenata* as treated in supercritical water.

Katsunobu Ehara, Daishi Takada, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: Softwood (*Cryptomeria japonica*) and hardwood (*Fagus crenata*) were treated in supercritical water (380°C, 100MPa) for 8 seconds. The treated woods were fractionated to the water-soluble portion, methanol-soluble portion and methanol-insoluble residues. For the methanol-soluble portion which mainly consists of lignin-derived products, GPC and GC-MS analyses were made to clarify the molecular weight distribution and to identify monomeric products, respectively. GPC analysis revealed that the methanol-soluble portion contains monomeric and some oligomeric products. Nineteen guaiacyl compounds in methanol-soluble portion from softwood, and 15 syringyl compounds in methanol-soluble portion from hardwood were identified by GC-MS analysis. These observations suggested that the lignin-derived products are useful products for substituting the chemicals from fossil resources.

2003-P20

中性抄紙における硫酸リグニン由来のロジンサイズ定着剤の調製とその評価

松下泰幸、岩月亜佑子、安田征市

名古屋大学大学院生命農学研究科

Preparation and evaluation of retention aids for rosin sizes from sulfuric acid lignin in neutral papermaking condition

Yasuyuki Matsushita, Ayuko Iwatsuki and Seiichi Yasuda

Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: Cationic polymers as the retention aids for rosin sizes in neutral papermaking were prepared from sulfuric acid lignin (SAL), one type of acid lignin. To convert SAL to the cationic polymer (MP-SAL), SAL was phenolated followed by the Mannich reaction to introduce the amino groups. In the MP-SAL single system, MP-SAL exhibited high sizing effectiveness in neutral papermaking with the rosin emulsion size. However, MP-SAL showed no sizing effectiveness when soap rosin size was used. In the alum-MP-SAL dual system, alum and MP-SAL, synergistically enhanced the sizing effectiveness in the rosin emulsion sizing at neutral pH.

2003-P21

ヒドロキシプロピル化未漂白パルプより調製したゲルの膨潤挙動

井村 健、浦木康光、岸本崇生、生方 信

北海道大学大学院農学研究科

Swelling behavior of hydroxypropylated unbleached pulp gels.

Takeshi Imura, Yasumitu Uraki, Takao Kishimoto, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: Urethane- and epoxy-types of gels were prepared from hydroxypropylated unbleached acetic acid pulps (HP-AP's) using hexamethylen diisocyanate (HDI) and ethyleneglycol diglycidyl ether (ED) as cross-linkers. The residual lignin content influenced thermoresponse of the gels; the volume-transition temperature of the gel upon heating was lowered by the lignin. The epoxy-type gel from HP-softwood AP showed the volume transition at 38°C, suggesting its possibility as a support in the drug delivery system. In addition, all the gels showed very unique swelling behavior in aqueous solution of cationic surfactants. Although the mechanism have not been clarified yet, the behavior seems to contribute to explore novel utilization of the gels.

2003-P22

リグニンゲルの膨潤と応用

臼倉ゆり子<sup>\*1</sup>、浦木康光<sup>\*1</sup>、岸本崇生<sup>\*1</sup>、生方 信<sup>\*1</sup>、平沖敏文<sup>\*2</sup>、福島和彦<sup>\*3</sup>

<sup>\*1</sup>北海道大学大学院農学研究科、<sup>\*2</sup>北海道大学大学院工学研究科、<sup>\*3</sup>名古屋大学大学院生命農学研究科

Swelling mechanism and application of lignin gel.

Yuriko Usukura<sup>\*1</sup>, Yasumitsu Uraki<sup>\*1</sup>, Takao Kishimoto<sup>\*1</sup>, Makoto Ubukata<sup>\*1</sup>, Toshifumi Hiraoki<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, <sup>\*2</sup>Graduate School of Engineering, Hokkaido University, <sup>\*3</sup>Graduate School of Bioagricultural Science, Nagoya University

Abstract: Lignin-gel was prepared from acetic acid lignin (AL) with polyethylene glycol diglycidyl ether (PE) at a high lignin concentration. This lignin gel was found to swell in aqueous organic solvents. The mobility of the solvated solvent was evaluated from the spin-spin lattice relaxation time ( $T_2$ ) using NMR to clarify the swelling mechanism.  $T_2$  of the solvents decreased with increasing the gel swelling degree. In particular, this tendency of the organic solvent was remarkable. This result suggests that the adsorption of solvent molecules onto gel polymer chain reduces the mobility of the solvent. As one of the applications of lignin gel, we attempted to utilize it as a membrane for solvent separation by pervaporation. As a result, ethanol selectively permeated at the low ethanol concentration, but the selectivity changes at the high concentration.

2003-P23

リグノスルホン酸塩系ポリウレタンゲルの調製と物性

伊藤孝志<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>大妻女子大学

DSC and AFM studies on sodium lignosulfonate-based PU hydrogels.

Takashi Itoh<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui University of Technology, <sup>\*2</sup>Otsuma Women's University

Abstract: Sodium lignosulfonate (LS)-based polyurethane (PU) hydrogels were prepared from LS and hexamethylene diisocyanate (HDI) derivatives. Water content (Wc) of the obtained PU hydrogels was less than 3.0 g g<sup>-1</sup> and NCO/OH ratio was varied from 0.2 to 0.6 mol mol<sup>-1</sup>. Phase transitions of LS and PU hydrogels were measured by differential scanning calorimetry (DSC). From DSC curves, glass transition temperature ( $T_g$ ), melting peak at low temperature ( $T_{ml}$ ) and melting peak at high temperature ( $T_{mh}$ ) were observed. It was also confirmed that there were three kinds of water, non-freezing water, freezing bound water, and freezing water.

2003-P24

アルコリシスリグニン、エチレングリコール及びグリセリンのエステル-カルボン酸誘導体を原料と

## するエポキシ樹脂の合成とその熱的性質

廣瀬重雄<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>

<sup>\*1</sup> 産業技術総合研究所、<sup>\*2</sup> 福井工業大学工学部

Synthesis and thermal properties of epoxy resins from ester-carboxylic acid derivatives of alcoholysis lignin, ethylene glycol and glycerin.

Shigeo Hirose<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>

<sup>\*1</sup> Research Institute of Materials and Chemical Process, AIST, <sup>\*2</sup> Fukui University of Technology

Abstract: Alcoholysis lignin (AL) was dissolved in ethylene glycol (EG) and the obtained mixture was reacted with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (AL-EG polyacid, ALEGPA). Glycerin-polyacid (ALGLYPA) was also prepared from AL and glycerin. The mixture of ALEGPA and ALGLYPA was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ( $[EPOXY]/[AA]$  ratios, mol/mol) was maintained at 1.1. The contents of ALGLYPA in the mixture of ALEGPA and ALGLYPA (ALGLYPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures ( $T_g$ 's) of epoxy resins increased with increasing ALGLYPA contents suggesting that glycerin structure acts as a hard segment in epoxy resin networks. Thermal decomposition temperatures ( $T_d$ 'S) of epoxy resins were almost constant regardless of ALGLYPA contents.

## 2003-P25

### クラフトリグニン及びリグノスルホン酸塩系木粉分散型ポリウレタン複合材料の熱的・機械的性質

栗本幹久<sup>\*1</sup>、藤井博知<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 大妻女子大学

Thermal and mechanical properties of PU composites containing wood powder with sodium lignosulfonate and kraft lignin.

M. Kurimoto<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup> Fukui University of Technology, <sup>\*2</sup> Otsuma Women's University

Abstract: Polyurethane (PU) composites were prepared from ground wood mixed with a kraft lignin (KL)-polyol solution and sodium lignosulfonate (LS)-polyol solution consisting of KL or LS dissolved in polyethylene glycol (PEG-200) triethylene glycol (TEG) and diethylene glycol (DEG). Mechanical and thermal properties of the above composites were studied. Thermal properties of the prepared PU composites were studied by thermogravimetry (TG). Sample weight for TG was ca. 7mg. Mechanical properties of PU composites were studied by compression tests, according to the Japanese Industrial Standard (JIS) A 1408 at room temperature.

## 2003-P26

### 無機粒子分散型クラフトリグニン系ポリウレタンの調製と物性

松村博司<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 大妻女子大学

Mechanical properties of kraft lignin-based PU foams containing inorganic fillers.

Hiroshi Matsumura<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup> Fukui University of Technology, <sup>\*2</sup> Otsuma Women's University

Abstract: Rigid polyurethane (PU) foams were prepared from kraft lignin (KL) which was dissolved in diethylene glycol (DEG), triethylene glycol (TEG) or polyethylene glycol (molecular weight 200: PEG200). The obtained solution containing filler was reacted with isocyanate in the presence of small amounts of silicone surfactant, catalyst and water. Mechanical properties of these

polyurethanes (PU's) were studied by compression tests. It was found that compression strength and compression elasticity of KLPU show maximum values at a certain filler content from 10 to 40%. Compression strength decreased with increasing molecular weight of ethylene glycol.

2003-P27

植物性廃棄物に由来するリグニンの油脂に対する参加防止効果

藤加珠子, 野田博行

生物ラジカル研究所

Antioxidant effect of lignin obtained from botanical wastes.

Kazuko Toh, Hiroyuki Noda

Institute for Life Support Technology

Abstract: Antioxidant effect of lignin and lignophenol, which were prepared from botanical wastes, was investigated. As the botanical wastes, used tea leaves (green tea), peanut husk, rice bran, and wood meal were used. The antioxidant effect was evaluated on the basis of the changes in peroxide value by auto-oxidation of linoleic acid. It was found that all samples showed high antioxidant effect. Especially, a lignophenol from tea leaves had the highest activity. In comparison with commercially available antioxidants, the antioxidant effect of the lignophenol from tea leaves was higher than that, of vitamin E, but lower than those of t-butylhydroxyanisol (=BHA) and ferulic acid.

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2004-101

表面プラズモン共鳴を用いたモノリグノール類とヘミセルロースの相互作用解析

浦木康光、中村 淳、岸本崇生、生方 信

北海道大学大学院農学研究科

Investigation on interaction between monolignols and hemicellulose using surface plasmon resonance.

Yasumitsu Uraki, Atsushi Nakamura, Takao Kishimoto, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: Interactions of monolignol (coniferyl alcohol) or its glucoside (coniferin) with xylan was investigated by the surface plasmon resonance (Biacore™) to clarify the transportation of lignin precursor from cytoplasm in the lignification process. Xylan isolated from birch was oxidized with periodate to generate aldehyde group, and then the resulting xylan was immobilized onto carboxymethyl (CM)-dextran as a support of sensor chip by the reductive amination to give a ligand on the sensor chip. The adsorption capacity of the oxidized xylan to coniferin was much larger than that of its glucoside. It is proposed that coniferyl alcohol would be supplied from cytoplasm for lignification but not its glucoside.

2004-102

広葉樹放射組織におけるリグニン化学構造の特性について

近藤憲哉、秋山拓也、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Structure of lignin in ray parenchyma obtained by a direct sampling without chemical treatment.

Kenya Kondo, Takuya Akiyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Science, the University of Tokyo

Abstract: 'Ray' and 'ray-free' fractions were separated from heartwood of *Platanus orientalis* by direct cutting on naked eyes. Klason lignin content was higher in 'ray' and lower in 'ray-free' fraction. Diastereomer ratio of  $\beta$ -O-4 structure obtained by ozonation method (E/T ratio) and ratio of aromatic ring type obtained by nitrobenzene oxidation (S/V ratio) were also higher in 'ray' and lower in 'ray-free' fraction. These tendencies were the same as those in sapwood. However, both S/V and E/T ratios obtained for whole wood of heartwood didn't exhibit the intermediate values of 'ray' and 'ray-free' fraction of heartwood. Although this result can't be explained at this moment, it was implied that alcohol-benzene extractives could affect significantly the results of nitrobenzene oxidation and ozonation. When all values of E/T ratio obtained in this experiment were plotted against those of SN ratio, they were correlated well each other, which confirmed the recent finding by Akiyama et al.

2004-103

高分子鑄型存在下でのコニフェリルアルコールの酵素重合  
中村力也<sup>\*1</sup>、松下泰幸<sup>\*1</sup>、福島和彦<sup>\*1</sup>、梅本和彦<sup>\*2</sup>、臼杵有光<sup>\*2</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科, <sup>\*2</sup>豊田中研

Enzymatic polymerization of coniferyl alcohol in the presence of polymer templates.

Rikiya Nakamura<sup>\*1</sup>, Yasuyuki Matsusita<sup>\*1</sup>, Kazuhiko Fukushima<sup>\*1</sup>, Kazuhiko Umemoto<sup>\*1</sup>, Arimitsu Usuki<sup>\*2</sup>

<sup>\*1</sup>Graduated School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>Toyota Central R & D Laboratories

Abstract: Dehydrogenative polymerisate (DHP) of coniferyl alcohol, a main monomer of lignin, was prepared by the use of horseradish peroxidase/H<sub>2</sub>O<sub>2</sub> system in the presence of polymer templates, e.g., poly(ethylene glycol), cellulose, xylan, and cyclodextrins (CDs). DHP was characterized by <sup>1</sup>H NMR and size exclusion chromatography. The chemical bonds ratio ( $\beta$ -O-4':  $\beta$ -5':  $\beta$ - $\beta$ ') was calculated by using the signal of <sup>1</sup>H NMR of acetylated DHP. Addition of xylan and  $\alpha$ -CD led to the increase of  $\beta$ -5' and  $\beta$ -O-4' structure, respectively. This result indicated that chemical structure of DHP was regulated by the additions of xylan and  $\alpha$ -CD in the reaction medium.

2004-104

細胞壁中における高分子リグニン形成過程の電顕観察 III イチヨウの Purves リグニンの観察  
寺島典二<sup>\*1</sup>、吉田正人<sup>\*2</sup>

<sup>\*1</sup>名古屋大学、<sup>\*2</sup>名古屋大学大学院生命農学研究科

Formation of macromolecular lignin in the cell wall as observed by electron microscopy. III.

Observation of Purves lignin prepared from differentiating xylem of *Ginkgo biloba*.

Noritsugu Terashima<sup>\*1</sup>, Masato Yoshida<sup>\*1</sup>

<sup>\*1</sup>Professor emeritus, Nagoya University, <sup>\*2</sup>Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: In the lignifying cell wall, lignin is formed as beads-like modules of lignin-hemicellulose complexes surrounding cellulose microfibrils as observed by FE-SEM. It was assumed that fusion of the modules in a final stage of cell wall lignification form a super high-molecular lignin-hemicellulose complex. Purves lignin was isolated from the differentiating ginkgo xylem by selective removal of polysaccharides by periodate oxidation. The lignin retained morphological features of tracheids even if it is isolated from the wood in which phenolic hydroxyl groups of lignin were protected by methylation from undesirable modification during periodate oxidation. The results support the assumed ultrastructural assembly of the cell wall polymers in ginkgo tracheids.

2004-105

イソコニフェリン化学合成法の改良とその脱水兼重合  
飛松裕基, 細谷隆史, 上高原浩、高野俊幸、中坪文明  
京都大学大学院農学研究科

Improvement of chemical synthesis of isoconiferin and its dehydrogenative polymerization.

Yuki Tobimatsu, Takashi Hosoya, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo  
Graduate School of Agriculture, Kyoto University

Abstract: To obtain highly polymerized DHP (Dehydrogenation polymer) by an introduction of hydrophilic glucose unit to monolignol, isoconiferin was successively prepared by the use of imidate method and polymerized by Peroxidase/ Hydrogen peroxide. The polymerization of isoconiferin proceeded in a completely homogeneous way and the resulting polymer was water-soluble. The molecular weight of isoconiferin-DHP depended on monomer addition times, concentrations of monomer and most strongly on amounts of peroxidase, while the molecular weight of coniferyl alcohol-DHP had no dependence on the amount of Peroxidase. As the results, maximum DP of isoconiferin-DHP was 31, while that of comiferyl alcohol was 15.

2004-106

$\beta$ -O-4 型規則性人工リグニンポリマーの合成(2)

岸本崇生, 浦木康光, 生方 信  
北海道大学大学院農学研究科

Synthesis of artificial lignin polymer composed of  $\beta$ -O-4 structure.

Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata  
Graduate School of Agriculture, Hokkaido University

Abstract: The  $\beta$ -O-4 structure is one of the most important substructures in lignin. We are working on the synthesis of lignin polymers composed of only  $\beta$ -O-4 structure from simple aromatic compounds as starting materials by a solution polymerization method. New monomer was selected and polymerized in the presence of alkali. The obtained polymeric material was analyzed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy, which suggests that the polymer has a regular structure. Molecular weight of the polymer will be determined by GPC analysis.

2004-107

ポプラペルオキシダーゼ遺伝子の単離とそれらのストレス誘導発現解析

森永紗也佳<sup>\*1</sup>、佐々木慎弥<sup>\*1</sup>、楠城時彦<sup>\*2</sup>、篠原健司<sup>\*2</sup>、堤 裕司<sup>\*3</sup>、近藤隆一郎<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>九州大学大学院農学研究科

Isolation and expression analysis of peroxidase genes in poplar under stress treatments.

Sayaka Morinaga<sup>\*1</sup>, Shinya Saaki<sup>\*1</sup>, Tokihiko Nanjo<sup>\*2</sup>, Kenji Shinohara<sup>\*2</sup>, Yuji Tsutsumi<sup>\*3</sup>, Ryuichiro Kondo<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Forestry and Forest Products Research Institute, <sup>\*3</sup>Graduate School of Agriculture, Kyushu University

Abstract: In higher plants, the peroxidase (PO) activity is generally upregulated by environmental stresses. However, PO comprise a multigene family, and therefore the most of physiological functions of isoenzymes have yet been unclear. In this Study, we analyzed the gene expression of some POs from poplar, a model tree. ESTs generated from the stress-treated leaves of *Populus nigra* were subjected to the screening of poplar PO clones, and 198 PO candidates were isolated. Of the 198 candidates, we selected 11 PO clones. A cationic PO clone was abundantly expressed in the poplar stress-related ESTs (104/198), suggesting its stress inducibility. In fact, it

was confirmed to be induced by environmental stress treatments such as dry, cold, heat, and H<sub>2</sub>O<sub>2</sub> by northern analysis. The exhaustive expression analysis of other PO genes and additional 17 PO clones isolated from the leaf, shoot, and xylem of *P. alba* with respect to the stress-induction is now undergoing.

2004-108

LIM様転写因子の発現抑制による低リグニン樹木の開発

河岡明義, 渡邊恵子, 南藤和也, 海老沼宏安

日本製紙株式会社森林科学研究所

Production and characterization of lignin-reduced woody plants by suppression of LIM transcription factor.

Akiyoshi Kawaoka, Keiko Watanabe, Kazuya Nanto, Hiroyasu Ebinuma

Nippon Paper Industries Co., Ltd.

Abstract: Lignins are phenolic polymers that are embedded in the cell walls of specialized plant cells. Our research purpose is to produce woody plants with low level of lignin for environmental and economical benefits of pulp production. Previously, we identified a cDNA encoding transcription factor from tobacco (*Nicotiana tabacum*), namely Nt1im1 that regulates the gene expression involved in lignin biosynthesis. The antisense Nt1im1 construct was introduced into *Eucalyptus camaldulensis* that is one of the most important hardwood for afforestation. The transgenic Eucalyptus grown in the greenhouse showed 5% reduction of lignin content and 5% increase of holocellulose content.

2004-109

リグナンの位置選択的メチル化を触媒する新規 *O*-メチルトランスフェラーゼ

梅澤俊明<sup>\*1</sup>, Laigeng Li<sup>\*2</sup>, 鈴木史朗<sup>\*1\*2</sup>, 榑原紀和<sup>\*1</sup>, 中坪朋文<sup>\*1</sup>, Vincent L. Chang<sup>\*2</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> ノースカロライナ州立大学

A novel *O*-methyltransferase catalyzing a regioselective methylation of lignan.

Toshiaki Umezawa<sup>\*1</sup>, Laigeng Li<sup>\*2</sup>, Shiro Suzuki<sup>\*1\*2</sup>, Norikazu Sakakibara<sup>\*1</sup>, Tomoyuki Nakatsubo<sup>\*1</sup>, Vincent L. Chiang<sup>\*2</sup>

<sup>\*1</sup> Research Institute for Sustainable Humanosphere, Kyoto University, <sup>\*2</sup> North Carolina State University

Abstract: In spite of frequent occurrence of methoxyl groups in lignan molecules, little is known about *O*-methyltransferases (OMTs) involved in lignan *O*-methylation. The present study reports the isolation of a novel safflower (*Carthamus tinctorius*) gene encoding a lignan *O*-methyltransferase which catalyzes regioselective methylation of matairesinol giving rise to arctigenin, but not isoarctigenin. A recombinant protein of the enzyme, matairesinol *O*-methyltransferase (CtMROMT), expressed in *E. coli*, exhibited the regioselectivity, like the plant protein, while the recombinant CtMROMT did not catalyze *O*-methylation of hydroxymonolignols and cinnamates, suggesting that the OMT is a novel type of plant OMT specific to lignan methylation.

2004-110

トチュウ粗酵素によってコニフェリルアルコールから生じる(+)-エリトロ-及び(-)-トレオ-グアイアシルグリセロール-β-コニフェリルエーテルの絶対立体配置とその新奇な立体選択的生成機構の提案

片山健至、田淵ゆかり、鈴木利貞

香川大学農学部

Absolute configuration of (+)-*erythro*- and (-)-*threo*-guaiacylglycerol-β-coniferyl ethers formed by

the incubation of coniferyl alcohol with cell-free extracts of *Eucommia ulmoides* and their novel stereoselective formation.

Thkeshi Katayama, Yukari Tabuchi, Toshisda Suzuki

Faculty of Agriculture, Kagawa University

Abstract: Incubation of coniferyl alcohol with cell-free extracts of *Eucommia ulmoides* in the presence of hydrogen peroxide gave (+)-*erythro*- and (-)-*threo*-guaiacylglycerol- $\beta$ -coniferyl ethers (GGCE), and the *erythro* isomer was formed more than the *threo* isomer. Absolute configuration of (+)-*erythro*, (-)-*erythro*, (+)-*threo*, and (-)-*threo* GGCE was determined as (7R, 8S), (7S, 8R), (7S, 8S), and (7R, 8R), respectively, by Mosher's method. Quantitative analysis of the four stereoisomers, (7R, 8S)-(+)-*erythro*-, (7S, 8R)-(-)-*erythro*-, (7S, 8S)-(+)-*threo*-, and (7R, 8R)-(-)-*threo*-GGCE, showed that their percentages were 44.45%, 25.55%, 5.25%, and 24.75%, respectively. We found for the first time an enzyme activity that catalyzes the stereoselective addition of water to (8R)-quinonemethide giving (7R, 8S)-(+)-*erythro*-GGCE. Non-enzymatic addition of water to the (8S)-quinonemethide gave (7S, 8R)-(-)-*erythro*- and (7R, 8R)-(-)-*threo*-GGCE in the almost same ratio.

2004-111

Evolution of lignin. —Structural characteristics of polyphenolic components of bryophytes, pteridophytes and spermatophytes.

Zenfu Jin<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>, Takeshi Tange<sup>\*1</sup>, Kenji Iiyama<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Tokyo University of Agriculture

Abstract: Polyphenolic components of several species of bryophytes and pteridophytes, which have been gifted by Dr. T. Ishii, Forestry and Forest Products Research Institute and Dr. M. Higuchi, National Science Museum, were examined by the yield of residues after Klason treatment. An alkaline nitrobenzene oxidation for aromatic composition, analytical ozonolysis to investigate the presence of  $\beta$ -O-4 intermonomer linkages and methoxyl content. Syringyl unit was detected in alkaline nitrobenzene oxidation products of *Selaginella tamariscina* (Beauv.) Spring and molar ratio of syringyl to guaiacyl nuclei (S/V ratio) was 2.31. Björkman lignins were prepared from *S. tamariscina* and *Polystichum polyblepharum* after extraction with 80% EtOH followed by water to investigate structural characteristics of lignins. The presence of syringyl unit as the major component of lignin in *S. tamariscina*, but not in *P. polyblepharum*, was also supported by <sup>1</sup>H NMR and FTIR spectroscopies, and confirmed by acidolysis and ozonation, that syringyl unit of *S. tamariscina* lignin is involved in  $\beta$ -O-4 linkages. The low content of methoxyl group and low total yield of alkaline nitrobenzene oxidation products and ozonation products suggest that Klason residue is not representative real lignin of *S. tamariscina* and *P. polyblepharum*.

2004-112

$\beta$ -O-4型構造の側鎖の立体構造を規定する要因(その2)—*erythro*/*threo*比とS/V比の相関—  
秋山拓也<sup>\*1</sup>、後藤仁志<sup>\*1</sup>、松本雄二<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、Deded S. Nawawi<sup>\*2</sup>、Wasrin Syafii<sup>\*2</sup>

<sup>\*1</sup>東京大学院農学生命科学研究科、<sup>\*2</sup>Bogor Agricultural University

A factor determining the diastereomeric forms of  $\beta$ -O-4 structures. —Relationships between *erythro*/*threo* ratio and syringyl/guaiacyl ratio among different wood species.

Takuya Akiyama<sup>\*1</sup>, Hitoshi Goto<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>, Gyosuke Meshitsuka<sup>\*1</sup>, Deded S. Nawawi<sup>\*2</sup>, Wasrin Syafii<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Bogor Agricultural University

Abstract: Twenty-one wood species containing softwoods and hardwoods were subjected to

nitrobenzene oxidation. The S/V ratio obtained was widely varied depending on wood species (0 to 6.1). The *erythro*/(*erythro* + *threo*) ratios of  $\beta$ -O-4 structures were strongly correlated with the S/(S+V) ratios ( $R^2 = 0.99$ ), as well as with the previously reported methoxyl group content in lignin ( $R^2 = 0.83$ ). It was suggested that syringyl/guaiacyl composition is one of the factors which control the proportion of *erythro* and *threo* forms of  $\beta$ -O-4 structures during the process of lignin formation. By nitrobenzene oxidation, a variation in the content of biphenyl type (5-5 linkage type) structure was also investigated based on divanillin yield.

#### 2004-特別講演

リグニン科学の新たな展開 –リグニン科学者に求められている課題–

飯山賢治

東京農業大学、東京大学アジア生物資源環境研究センター

Let's advance a fresh lignin science: Assignments asked for lignin scientists.

Kenji Iiyama

Tokyo University of Agriculture and the University of Tokyo

Abstract: The most abundant organic compound on the earth is "Lignin", but not cellulose, because lignin resists strongly against mineralization by the activities of microorganisms. Presence of lignin, therefore, plays a key part in global carbon circulation, global environment and accumulation of fossil resources. In addition, the term of lignin is discussed widely in various disciplines such as agricultural science, botany, environmental science, ecology, animal husbandry, pharmacy, oceanography, archaeology, and so on. Lignin scientists are looked forward to advancing such disciplines. The assignments asked for lignin scientists are discussed.

#### 2004-201

*Phanerochaete crassa* WD1694 菌の菌糸先端部のペルオキシダーゼ活性の定量

高野麻理子、安部 久、林 徳子

森林総合研究所

Extracellular peroxidase activity at the apical tip of *Phanerochaete crassa* WD1694.

Mariko Takano, Hisashi Abe, Noriko Hayashi

Forestry and Forest Products Research Institute

Abstract: Extracellular peroxidase activity of *Phanerochaete crassa* WD1694 was visualized by staining with a peroxidase substrate, 3,3'-5,5'-Tetramethylbenzidine precipitate. The staining occurred directly on and along the apical tip of the mycelium. Visible spectra and absorbance of the staining at the apical tip was analyzed by microspectrophotometry, and catalytic velocity was calculated. The maximum catalytic velocity was estimated 1135 $\mu$ M/min. The result clearly showed that the catalytic velocity of the extracellular peroxidase reaction at the apical tip of *P. crassa* WD1694 was much higher than that reported on MnP and Lip of *Phanerochaete chrysosporium* that caused the depolymerization of lignin in vitro.

#### 2004-202

$^{13}\text{C}$  シアン配位型ペルオキシダーゼの NMR 解析 –過酸化水素との反応における活性部位アミノ酸残基の役割–

野中大輔<sup>\*1</sup>、親泊政二三<sup>\*2</sup>、藤井 浩<sup>\*3</sup>、割石博之<sup>\*4</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>科学技術振興機構、<sup>\*3</sup>大学共同利用機関法人自然科学研究機構岡崎統合バイオサイエンスセンター、<sup>\*4</sup>九州大学大学院農学研究科

NMR Analysis of  $^{13}\text{C}^{15}\text{N}$ -ligated lignin peroxidase and manganese peroxidase. – Role of active-site amino acids in hydrogen peroxide activation.

Daisuke Nonaka<sup>\*1</sup>, Masafumi Oyadomari<sup>\*2</sup>, Hiroshi Fujii<sup>\*3</sup>, Hiroyuki Wariishi<sup>\*4</sup>

<sup>\*1</sup>Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Japan Science and Technology Agency, <sup>\*3</sup>Institute for Molecular Science and Center for Integrative Bioscience, <sup>\*4</sup>National Institutes of Natural Science, Faculty of Agriculture, Kyushu University

Abstract: To investigate the heme environment of lignin peroxidase and manganese peroxidase from *Phanerochaete chrysosporium*, <sup>13</sup>C- and <sup>15</sup>N-NMR spectroscopic techniques were utilized. <sup>13</sup>C-NMR signals of cyanide bound to the heme iron of LiP and MnP (-3860 ppm and -3863 ppm, respectively) indicated that electron push effect from axial ligands of both enzymes were much lower than that of common peroxidases, e.g. horseradish peroxidase. On the other hand, <sup>15</sup>N-NMR analysis of these enzymes revealed that the electron pull effect of both enzymes were strong as observed in other peroxidases. These results indicated that LiP and MnP were shown to share unique features, significantly weak electron push effect but with strong pull effect, which may explain slower rates of compound I formation for either LiP or MnP.

2004-203

*Phanerochaete chrysosporium* におけるパスウェイクロストーク

割石博之<sup>\*1</sup>, 三浦大典<sup>\*2</sup>, 志水元亨<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院農学研究科、<sup>\*2</sup>九州大学大学院生物資源環境科学研究科

Pathway crosstalk involved in lignin degradation system of *Phanerochaete chrysosporium*.

Hiroyuki Wariishi, Daisuke Miura, Motoyuki Shimizu

Faculty of Agriculture, Kyushu University

Abstract: A proteomic analysis for surveying heme-binding proteins produced by the white-rot basidiomycete *Phanerochaete chrysosporium* was performed utilizing a biotinylated heme-streptavidin beads system. Mitochondrial citrate synthase (CS) and glyceraldehyde 3-phosphate dehydrogenase (GAPDH) were identified as a heme binding protein. CS was shown to possess a Cys-Pro motif, a well-known heme responsive motif, in its amino acid sequences. A homology modeling via MOE using the crystal structure of citrate synthase from pig as a template revealed the existence of the Cys-Pro motif on the surface of the protein. A genomic analysis revealed that 5-Aminolevulinic acid synthase (ALAS) also possesses the Cys-Pro motif. These data, combined with our previous data showing the involvement of CS, GAPDH, and ALAS in the metabolic control of carbon flux and redox regulation, strongly suggested that the existence of a unique pathway crosstalk between the glycolysis, TCA cycle, and heme biosynthetic pathway. This pathway crosstalk is thought necessary for optimizing fungal lignin degradation system.

2004-204

多糖加水分解酵素による MWL 抽出残渣の分解挙動(II) -特にキシラナーゼ処理について-

吉野寛之、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

The behavior of degradation of wood meal after extraction of the MWL by carbohydrate-degrading enzymes. (II). -Structural analysis by xylanase.

Hiroyuki Furuno, Hiroshi Kamitakahara, Toshiyuki Tbkano, Fumiaki Nakatsubo

Graduate school of Agriculture, Kyoto University

Abstract: The xylanase treatment of Cellulose-Lignin fracdon (CL), which was extracted from MWL extracted residue with LiCl/ DMAc, was carried out. From neutral sugar and lignin analyses data, it was found that xylanase solubilized approximately 75% of xylose and 41% of lignin CL. From GPC data, it was found that the molecular weight of the solubilized lignin was much lower than MWL. These indicated that no less than 40% of lignin in CL, with a low molecular weight, formed xylan-lignin

complex. The solubilized lignin apparently had the native structure derived from LCC.

2004-205

酸素アルカリ処理におけるクラフトリグニンの酸素消費量の測定

今井愛子、友日生織、松本雄二、飯塚堯介

東京大学院農学生命科学研究科

Accurate measurement of oxygen consumption during oxygen-alkali treatment of kraft lignin and lignin model compounds.

Aiko Imai, Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: During oxygen-alkali bleaching, the progress of lignin oxidation is believed to govern the delignification. However there seems to be no clear relationships established between the oxidation reaction and delignification. In order to directly analyze the progress of lignin oxidation, we designed a measuring device by which oxygen consumption can be precisely followed based on the accurate measurement of oxygen supply to the reactor. By use of this device, oxygen consumption of isolated softwood kraft lignin and several lignin model compounds was measured under 0.80 MPa of oxygen pressure at 95°C. The results were that one aromatic ring consumed about 3 oxygen molecules. Although non-phenolic lignin model compound didn't consume any oxygen, results obtained for kraft lignin suggested that non-phenolic unit as well as phenolic unit in lignin consumed oxygen during oxygen-alkali treatment.

2004-205

化学パルプの温和なアルカリ処理による過マンガン酸カリウム消費物質の生成

友田生織、童国林、松本雄二、飯塚堯介

東京大学院農学生命科学研究科

Formation of permanganate consuming substances by mild alkali treatment of chemical pulp.

Iori Tomoda, Guolin Tong, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Permanganate consuming structures were produced from kraft pulp by mild alkali treatment. Its formation was suppressed when hydrogen peroxide was present during the reaction. In order to fully understand the role of hydrogen peroxide, pulp was treated by alkali in the presence or absence of hydrogen peroxide under different pH and the permanganate consumption of both pulp and reaction liquor were analyzed. As roles of hydrogen peroxide, (i) destruction of permanganate consuming structures, (ii) suppression of the formation of permanganate consuming structures, and (iii) prohibition of incorporation of permanganate consuming structures into pulp were suggested.

2004-207

リグニンの嫌気条件下での微生物変性 –シロアリ原腸を通過したリグニンの性状–

勝亦京子\*<sup>1</sup>、堀啓映子\*<sup>1</sup>、飯山賢治\*<sup>2</sup>

\*<sup>1</sup>東京大学院農学生命科学研究科、\*<sup>2</sup>東京農業大学

Changes in structural feature of lignin by microorganism under anaerobic condition. –Property of lignin after digestion by termite.

Kyoko S. Katsumata\*<sup>1</sup>, Keko Hori\*<sup>1</sup>, Kenji Iiyama\*<sup>2</sup>

\*<sup>1</sup>Graduate School of Agricultural and Life Science, the University of Tokyo, \*<sup>2</sup>Tokyo University of Agriculture

Abstract: Behavior of biodegradation (biomodification) of plant cell wall components under aerobic condition is well documented, but not enough for especially lignin under anaerobic system.

Biomodification of lignin is greatly due to the activities of peroxidase group, it is not clear yet the behavior of peroxidases under anaerobic condition. Digestion of woody materials by termites is the typical anaerobic modification of plant cell wall components together with digestion of forages in rumen of ruminants. Changes in chemical feature of lignin by microorganism under anaerobic condition were investigated by the comparison of cell wall components of wood before and after digestion by termite. Wood of Ilang-Ilang (*Ilang-Ilang C. dadloyi*) and Apitong (*Dipterocarpus grandiflorua*) and excrements of termites which feed each wood were collected from University of the Philippines. Los Baños. Björkman lignin of each samples were isolated. There were no significant differences on <sup>1</sup>H-NMR spectra between acetylated Björkman lignin from excrements and original woods. Methoxyl contents of Björkman lignins from excrements of termite were also similar to those of original wood. Small differences for only contents of aliphatic hydroxyl and conjugated phenolic hydroxyl group were detected.

2004-208

リグニンエーテル構造の熱分解開裂機構

河本晴雄、中村健史、坂 志朗

京都大学大学院エネルギー科学研究科

Mechanism of the pyrolytic cleavage of ether structures in lignin.

Haruo Kawamoto, Takeshi Nakamura, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: Mechanism of the pyrolytic cleavage of  $\alpha$ - and  $\beta$ -ether structures in lignin was studied with  $\alpha$ -ether types of dimeric and  $\alpha$ ,  $\beta$ -diether types of trimeric model compounds having differently substituted C  $\alpha$ -phenyl ether groups. As a result, phenolic and non-phenolic  $\alpha$ -ether structures were cleaved in ionic and homolytic (radical) mechanisms, respectively, in dimers. In trimers, additional  $\beta$ -ether groups did not change the mechanism of the  $\alpha$ -ether cleavage of the non-phenolic trimers, whereas the ionic mechanism was changed to radical in the phenolic trimers. The latter results are reasonably explained with the formation of radical species through homolytic cleavage of the  $\beta$ -ether structure, although the pyrolytic cleavage of the phenolic  $\alpha$ -ether structures in the phenolic trimers is initiated with the ionic mechanism.

2004-209

木材の光劣化(II) -光照射によるスギ材表面のリグニン構造変化-

砂原 寛<sup>\*1</sup>、中川明子<sup>\*2</sup>、富田文一郎<sup>\*2</sup>、黒田健一<sup>\*3</sup>

<sup>\*1</sup>ケミプロ化成株式会社、<sup>\*2</sup>筑波大学大学院生命環境科学研究科、<sup>\*3</sup>九州大学大学院農学研究院  
Photodegradation of wood. (2). -Change of lignin structure of *Cryptomeria japonica* D. Don by UV irradiation.

Hiroshi Sunahara<sup>\*1</sup>, Akiko Nakagawa<sup>\*2</sup>, Bunichiro Tomita<sup>\*2</sup>, Ken-ichi Kuroda<sup>\*3</sup>

<sup>\*1</sup>Chemipro Lasei Kaisha Ltd., <sup>\*2</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, <sup>\*3</sup>Department of Forest and Forest Products Science, Faculty of Agriculture, Kyushu University

Abstract: When lumber is left for out side for long time, the color of the lumber's surface is changed, yellow to white-brown and the surface was cracking. These are due to the participation of photo degradation of lignin by UV irradiation. We then started to the study of photo degradation of lignin. The results suggested that lignin is degraded early time (acceleration by UV irradiation for 1 to 5 hours). A decrease in  $\beta$ -O-4 subunits was found by pyrolysis gas chromatography.

2004-210

## リグニン含有フェノール樹脂の表面特性

松下泰幸、和田沙織、福島和彦

名古屋大学大学院生命農学研究科

Surface characteristics of phenol resins contained lignin

Yasuyuki Matsushita, Saori Wada and Kazuhiko Fukushima

Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: The surface characteristics of phenol-formaldehyde (PF) resin with lignosulfonate and kraft lignin were determined by contact angle measurement and inverse gas chromatography (IGC). In the contact angle measurement, the three-liquid method was utilized to determine the Lifshitz-van der Waals components ( $\gamma^{LW}$ ), electron-acceptor parameter ( $\gamma^+$ ), and electron-donor parameter ( $\gamma^-$ ) of the prepared resins and calculation of the acid-base component of the work of adhesion between water and the resins. The result of IGC showed the same  $\gamma^{LW}$  trends obtained from the contact angle measurement.

2004-211

## セルロース微粒子充填クラフトリグニン系エポキシ樹脂複合材料の製造

船橋正弘

産業技術総合研究所

Preparation of composites of kraft-lignin based epoxy resin filled with cellulose particle.

Masahiro Funabashi

National Institute of Advanced Industrial Science and Technology (AIST).

Abstract: A mixture of ester-carboxylic acid derivatives (KLPA) was obtained by reaction of an ethylene glycol solution of Kraft lignin (KL) and succinic anhydride in the presence of a catalytic amount of dimethylbenzylamine at 80 °C. Composite samples were prepared by a reaction of the mixture of KLPA and cellulose particles with ethylene glycol diglycidyl ether (EGDGE) at 70 °C. Cellulose contents ranged from 0 to 60 wt%. The above mixtures were molded into sheets at 130 °C for 5 hours. The mechanical properties of the samples were investigated by tensile tests using plate type specimens.

2004-212

## 断熱材用リグニンベースポリウレタンフォームの熱的機械的性質

畠山兵衛<sup>\*1</sup>、松村博司<sup>\*1</sup>、廣瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 産業技術総合研究所、<sup>\*3</sup> 大妻女子大学

Thermal and mechanical properties of lignin-based rigid polyurethane foams for insulation.

Hyo Hatakeyama<sup>\*1</sup>, Hiroshi Matsumura<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Fukui University of Technology, <sup>\*2</sup>National Institute of Advanced Industrial Science and Technology, <sup>\*3</sup>Otsu Women's University

Abstract: Rigid polymethane (PU) foams for insulation were prepared from various kinds of lignins such as kraft lignin (KL), sodium lignosulfonate (LS), solvolysis lignin (SL) and alcoholysis lignin (AL). Thermal and mechanical properties of the above polyurethane foams (PU's) were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), and compression tests. It was found that glass transition temperatures ( $T_g$ 's), thermal degradation temperatures ( $T_d$ 'S) and mechanical properties of the PU's were not prominently dependent on kinds of lignin and that all of the above lignin-based PU's are available for insulation. From the viewpoints of practical utilization, KL- and LS-based PU's were compared in this study.

2004-213

リピッドペルオキシレーションにおけるリグニン分解のラジカル反応化学的考察 –カーボンセンターラジカルについて

大橋康典、渡邊崇人、本田与一、渡辺隆司  
京都大学生存圏研究所

Radical chemistry of lipid peroxidation for lignin degradation: On the roles of carbon-centered radicals.

Yasunori Ohashi, Takahito Watanabe, Yoichi Honda, Takashi Watanabe  
Research Institute for Sustainable Humanosphere, Kyoto University

Abstract: In 1999, Kapich et al. reported that peroxy radicals produced by thermal decomposition of azo compounds degraded a non-phenolic lignin model compound. However, there was no direct evidence showing that carbon-centered radicals were responsible for the degradation. In the present study, mechanisms for the non-phenolic  $\beta$ -O-4 lignin model degradation by carbon-centered radicals from azo compounds were investigated. The results suggested that carbon-centered radicals are able to degrade the model compound by a mechanism different from that for peroxy radicals.

2004-214 カワラタケによるフタル酸ジブチルの分解とそれに関与する酵素

山田喜彦、平井浩文、河合真吾、西田友昭  
静岡大学農学部

Degradation of di-*n*-butyl phthalate by white rot fungus *Trametes versicolor* and its related enzyme.  
Yoshihiko Yamada, Hirofumi Hirai, Shingo Kawai, Tomoaki Nishida  
Faculty of Agriculture, Shizuoka University

Abstract: Di-*n*-butyl phthalate (DBP) is widely used in a variety of industrial applications as a plasticizer, and is suspected of having estrogenic (endocrine-disrupting) activity, mutagenicity, teratogenicity, and carcinogenicity. In this study, therefore, we attempted the degradation of DBP by white rot fungus *Trametes versicolor*. DBP decreased by 85% and 95% after 2 days and 3 days of fungal treatment, respectively, and DBP was converted into mono-*n*-butyl phthalate (MBP) and an unidentified product. Although no appreciable decrease of DBP was obtained by manganese peroxidase and laccase, the cell-free extract prepared from the mycelium of *T. versicolor* decreased DBP and converted DBP into MBP. This result indicated that the intracellular enzyme(s) produced by white rot fungus is involved in DBP degradation.

2004-215

白色腐朽担子菌とその菌体外酵素による異常プリオンタンパクの分解

岩村 翼<sup>\*1</sup>、山口 同<sup>\*1</sup>、堤 祐司<sup>\*1</sup>、松浦裕一<sup>\*2</sup>、毛利資郎<sup>\*2</sup>、近藤隆一郎<sup>\*1</sup>

<sup>\*1</sup>九州大学大学院農学研究院、<sup>\*2</sup>九州大学大学院医学研究院

Biodegradation of protease-resistant prion protein by white-rot fungi and their ligninolytic enzymes.  
Tsubasa Iwanura<sup>\*1</sup>, Atsumu Yanaguchi<sup>\*1</sup>, Yuji Tsutsumi<sup>\*1</sup>, Yuichi Matsumura<sup>\*2</sup>, Shirou Mohri<sup>\*2</sup>,  
Ryuichiro Kondo<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agriculture, Kyushu University, <sup>\*2</sup>Graduate School of Medical Sciences, Kyushu University

Abstract: Protease Resistant Prion Protein (PrP<sup>Res</sup>) is cause substance of bovine spongiform encephalopathy (BSE) and other diseases. PrP<sup>Res</sup> can not be degraded either by proteases or usual chemical treatments. Thus, validated method for the decontamination of PrP<sup>Res</sup> is urgently required. Recently, white-rot fungi have received worldwide attention for bioremediation because of their abilities for the degradation and detoxification of environmental pollutants, such as dioxins and chlorophenols. In this study, PrP<sup>Res</sup> was treated by 14 white-rot fungi and 1 brown-rot fungus. The

PrP<sup>Res</sup> was completely degraded by 8 white-rot fungi, and all these fungi produced manganese peroxidase (MnP) during the treatment. The crude extracellular enzyme also degraded PrP<sup>Res</sup> in the condition containing Mn( II ) and H<sub>2</sub>O<sub>2</sub>. These results support that MnP is a key enzyme for PrP<sup>Res</sup> degradation.

2004-P01

LCC の両親媒的性質

臼倉ゆり子、植木飛鳥、浦木康光、岸本崇生、生方 信

北海道大学大学院農学研究科

Amphiphilic characteristics of LCC.

Yuriko Usukura, Asuka Ueki, Yasumitsu Uraki, Takao Kishimoto, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: Lignin-Carbohydrate Complex (LCC) was isolated from wood meal residue with DMSO after extraction of milled wood lignin (MWL). Transmission electron micrographs after negative staining indicated that LCC formed self-aggregates in water with diameters in the range of nano-meter. The aggregates revealed to have strong hydrophobic domains by the fluorometric study of their complexes with fluorescent reagents as indicators for hydrophobicity. The surface pressure ( $\pi$ )-area (A) isotherms of LCC also indicated self-assembly and the possibility of formation of LB film.

2004-P02

リグニン・炭水化物結合体の単離(IV)アカマツ材からの単離

池田 努、杉元倫子、田中良平、真柄謙吾、加藤 厚、細谷修二

森林総合研究所

Isolation of lignin-carbohydrate complexes. (IV). Application to red pine wood.

Tsutomu Ikeda, Tomoko Sugimoto, Ryohei Tanaka, Kengo Magara, Atsushi Kato, Shuji Hosoya

Forestry and Forest Products Research Institute

Abstract: Ozonation followed by acid hydrolysis was applied to red pine wood meal to isolate the benzylic ether type lignin-carbohydrate bonds (LCC bonds). The yield of the acidic fraction which contained LCC products was increased by extending ozonation and using weak anion exchange resin for anion exchange chromatography. There were many products in the acidic fraction with similar retention time on GC chromatogram after trimethylsilylation. Therefore, the identification of the products was difficult. It was improved by applying acetylation instead of trimethylsilylation. Some peaks on GC chromatogram of the samples from red pine wood showed the same retention time and the similar mass fragment pattern compared with the authentic compounds from LCC model compounds. These results suggested that benzylic ether type LCC bonds existed in red pine wood.

2004-P03

ケナフの成熟段階と部位の違いによる化学成分の変化

金光範<sup>\*1</sup>、中川明子<sup>\*1</sup>、大井 洋<sup>\*1</sup>、黒田健一<sup>\*2</sup>

<sup>\*1</sup>筑波大学大学院生命環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院

Difference of chemical components of *Hibiscus cannabinus* bast and core between various maturation steps.

Guang-Fan Jin<sup>\*1</sup>, Akiko Nakagawa<sup>\*1</sup>, Hiroshi Ohi<sup>\*1</sup>, Ken-ichi Kuroda<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, <sup>\*2</sup>Faculty of Agriculture, Kyushu University

Abstract: *Hibiscus cannabinus* plant grown in the Agricultural and Forestry Research Center at

the University of Tsukuba were separated into three parts (up, middle and bottom), and their bast and core parts were subjected to lignin and carbohydrates analyses. The middle and bottom parts of the bast were treated under soda-anthraquinone pulping and totally chlorine-free bleaching conditions, and the results were compared with those from *Acacia mearnsii*.

2004-P04

SEC-UV-MALS 法を用いた針葉樹クラフトパルプの特性解析

柳澤正弘、磯貝 明

東京大学大学院農学生命科学研究科

SEC-UV-MALS analysis of softwood kraft pulp.

Masahiro Yanagisawa, Akira Isogai

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Various cellulose and pulp samples including softwood kraft pulp (SKP) were dissolved in 8% lithium chloride/1,3-dimethyl-2-imidazolidinone (LiCl/DMI) and 8% LiCl/N,N-dimethylacetamide (LiCl/DMAc), and the obtained solutions were analyzed by size-exclusion chromatography equipped with ultraviolet and multi-angle light scattering detectors (SEC-UV-MALS). The conformation analysis using 1% LiCl/DMI as an eluent revealed that some compact structures consisting of cellulose, hemicellulose and lignin are present in the high MM part of SKP/LiCl/DMI. This structure was not broken by bleaching or removal of lignin, while it was susceptible to acid treatments and  $\beta$ -1,4-mannanase treatments. Thus, glucomannan seems to be a key component of the structure.

2004-P05

分轄添加型ラボ蒸解装置を用いたキノン蒸解法の検討

田中潤治

川崎化成工業株式会社

Studies on quinone cooking using laboratory cooking equipment applied to modified cooking processes.

Junji Tanaka

Kawasaki Kasei Chemicals Co., Ltd

Abstract: Quinone has been used as a cooking additive in many KP mills. This paper shows how quinone is applied to recent modified cooking processes. In order to make conditions of laboratory test similar to the ones of a real digester, we developed a small scale digester in which addition and extraction of cooking liquors are possible. Using this equipment, the following results became clear. 1. Addition of quinone at the top of digester is most effective. The effect of quinone is decreased if it is added after the start of cooking. 2. The amount of extracted SAG (solution-type quinone) from a digester accompanying the extraction of black liquor is very small. But the large amount of AQ (slurry-type quinone) is extracted under the lower concentration of active alkali.

2004-P06

摩砕によるリグニン構造の変化について

藤本 文<sup>\*1</sup>、松本雄二<sup>\*1</sup>、Hou-min Chang<sup>\*2</sup>、飯塚堯介<sup>\*1</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup>North Carolina state University

Changes of lignin structures caused by milling.

Aya Fuiimoto<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>, Hou-min Chang<sup>\*2</sup>, Gyosuke Meshitsuka<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>North Carolina State University

Abstract: In this paper, we tried to investigate the effect of milling on the structural change of lignin under various milling conditions. Milled woods prepared under different conditions were analyzed by ozonation method<sup>4)</sup>. Both the content of  $\beta$ -O-4 structure and the diastereomer ratio (*erythro* / *erythro* + *threo*) decreased with the progress of milling. It was found that lignin undergoes the same degree of structural change when woods were milled to the same extent regardless of the difference of milling condition.

2004-P07

リグニン構造論におけるオゾン分解法の最近の展開

松本雄二

東京大学大学院農学生命科学研究科

Recent contribution of ozonation method to structural analysis of lignin.

Yuji Matsumoto

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Recent development of ozonation method and its contribution to lignin chemistry is reviewed. The presence of simple relationships between stereo structure of  $\beta$ -O-4 linkage and aromatic ring type has been suggested. This relationship seems to be valid not only to woods but also to lower plant. Stereo preferential reactions of lignin during many kinds of chemical and mechanical treatments were detected by ozonation analysis.

2004-P08

腸内細菌に対するリグニンの影響

藤加珠子、野田博行

生物ラジカル研究所

Effect of lignin on the growth of enterobacteria.

Kazuko Toh, Hiroyuki Noda

Institute for Life Support Technology

Abstract: Several kinds of enterobacteria were cultured with the medium containing lignin that had been derived from rice bran. Lignin was metabolized by *Escherichia coli* and *Staphylococcus epidermidis*. In the medium with lignin, the growth of *Lactobacillus acidophilus* and *Streptococcus intermedius* was augmented. On the other hand, the growth of other enterobacteria such as *Escherichia coli* was suppressed.

2004-P09

脱水素重合時におけるシナミルアルコール類と4-クロロアニリンとの反応

蓮見実理恵<sup>\*1</sup>、中川明子<sup>\*1</sup>、富田文一郎<sup>\*1</sup>、黒田健一<sup>\*2</sup>

<sup>\*1</sup>筑波大学大学院生命環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院

Structural elucidation of chloroaniline-lignin matrix by pyrolysis-gas chromatography with on-line methylation.

Mirie Hasumi<sup>\*1</sup>, Akiko Nakagawa-izumi<sup>\*1</sup>, Bun-ichiro Tomita<sup>\*1</sup>, Ken-ichi Kuroda<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, <sup>\*2</sup>Graduate Schools of Agriculture, Kyushu University,

Abstract: Agrochemicals containing organochlorine compounds remain in soil. These compounds are incorporated into lignin and humic acid. In order to clarify the fate of organochlorine compounds, bulk guaiacyl- and syringyl dehydrogenative polymers (DHPS) were prepared in the presence and absence of 4-chloroaniline, and analyzed with on-line methylation pyrolysis gas chromatography/ mass spectrometry using tetramethylammonium hydroxide (TMAH), TMAH-Py-

GC/MS. In TMAH-Py-GC/MS of coniferyl alcohol-DHP incorporating chloroaniline, (4-chloro-phenyl)-[1-(3,4-dimethoxyphenyl)-2,3-dimethoxypropyl] amine was detected as a pyrolysis product; a similar syringyl product was obtained from TMAH-Py-GC/MS of sinapyl alcohol/chloro-aniline-DHP. In TMAH-Py-GC/MS of DHPs incorporating chloroaniline, the amounts of  $\beta$ -O-4 substructure-derived products, *erythro/threo*-1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane and 1-(3,4,5-trimethoxyphenyl)-1,2,3-trimethoxypropane, were greatly decreased compared to those from DHPs without chloroaniline. The pyrolysis results directly proved that the incorporation of 4-chloroaniline into the C $\alpha$ -position of arylglycerol- $\beta$ -guaiacyl ether substructures.

2004-P10

スグリグニンの熱分解における各種単位構造の役割

河本晴雄、中村健史、坂 志朗

京都大学大学院エネルギー科学研究科

Role of substructure in pyrolysis of Japanese cedar lignin.

Haruo Kawamoto, Takeshi Nakamura, Shiro Saka

Graduate School of Energy Science, Kyoto University

Abstract: To elucidate the pyrolysis behavior of lignin in wood, pyrolysis behavior of milled wood lignin (MWL) isolated from Japanese cedar (*Cryptomeria japonica*) was studied at 200–400°C in nitrogen. As a result, condensation preferentially occurred at 200–300°C rather than depolymerization, substantial depolymerization started at 300–350°C, and carbonization started at 350–400°C. Methylation of the OH groups stabilized the MWL sample for condensation as indicated by raising the condensation temperature by 50–100°C, while the methylation did not change the reactivities of depolymerization and carbonization. With the results of dimeric model compounds, role of the substructure in lignin in these pyrolysis behaviors is also discussed. These results will give useful suggestions for controlling the product selectivity, low molecular weight substances vs. char, from lignin in wood.

2004-P11

リグノフェノールエポキシ樹脂の合成と物性

八木雅史、梶山幹夫、富田文一郎

筑波大学大学院生命環境科学研究科

Synthesis and properties of lignophenol/epoxy resins.

Masashi Yagi, Mikio Kajiyama, Bunichiro Tomita

Graduate School of Life and Environmental Sciences, University of Tsukuba

Abstract: Lignophenol/epoxy resins were prepared from lignophenols (LP), epoxy compounds (E), and triethylene tetramine. They were prepared at various weight ratios of LP and E, LP/E, and various molar ratios of N-H and epoxy group, [NH]/[Epoxy]. N,N-dimethylformamide (DMF) solubility and the viscoelastic properties of cured resins were investigated. The solubility of DMF increased with increasing LP/E ratios. The resins with LP/E=1/1 and [NH]/[Epoxy]=0.5 had the highest peak temperature of loss modulus. The breadth of the temperature-modulus curve in the transition region was estimated quantitatively according to the Kwei's equation which indicates the steepness of the dispersion curve.

2004-P12

アカマツ硫酸リグニンのレゾルシノール化

今井将徳、松下泰幸、今井貴規、福島和彦

名古屋大学大学院生命農学研究科

Resorcinolization of red pine sulfuric Acid Lignin

Masanori Imai, Yasuyuki Matsushita, Takanori Imai, and Kazuhiko, Fukusima

Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: To enhance the reactivity and the solubility of sulfuric acid lignin (SAL), treatments with resorcinol in the presence of 72% sulfuric acid catalyst were performed. When resorcinol concentration was sufficiently high, resorcinolized sulfuric acid lignin with higher solubility to organic solvent was obtained. Compared with phenolization of SAL, larger amount of acid soluble fraction of reaction product was yielded. But molecule weight of resorcinolized product was larger than that of phenolized one. This may be interpreted that decomposed SAL was re-polymerized during the resorcinolized reaction.

2004-P13

ヒラタケにおける多機能型ペルオキシダーゼ MnP2 組換え遺伝子の発現

月原多佳久、本田与一、渡邊崇人、渡辺隆司

京都大学生存圏研究所

Expression of recombinant versatile peroxidase MnP2 in *Pleurotus ostreatus*.

Takahisa Tsukihara, Yoichi Honda, Takahito Watanabe, Takashi Watanabe

Research Institute for Sustainable Humanosphere, Kyoto University

Abstract: *Pleurotus ostreatus* secretes an unique peroxidase, MnP2 predominantly in low nitrogen condition. MnP2 can oxidize not only Mn<sup>2+</sup> but also non-phenolic and high-molecular weight compounds directly [1]. To express MnP2, we made expression plasmid containing the coding sequence of *mnp2* between *P. ostreatus sdi1* promoter and terminator sequences and introduced the plasmid to *P. ostreatus*. We isolated 33 transformants containing the recombinant *mnp2* sequence. Through screenings for elevated decolorizing activity of Poly R-478, one of the recombinants, TM2-10 was selected. On a synthetic medium containing 15 mM ammonium oxalate, specific expression of rMnP2 by TM2-10, but not wild-type control, was demonstrated with anion-exchange chromatography.

2004-P14

白色腐朽菌 *Ceriporiopsis subvermispora* の産生するジカルボン酸 ceriporic acid B アナログの合成と機能解析

菅 祥彦、大橋康典、渡邊崇人、本田与一、渡辺隆司

京都大学生存圏研究所

Synthesis and functional analysis of dicarboxylic acid, ceriporic acid B produced by a white rot fungus *Ceriporiopsis subvermispora*.

Yoshihiko Kan, Yasunori Ohashi, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Research Institute for Sustainable Humanosphere, Kyoto University

Abstract: Previously, we reported that 1-nonadecene-2, 3-dicarboxylic acid (ceriporic acid B, NDA) inhibited production of ·OH by the Fenton reaction. The present research aimed at elucidating effects of the alkyl side chain of this metabolite on iron redox reactions and the Fenton reaction. To discuss on the structure-function relationship, we synthesized 1-undecene-2, 3-dicarboxylic acid (UDA), an analogue of ceriporic acid B. Using UDA, NDA and itaconic acid, we analyzed surfactant activities, suppression of Fe<sup>3+</sup> redox reaction and inhibition of ·OH production. As a result, we found that UDA suppressed ·OH production by the Fenton reaction less effectively than NDA. No inhibitory effects were found for itaconic acid. These results indicate that chain length of the alkyl side chain is a key factor for controlling iron redox reactions and inhibition of ·OH production by the Fenton

reaction.

2004-P15

担子菌カワラタケの遺伝子組換えによるラッカーゼの高生産

梶田真也<sup>\*1</sup>、宮崎安将<sup>\*2</sup>、中村雅哉<sup>\*2</sup>、片山義博<sup>\*1</sup>、飯村洋介<sup>\*3</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>産業技術総合研究所

Overproduction of recombinant laccase using a homologous expression system in *Coriolus versicolor*.

Shinya Kajita<sup>\*1</sup>, Yasumasa Miyazaki<sup>\*2</sup>, Masaya Nakamura<sup>\*2</sup>, Yoshihiro Katayama<sup>\*1</sup>, Yosuke Iimura<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Forestry and Forest Products Research Institute, <sup>\*3</sup>National Institute of Advanced Industrial Science and Technology

Abstract: One of the major extracellular enzymes of the white-rot fungus *Coriolus versicolor* is laccase, which is involved in the degradation of lignin. We constructed a homologous system for the expression of a gene for laccase III in *C. versicolor* using a chimeric laccase gene driven by the promoter of a gene for glyceraldehyde-3-phosphate dehydrogenase from this fungus. We transformed *C. versicolor* successfully by introducing both a gene for hygromycin B phosphotransferase and the chimeric laccase gene. We examined one of the transformants that had the highest laccase activity and found that its activity was significantly higher than that of the wild type.

2004-P16

マンガンペルオキシダーゼによる変異原性物質の分解と無毒化

待井芳晴、平井浩文、河合真吾、西田友昭

静岡大学農学部

Degradation and detoxification of mutagen by manganese peroxidase.

Yoshiharu Machii, Hirofumi Hirai, Shingo Kawai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: 3-*Tert*-butyl-4-hydroxyanisole (BHA), which is a phenolic compound widely used as an antioxidant for foods and cosmetics, displays both mutagenic and estrogenic activities. Therefore, we investigated whether manganese peroxidase (MnP) can degrade and remove the mutagenic activity. BHA completely disappeared in the reaction mixture after a 24-h treatment with MnP, and the mutagenic activity of BHA was also completely removed. These results indicate that the MnP is effective in degradation and detoxification of BHA. The GC-MS analyses indicated that the major metabolite of BHA is 2,2'-dihydroxy-5,5'-dimethoxy-3,3'-di-*tert*-butylbiphenyl (M1).

2004-P17

白色腐朽担子菌による塩素化ダイオキシン類の分解特異性

<sup>\*1</sup> 亀井一郎、<sup>\*2</sup> 近藤隆一郎

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究院

Specificity for the degradation of polychlorinated dioxins by white-rot fungi

Ichiro Kamei<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Graduate School of Agriculture, Kyushu University

Abstract: The model compounds of polychlorinated dibenzo-*p*-dioxins (PCDDs), 2,7-dichloro-, 2,3,7-trichloro-, 1,2,6,7-, 1,2,8,9-, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin and the model compounds of polychlorinated dibenzofuran, 2,8-dichloro-, 2,4,8-trichlorodibenzofuran were used as substrate for degradation experiment by white-rot fungi *Phlebia lindtneri*, and *Phlebia brevispora*. In the cultures

treated with *P. lindtneri*, the degradation rate of 1,2,6,7-tetraCDD was higher than that of 2,3,7-triCDD, and no degradation of 1,3,6,8-tetraCDD was observed. These results indicate that the degradation of PCDDs depend more strongly chlorinated position than the number of chlorinated substituents. Degradation rate of polychlorinated dibenzofuran was lower than that of polychlorinated dibenzo-*p*-dioxin. On the other hand, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin, 2,8-dichloro, and 2,4,8-trichlorodibenzofuran were degraded by *P. brevispora*. Monohydroxylated and monomethoxylated compounds were detected as metabolite from the cultures treated with *P. brevispora*.

## 第 50 回 (2005.10.19-20)名古屋大学 野依記念学術交流館

2005-101

マツ木部組織における過ヨウ素酸リグニンの ToF-SIMS 測定

斉藤香織<sup>\*1</sup>、寺島典二<sup>\*2</sup>、加藤俊之<sup>\*3</sup>、福島和彦<sup>\*1</sup>

<sup>1</sup>名古屋大学大学院生命農学研究科、<sup>2</sup>名古屋、<sup>3</sup>名古屋大学全学技術センター

Investigation of periodate lignin from *Pinus thunbergii* xylem using ToF-SIMS

Kaori Saito<sup>\*1</sup>, Noritsugu Terashima<sup>\*2</sup>, Toshiyuki Kato<sup>\*3</sup>, and Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, <sup>\*2</sup>2-61 0 Uedayama, Tenpaku, Nagoya, <sup>\*3</sup>Technical Center, Nagoya University

Abstract: Periodate lignin structures of the differentiating xylem of normal and compression wood of pine were investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS). In a previous study, the morphological features of lignin have shown to be retained after the removal of polysaccharides by periodate oxidation. Xylem tissue samples were pre-methylated with CH<sub>2</sub>N<sub>2</sub> to protect free-phenolic groups in lignin from undesirable oxidative modification, and then were treated with periodate. The spectra of compression wood treated with periodate showed both the ions derived from units having free-phenolic groups and the ions derived from lignin units having a methylated phenolic hydroxyl group at m/z 165 for guaiacyl and at m/z 135 for *p*-hydroxyphenyl units. Comparison of the ToF-SIMS spectra of untreated, CH<sub>2</sub>N<sub>2</sub>-treated, and CH<sub>2</sub>N<sub>2</sub>-periodate-treated samples gave a good explanation for the behavior of periodate oxidation observed in intact xylem tissues of wood.

2005-102

<sup>13</sup>C 標識テトラメチルアンモニウムヒドロキシドを用いた熱分解-メチル化によるリグニンの分析  
黒田健一<sup>\*1</sup>、中川明子<sup>\*2</sup>、T. R. Filley<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院農学研究院、<sup>\*2</sup>筑波大学大学院生命環境科学研究科、<sup>\*3</sup>Purdue University

<sup>13</sup>C-Labeled tetramethylammonium hydroxide (TMAH) thermochemolysis of lignin.

Ken-ichi Kuroda<sup>\*1</sup>, Akiko Nakagawa-izumi<sup>\*2</sup>, Timothy R. Filley<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Agriculture, Kyushu University, <sup>\*2</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, <sup>\*3</sup>Department of Earth and Atmospheric Sciences, Purdue University

Abstract: A bulk dehydrogenation polymer of coniferyl alcohol (G-DHP) and a Japanese cedar wood were methylated with diazomethane and subjected to <sup>13</sup>C-labeled tetramethylammonium hydroxide (<sup>13</sup>C-TMAH) thermochemolysis (315°C/4s). Products having diazomethane- and analytically-added methyl groups were transferred to GC/MS. MS data of the products showed that

(1) veratrylaldehyde (2),  $\beta$ ,3,4-trimethoxystyrene (5) extensively stemmed from nonphenolic  $\beta$ -aryl ether subunits, and 1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane (7) stemmed from both phenolic and nonphenolic  $\beta$ -aryl ether subunits, (2) the DHP had phenolic guaiacylglycerol moieties involved in  $\beta$ -aryl ether linkages in a larger abundance than nonphenolic ones, in contrast to the wood lignin, (3) coniferyl alcohol dimethyl ether (6) observed in the DHP pyrogram stemmed from 4-*O*-etherified coniferyl alcohol and 6 produced from the wood stemmed from both 4-*O*- and  $\gamma$ -*O*-etherified coniferyl alcohols in roughly equal amounts, (4) pinoresinol dimethyl ether (11) showed the  $M^+$  ions both at  $m/z$  387 and  $m/z$  388 in a roughly 1:2 signal intensity ratio, suggesting that 1/3  $\beta$ - $\beta$  subunits are present at the terminal of the DHP network, and (4) stilbenes 8-10 showed the molecular ion at  $m/z$  373, suggesting that these stem from terminal  $\beta$ -5 subunits.

2005-103

酸性条件下におけるリグニン  $\beta$ -O-4 結合解裂機構の再評価(1)

横山朝哉、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Reinvestigation of the mechanism of lignin  $\beta$ -O-4 bond cleavage under acidic conditions. (1).  
-Experiments using  $C_6-C_2$  model compounds.

Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, The University of Tokyo

Abstract: Acidolysis of lignin containing materials has widely been applied as a method for isolation as well as structural analysis of lignin. The most important chemical reaction in these methods is the cleavage of  $\beta$ -O-4 bond in lignin. Although the mechanism of the cleavage has been postulated, it seems not to be rationale when the known phenomenon, the rate of the cleavage is dependent on the concentration and kind of acid, is taken into consideration. The objective of this research is to propose a more rationale mechanism for the cleavage of lignin  $\beta$ -O-4 bond in acidolysis and to examine its kinetic in detail. To avoid complexities of the reaction caused by the presence of  $\gamma$ -hydroxymethyl group, a  $C_6-C_2$  model compound was used in this paper. The model was subjected to an acidolysis under various conditions and its degradation and kinetic were thoroughly examined.

2005-104

モノリグノール配糖体の HRP 触媒脱水素重合

飛松裕基、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

HRP catalyzed dehydrogenative polymerization of monolignol glucosides.

Yuki Tobimatsu, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Graduate School of Agriculture, Kyoto University

Abstract: High yields synthesis of (*E*)-isoconiferin, (*E*)-triandrin and (*E*)-isosyringin, which had a hydrophilic D-glucose unit on their  $\gamma$  positions of the respective monolignols, were established and their HRP catalyzed polymerizations in homogeneous systems were conducted. Under optimum conditions, isoconiferin and triandrin gave polymers with  $DP_n = 42-47$  in high yields, while the  $DP_n$  of conventional DHPs were around 10. But the polymerization of isosyringin gave a polymer in only 28% yield and the  $DP_n$  of the polymer was in the same range with that of DHP from sinapyl alcohol. The copolymerization of isosyringin and isoconiferin, however, gave a copolymer with  $DP_n = 27$  in 80% yield.

2005-105

形質転換樹木リグニンの迅速分析 —透過型近赤外分光法の応用—

山田竜彦<sup>\*1\*2</sup>、Ting-Feng Yeh<sup>\*1</sup>、Hou-min Chang<sup>\*1</sup>、John F. Kadla<sup>\*3</sup>、Laigeng Li<sup>\*1</sup>、Vincent L Chiang<sup>\*2</sup>  
<sup>\*1</sup> ノースカロライナ州立大学、<sup>\*2</sup> 森林総合研究所、<sup>\*3</sup> ブリティッシュコロンビア大学

Rapid analysis of transgenic tree lignin. Application of transmittance near infrared spectroscopy.  
Tatsuhiko Yamada<sup>\*1\*2</sup>, Ting-Feng Yeh<sup>\*1</sup>, Hou-min Chang<sup>\*1</sup>, John F. Kadla<sup>\*3</sup>, Laigeng Li<sup>\*1</sup>, Vincent L Chiang<sup>\*1</sup>

<sup>\*1</sup>North Carolina State University, <sup>\*2</sup>Forestry and Forest Products Research Institute, <sup>\*3</sup>University of British Columbia

Abstract: Our extensive functional genomic research on lignin biosynthesis has produced highly improved transgenic trees. To efficiently monitor and control the properties of the transgenic products a rapid mini scale analytical method is required. Transmittance near infrared (NIR) spectroscopy was chosen as a rapid lignin analysis tool. Pellets were prepared from 75 mg of wood meal and directly scanned. Very strong correlations were obtained between the conventional wet chemistry results and the NIR data for lignin content and S/G ratio. The results indicate that transmittance NIR is a powerful tool for determining and screening the chemical properties of transgenic trees.

2005-106

酸素処理過程におけるリグニン構造変化の赤外分光法による解析(4) —酸素処理に抵抗性を示すフェノール類の生成について—

矢田実、飯塚堯介

東京大学大学院農学生命科学研究科

Infrared study of structural changes of lignin during oxygen treatment : part 4. Generation of resistant phenolic structure to oxygen treatment.

Minoru Yada, Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: For the fundamental study of oxygen delignification of kraft pulp, structural changes of kraft lignin during alkaline oxygen treatment was studied. At the early phase of the treatment, not only the generation of muconate substructure but the generation of some resistant phenolic substructures toward the treatment were suggested from the measurement of UV-VIS spectra at various pH. Furthermore formation of carbonyl groups was indicated by the time series analysis of infrared ATR spectra. Correlation analysis between this carbonyl band and other infrared bands under pH perturbation indicated that a part of carbonyl groups should be conjugated with phenolic substructure. In addition, the time series analysis of <sup>1</sup>H-NMR indicated that changes of the structural circumstance of a methoxyl group were occurred by the modification of a side chain part of lignin structure. These three results could be explained by the generation of a phenolic substructure conjugated with a carbonyl group, and  $\sigma$ -vanillin type phenolic structure formed by the olefinic side chain cleavage of  $\sigma$ - $p$ -stilbene moiety can be a possible structure. Here, a stilbene structure should be generated from a phenolic phenylcoumaran moiety as the result of kraft cooking.

2005-107

美唄泥炭湿地からの水溶性有機物の分析

勝亦京子、Zhenfu Jin、堀啓映子、飯山賢治

東京大学大学院農学生命科学研究科

Chemical feature of dissolved organic matter from Bibai swamp.

Kyoko S. Katsumata, Zhenfu Jim, Keeko Hori, Kenji Iiyama

Graduate School of Agricultural and Life Sciences, the University of Tokyo

**Abstract:** Water passed through peat swamp colored in brown to dark brown by dissolving organic matters (DOM). When the DOM in water now in ocean, such DOM could form chelates with metal ions in ocean water. The chelates would be insoluble in ocean water, and accumulate at the ocean bed as sediments. Lignin, which is significantly resist to biological decomposition, is the major component of DOM, has high ability of chelate formation. The behavior of water-soluble lignin is significantly important factor for global carbon circulation, but quite limited information is available. We started to investigate to make clear chemical structure of water-soluble lignin under natural condition and reaction under global system. The DOM was isolated from water at Bibai peat swamp in Hokkaido, the chemical feature of the DOM was analysed using some wet and spectrometric analyses. The major component of DOM would be highly modified lignin by activities of microorganisms.

2005-108

Characteristics of bast and core lignins of kenaf (*Hibiscus cannabinus*) and mulberry (*Morus bombycis*).

Zhenfu Jin, Kenji Iiyama

Graduate School of Agricultural and Life Sciences, the University of Tokyo

**Abstract:** Structural characteristics of bark and core lignins from kenaf (*Hibiscus cannabinus*), paper mulberry (*Broussonetia kazinoki*) and mulberry (*Morus bombycis*) were examined. All of bark fractions gave lower Klason lignin contents than those of core fractions. Kenaf bark exhibited significantly high S/V molar ratio. High ratio of *elythro*- to *threo*-form (E/T ratio) of  $\beta$ -O-4 structure in lignin of kenaf bark was confirmed by both ozonation and  $^1\text{H-NMR}$  analysis. Lignin structure of kenaf bark was comparable to core lignin while paper mulberry and mulberry bark exhibited quite different lignin characteristics comparing to core lignin.

2005-109

Feasibility of branch of young *Acacia mangium* Willd as raw material for pulp and paper manufacture.

Ridwan Yahya<sup>\*1\*2</sup>, Takuya Akiyama<sup>\*2</sup>, Gyosuke Meshitsuka<sup>\*2</sup>, Yuji Matsumoto<sup>\*2</sup>

<sup>\*1</sup>Bengkulu University, <sup>\*2</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo

**Abstract:** To examine the feasibility of branch of *Acacia mangium* with diameter less than 8 cm as a raw material for pulp production, we carried out a systematic fundamental study. Those branches are usually left on the ground as logging wastes in a plantation. Based on their chemical composition and fiber dimensions, we concluded that the quality of branches of *A. mangium* is as good as its trunks as raw materials for pulp and paper production. It was also suggested that yield and qualities of pulps might not be spoiled significantly even if branches with bark are subjected to pulping with trunks.

2005-110

Ozone bleaching for the low-kappa-number kraft pulp of wheat straw.

Miaomiao Cao<sup>\*1</sup>, Guolin Tong<sup>\*1</sup>, Guoxin Xue<sup>\*1\*2</sup>

<sup>\*1</sup>Nanjing Forestry University, <sup>\*2</sup>Zhejiang University of Science and Technology

**Abstract:** This study has investigated the ozone bleaching for low-kappa-number kraft pulp of wheat straw, and the low-kappa-number kraft pulp was produced by the one stage extended delignification technology. Results showed 86.9% (SBD) brightness of bleached pulp could be achieved and the viscosity of the pulp could be 551ml/g after the AZEYP bleaching sequences. Lignin is the natural protector to carbohydrate. The Ozone delignification is important and benefit for

TCF bleaching.

2005-111

Synthesis and properties of cationic lignin surfactant.

Yiqin Yang, Guolin Tong, Zhongzheng Li

College of Chemical Engineering, Nanjing Forestry University

Abstract: Cationic lignin surfactant was synthesized by reacting kraft lignin with quaternary ammonium salt cationic 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTMAC). The effects of CHPTMAC dosage, NaOH dosage, reaction temperature and reaction time on the surface activity, nitrogen content and solubility of cationic lignin surfactants were studied. The results indicated the suitable synthesis conditions of cationic lignin surfactant were as follows: the dosage of quaternary ammonium salt (CHPTMAC) was 4 mol/kg lignin, the molar ratio of NaOH to quaternary ammonium salt agent was 1.3, reaction temperature was 50°C and reaction time was 4 h. Synthesized cationic lignin surfactant had good solubility under different pH value, the highest nitrogen content was 2.57% and the lowest surface tension of them was reached 42.7 mN/m.

Keywords: kraft lignin, quaternary ammonium salt, cationic lignin surfactant, nitrogen content, surfactivity.

2005-112

リグニン含有するヒドロキシプロピルセルロースゲルの熱的性質とゲスト分子との相互作用

浦木康光、井村健、岸本崇生、生方信

北海道大学大学院農学研究科

Thermal property of hydroxypropylcellulose bearing lignin gel and its interaction with guest molecules.

Yasumitsu Uraki, Takeshi Imura, Takao Kishimoto, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: Hydroxypropylcellulose bearing lignin (HPC-L) was prepared from unbleached acetic acid pulp of Todo-fir. The pulp derivative was converted to hydrogel with ethyleneglycol diglycidyl-ether as a crosslinker. The resultant gel showed exothermic peak in differential scanning calorimetry, of which temperature was consistent with that of gel shrinking. The temperature was elevated by adsorption of ionized dye. Thus, the thermal property was altered by the interaction with guest molecules. In addition, the gel showed different swelling behaviors upon interaction with ionic and nonionic surfactants.

2005-113

HBS パルプ化の実証試験—リグニン利用の可能性—

生方信<sup>\*1</sup>、植木飛鳥<sup>\*1</sup>、三橋進也<sup>\*1</sup>、岸本崇生<sup>\*1</sup>、浦木康光<sup>\*1</sup>、藤田進一郎<sup>\*2</sup>

<sup>\*1</sup>北海道大学大学院農学研究科, <sup>\*2</sup>北海道大学大学院工学研究科

Verification test of HBS-pulping: Possibility of lignin utilization.

Makoto Ubukata<sup>\*1</sup>, Asuka Ueki<sup>\*1</sup>, Shinya Mitsuhashi<sup>\*1</sup>, Yasumitsu Uraki<sup>\*1</sup>, Shinichiro Fujita<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, <sup>\*2</sup>Graduate School of Engineering, Hokkaido University

Abstract: Y. Sano et al. developed the HBS-pulping method that could operate even on a small scale at a native locality of woody biomass. We undertook a verification test of this method including HBS pulping of softwood and agricultural husks, preparation of monosaccharide by pre-hydrolysis, enzymatic saccharization of HBS pulp, quality of silica contained in agricultural husks, preparation of fiberboard, application of HBS lignin to medical field, feasibility study and conceptual design of HBS-

pulping process. In this symposium, we report the results of the verification test of HBS pulping from the point of view of lignin utilization.

2005-114

酢酸リグニン/合成ポリマー複合体の調製と分子間相互作用の評価

寺本好邦、田中紀子、遠藤貴士

産業技術総合研究所

Preparation and characterization of intermolecular interaction of organosolv lignin, acetate / synthetic polymer composites.

Yoshikuni Teramoto, Noriko Tanaka, Takashi Endo

National Institute of Advanced Industrial Science and Technology

Abstract: Binary blends and pseudo complexes of organosolv lignin, acetate (OSL-Ac) with poly(*N*-vinyl pyrrolidone) were prepared, respectively, by casting from mixed polymer solution in *N,N*-dimethylformamide as good solvent and by spontaneous co-precipitation from solutions in tetrahydrofuran as comparatively poor solvent. Fourier transform infrared measurements revealed the presence of rather stronger hydrogen-bonding interactions between hydroxyls of OSL-Ac and carbonyls of *N*-vinyl pyrrolidone units for the complexes than those for the blends. Thermal transition data obtained by differential scanning calorimetry suggested that the blends are miscible, whereas, for the complexes, a high frequency of interactions combined OSL-Ac with PVP intimately in the complexes to reduce the mobilities of the individual polymer chains.

2005-115

リグニンベースのポリイオンコンプレックスの調製と機能開拓

長谷川大輔<sup>\*1</sup>、寺本好邦<sup>\*2</sup>、西尾嘉之<sup>\*1</sup>

<sup>\*1</sup> 京都大学大学院農学研究科、<sup>\*2</sup> 産業技術総合研究所

Preparation and functionalization of lignin-based poly-ion complex.

Daisuke Hasegawa<sup>\*1</sup>, Yoshikuni Teramoto<sup>\*2</sup>, Yoshiyuki Nishio<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Agriculture, Kyoto University, <sup>\*2</sup> National Institute of Advanced Industrial Science and Technology

Abstract: Poly-ion complexes of anionic lignosulfonic acid (LSA) with cationic poly(2-vinyl pyridine) or poly(4-vinyl pyridine) were prepared by spontaneous precipitation from solutions in dimethyl sulfoxide or diluted hydrochloric acid. Fourier transform infrared measurement for the complexes revealed the presence of strong ionic interactions between sulfonic anion of LSA and pyridinium cation of vinylpyridine (VPy) polymer. The emergence of the strong interaction was supported by striking elevation of glass transition temperature in differential scanning calorimetry measurements. Subsequently, thin-layered coating of lignin on VPy polymer films was conducted successfully to vary their surface property, as evidenced through visualization of the LSA component by atomic force microscopy.

2005-116

リグニンベース木質粒子分散型ポリウレタン複合体パネルの調製と物性

畠山兵衛<sup>\*1</sup>、南保貴士<sup>\*1</sup>、廣瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

<sup>\*1</sup> 福井工業大学工学部、<sup>\*2</sup> 産業技術総合研究所、<sup>\*3</sup> リグノセルリサーチ

Preparation and mechanical properties of wood panel with lignin-based polyurethane composites.

Hyo Hatakeyama<sup>\*1</sup>, Takashi Nanbo<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup> Fukui University of Technology, <sup>\*2</sup> National Institute of Advanced Industrial Science and Technology

<sup>\*3</sup> Lignocell Research Co.

Abstract: Wood panels with kraft lignin (KL)-based polyurethane (PU) composites were prepared using three kinds of ethylene glycols, such as diethylene glycol, triethylene glycol or polyethylene glycol. Wood powder and coffee residue were used as fillers. Filler content (=filler/polyol, g/g) in KL polyol was varied from 50 to 100 %. Apparent density and mechanical properties of wood panels with the above PU composites were investigated as functions of filler contents and molecular mass of ethylene glycol. Flexural strength calibrated with apparent density was correlated with filler content. For the panel with PU composites filled with wood powder, the optimum point was observed at around filler content 70 to 80 %. Modulus of elasticity ranged from 3 to 6 GPa, suggested that panels obtained in this study are sufficiently strong for practical applications.

2005-特別講演

リグニン化学構造の不均一性

飯塚 堯介

東京大学大学院農学生命科学研究科

Structural heterogeneity of lignin.

Gyosuke Meshitsuka

Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Structural heterogeneity seems to be a key to understand the real structure of lignin and to discuss how lignin is deposited in the course of cell wall formation. Structure of lignin is believed to be not homogeneous in wood, but to be different dependent on the tissues of wood fiber, vessel and ray cell, on the cell wall layers of middle lamella, primary wall and secondary wall, and even in a lignin molecule. In order to characterize a lignin in a particular layer of cell wall, the fractionation of disintegrated wood and the separation of differentiating xylem were introduced. By these methods, structural characteristics of lignin in the compound middle lamella were obtained. It is well known that Milled Wood Lignin (MWL) does not represent whole lignin in wood but is originated from the compound middle lamella at least in the case of hardwood MWL obtained at the early stage of milling. Ozonation is truly epoch-making for the structural analysis of lignin, by which stereostructural characteristics of lignin side chain part were obtained, and  $\beta$ -O-4 structure in lignin was for the first time confirmed to be in a racemic form and optically inactive. It is also important to note that syringaldehyde ratio by alkaline nitrobenzene oxidation and erythronic acid ratio by ozonation are in a linear relationship. Development of new and controlled degradation methods and advanced microscopic technologies may open a new stage for the study of the structural heterogeneity of lignin.

2005-201

イネをモデルとした植物細胞壁形成過程に関する研究 -糖代謝系とシキミ酸経路、フェニルプロパノイド経路との共役、及びその遺伝子発現制御機構-

中野仁美<sup>\*1</sup>、佐藤かな<sup>\*1</sup>、間瀬浩平<sup>\*1</sup>、半智史<sup>\*2</sup>、西窪伸之<sup>\*1\*3</sup>、北野秀己<sup>\*4</sup>、船田 良<sup>\*2</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 農工大院農学教育部、<sup>\*3</sup> 理化学研究所植物科学研究センター、<sup>\*4</sup> 名古屋大学生物機能開発利用研究センター

Study for the process of cell wall formation in rice plant. - Conjugation and regulation of gene expressions among three metabolic pathways, carbohydrate metabolism, shikimate pathway and phenylpropanoid pathway.

Yoshimi Nakano<sup>\*1</sup>, Kanna Sato<sup>\*1</sup>, Kohei Mase<sup>\*1</sup>, Satoshi Nakaba<sup>\*2</sup>, Nobuyuki Nishikubo<sup>\*1\*3</sup>, Hidemi

Kitano<sup>\*4</sup>, Ryo Funada<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Graduate School of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*3</sup>RIKEN Plant Science Center, <sup>\*4</sup>Bioscience and Biotechnology Center, Nagoya University

Abstract: Plant cell walls contain polysaccharides-linked hydroxycinnamoyl ethers (PHEs) which consist of the ester-linkages between hydroxycinnamic acid derivatives such as ferulic acid (PA), *p*-coumaric acid (*p*CA) and cell wall matrix polysaccharides. Those hydroxycinnamic acids, in the Gramineae, mainly compose the ester linkages mainly with arabinoxylan or slightly with xyloglucan. They also compose ether-linkages with cell wall lignin units to form covalent ester-ether bridges between polysaccharides and lignins. A novel rice dwarf mutant Fukei 71 is found ectopically accumulating PHEs in the cell walls of internode pith parenchyma. We have pursued molecular and genetic analyses with Fukei 71 in order to clear PHEs biosynthesis in rice.

2005-202

イネをモデルとした植物細胞壁形成過程に関する研究 -Glycosylphosphatidylinositol-anchored protein はイネの細胞壁高次構造形成にどのように関わるのか？

鈴木瑠<sup>\*1</sup>、武内佐知<sup>\*1</sup>、佐藤かな<sup>\*1</sup>、半智史<sup>\*2</sup>、北野英己<sup>\*3</sup>、船田良<sup>\*2</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>農工大院農学教育部、<sup>\*3</sup>名古屋大学生物機能開発利用研究センター

Study of plant cell wall formation in *Oryza sativa* L. -How does glycosylphosphatidylinositol-anchored protein relate to cell wall conformation in rice plant (*Oryza sativa* L.).

Ryu Suzuki<sup>\*1</sup>, Sachi Takenouchi<sup>\*1</sup>, Kanna Sato<sup>\*1</sup>, Satoshi Nakaba<sup>\*2</sup>, Hidemi Kitano<sup>\*3</sup>, Ryo Funada<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup>Graduate school of Agriculture, Tokyo University of Agriculture and Technology, <sup>\*3</sup>Bioscience and Biotechnology Center, Nagoya University

Abstract: The advances in microscopy, molecular biology and genomics converged to make work easier for biologists to study the mechanism and process of cell wall conformation. Many biologists used *Arabidopsis thaliana* as a model plant to study cell wall conformation, and they revealed there are many genes involved in plant cell wall conformation. But few knowledge came out about detailed mechanism and process of wall formation. In this study, we used brittle culm mutant called *cwa1*, recessive mutant rice plant (*Oryza sativa* L.), to obtain new information about plant cell wall conformation which are not revealed in *Arabidopsis* study.

2005-203

ゴマの機能性リグナン、特にセサミノールの生合成について

片山健至<sup>\*1</sup>、小堀里恵<sup>\*1</sup>、鈴木利貞<sup>\*1</sup>、並木満夫<sup>\*2</sup>、田代亨<sup>\*3</sup>

<sup>\*1</sup>香川大学農学部、<sup>\*2</sup>おいしさの科学研究所、<sup>\*3</sup>千葉大学園芸学部

Biosynthesis of functional lignans, particularly sesaminol, in *Sesamum indicum* seeds.

Takeshi Katayama<sup>\*1</sup>, Rie Kobori<sup>\*1</sup>, Toshisada Suzuki<sup>\*1</sup>, Mitsuo Namiki<sup>\*2</sup>, Toru Tashiro<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, <sup>\*2</sup>Institute of Oishisa Science, <sup>\*3</sup>Faculty of Horticulture, Chiba University

Abstract: To clarify biosynthesis of sesaminol, one of the strongest antioxidant lignans in sesame seeds, feeding experiments of L-[U-<sup>14</sup>C]phenylalanine (Phe) were carried out. A solution of L-[U-<sup>14</sup>C]Phe (10mM, 20μl) was injected into unripe capsules of 11 week-old (after seeding) intact *Sesamum indicum* plants cultivated in pots and then the plants were cultivated for a week at 26°C. The order of the percent incorporation of the radioactivity into the sesame lignans is as follows:

sesamin > sesamolin > sesaminol ≥ pinoresinol > 7-episesaminol. It was found for the first time that the radioactivity was clearly incorporated into free sesaminol and 7-episesaminol in the seeds in a 100 : 8-9 ratio, but not into those in the pods. The percent incorporation into sesamin, sesamolin, and (+)-pinoresinol, in the seeds was 5-38 times larger than that in the pods.

2005-204

MROMT に相同性の高い新規フラボノイド OMT について

中坪朋文<sup>\*1</sup>、Laigeng Li<sup>\*2</sup>、Vincent L. Chiang<sup>\*2</sup>、服部武文<sup>\*1</sup>、梅澤俊明<sup>\*1</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> ノースカロライナ州立大学

A novel flavonoid *O*-methyltransferase having a high sequence similarity to MROMT.

Tomoyuki Nakatsubo<sup>\*1</sup>, Laigeng Li<sup>\*2</sup>, Vincent L. Chiang<sup>\*2</sup>, Takefumi Hattori<sup>\*1</sup>, Toshiaki Umezawa<sup>\*1</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, <sup>\*2</sup>College of Natural Resources, North Carolina State University

Abstract: *Carthamus tinctorius* maturing seeds produce various secondary metabolites such as lignans, lignin, flavonoids, and serotonin amides of cinnamates. Recently, Umezawa et al. reported the cloning of the novel gene encoding lignan *O*-methyltransferase (matairesinol *O*-methyltransferase, *CtMROMT*) using *C. tinctorius* maturing seeds. In addition, they cloned a cDNA which shows a high sequence similarity to *CtMROMT* named *CtMROMTlike*. The present study identified the function of *CtMROMTlike*. Thus, the recombinant *CtMROMTlike*, expressed in *E. coli*, did not catalyze *O*-methylation of matairesinol, but catalyzed *O*-methylation of a flavonoid, apigenin, indicating clearly that *CtMROMTlike* was flavonoid *O*-methyltransferase (FOMT), but not MROMT.

2005-205

*Arabidopsis thaliana* の細胞分裂機構を用いた樹木資源の生産制御に関する研究

松井紀子<sup>\*1</sup>、武内 佐知<sup>\*1</sup>、西窪伸之<sup>\*1\*2</sup>、半智史<sup>\*3</sup>、船田良<sup>\*3</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 理化学研究所植物科学研究センター、<sup>\*3</sup> 農工大院農学教育部、  
Research on production control of woody resources with cell division mechanisms of *Arabidopsis thaliana*.

Noriko Matsui, Sachi Takenouchi, Nobuyuki Nishikubo, Satoshi Nakaba, Ryo Funada, Shinya Kajita, Yoshihiro Katayama

<sup>\*1</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, <sup>\*2</sup> Plant Science Center, RIKEN, <sup>\*3</sup> Graduate School of Agriculture, Tokyo University of Agriculture and Technology

Abstract: The mechanisms by which plants modulate their growth rate in response to environmental and developmental conditions are unknown, but are presumed to involve specialized regions meristems where cells division is concentrated. In plant, as in other eukaryotes, the cell cycle consists of four different phases-G1(gap1),S(DNA synthesis), G2(gap2),and M(mitosis) phases. The G1/S transition generally represents the principal point of commitment to cell division. Many of the components of the cell cycle core machinery regulating the G1/S transition in plant have been recently identified. In this study, we examined regulation cell division in vascular cambium with G1/S related genes, AtE2F, AtDP, AtCycD.

2005-206

植物ペルオキシダーゼの生理機能解明に向けたプロテオミクス

佐々木慎弥<sup>\*1</sup>、江藤佑<sup>\*2</sup>、志水元亨<sup>\*3</sup>、割石博之<sup>\*3</sup>、堤祐司<sup>\*3</sup>、近藤隆一郎<sup>\*3</sup>

<sup>\*1</sup> 九州大学大学院生物資源環境科学研究科、<sup>\*2</sup> 九州大学農学部、<sup>\*3</sup> 九州大学大学院農学研究院  
Proteomic studies for physiological function of plant peroxidases.

Shinya Sasaki\*<sup>1</sup>, Yu Eto\*<sup>2</sup>, Motoyuki Shimizu\*<sup>3</sup>, Hiroyuki Wariishi\*<sup>3</sup>, Yuji Tsutsumi\*<sup>3</sup>, Ryuichiro Kondo\*<sup>3</sup>  
\*<sup>1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, \*<sup>2</sup>Faculty of Agriculture, Kyushu University, \*<sup>3</sup>Graduate School of Agriculture, Kyushu University

Abstract: Higher plants possess a large set of the classical plant peroxidases. These peroxidases are thought to participate in a wide range of physiological functions. However, the most of them have been unclear. Using proteomic analysis, we surveyed the localization of plant peroxidase in various organs in *Populus alba* L. Peroxidase isoenzymes were extracted from the various organs and fractionated by a Concanavallin A Sepharose column. Approximately 20 protein spots were detected by the two-dimensional electrophoresis gels. Some anionic peroxidase isoenzymes were identified via the PMF analysis. One of the anionic peroxidases would be xylem and inner bark specific peroxidase.

2005-207

*Phanerochaete crassa* WD1694 の菌体外スライムと菌体外ペルオキシダーゼ活性染色について  
高野麻理子、林 徳子  
森林総合研究所

Slime of *Phanerochaete crassa* WD 1694 and its relationship to extracellular peroxidase activity staining.

Mariko Takano, Noriko Hayashi

Forestry and Forest Products Research Institute

Abstract: Distribution of slime of the white-rot fungi *Phanerochaete crassa* WD1694 was studied by a microscope with phloxine B coloration and phase contrast technique. The slime was occurred inside of each mycelial pellets grown in the shaken culture containing unbleached kraft pulp. Hyphal tips that caused extracellular peroxidase staining did not had slime around the hyphae. Besides the strong coloration of extracellular peroxidase staining at the hyphal tips and on the hyphae protruding from mycelial pellets, the staining also occurred on the hyphae inside of the mycelial pellets and in slime among the hyphae. The results suggested that the localization of extracellular peroxidase staining on the mycelium was mainly due to the generation of oxidant at the hyphal tips and on the hyphae, and was also caused by fungal slime that might keep the generated oxidants.

2005-208

MnP による異常プリオンタンパク  $\beta$ -シート構造の分解

岩村翼\*<sup>1</sup>、堤祐司\*<sup>2</sup>、近藤隆一郎\*<sup>2</sup>、松浦裕一\*<sup>3</sup>、毛利資郎\*<sup>3</sup>

\*<sup>1</sup>九州大学大学院生物資源環境科学研究科、\*<sup>2</sup>九州大学大学院農学研究院、\*<sup>3</sup>九州大学大学院医学研究院

Degradation of  $\beta$ -sheet structure of protease-resistant prion protein by MnP.

Tsubasa Iwamura, Yuji Tsutsumi, Ryuichiro Kondo, Yuichi Matsuura, Shirou Mohri

\*<sup>1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, \*<sup>2</sup> Graduate School of Agriculture, Kyushu University, \*<sup>3</sup>Graduate School of Medical Science, Kyushu University

Abstract: Protease Resistant Prion Protein (PrP<sup>Res</sup>) is a causal substance of bovine spongiform encephalopathy (BSE) and other prion diseases. PrP<sup>Res</sup> has a high content of  $\beta$ -sheet structure, and can not be degraded either by proteases or usual chemical treatments. Thus, convincing method for the decontamination of PrP<sup>Res</sup> is urgently required. We reported that PrP<sup>Res</sup> was completely degraded by 8 white-rot fungi and its crude extracellular enzyme. In this study, we assessed the PrP<sup>Res</sup> infectious after the treatment by white-rot fungi. When PrP<sup>Res</sup> was treated with *Ceriporia lacerata* MZ-340, intracerebral bioassay showed virtually no infectivity. In addition, keratin

that has a high content of  $\beta$ -sheet structure as well as PrP<sup>Res</sup> was also completely degraded by purified MnP from *C. lacerata* MZ-340. These results support that MnP produced by *C. lacerata* MZ-340 can degrade  $\beta$ -sheet structure.

2005-209

土壤浄化を指向した白色腐朽菌のスクリーニング

天野智絵、平井浩文、河合真吾、西田友昭

静岡大学農学部

Screening of white rot fungi aiming for soil remediation.

Chie Amano, Hirofumi Hirai, Shingo Kawai, Tomoaki Nisida

Faculty of Agriculture, Shizuoka University

Abstract: White rot fungus, tentatively named AG-200, which extensively degrades white birch (*Betula platyphylla* var *japonica*) wood-lignin was isolated by using hardwood kraft pulp and agar medium containing guaiacol. The partial sequencing data of 18S ribosomal DNA and the shape of fruit body suggested that the fungus AG-200 belongs to *Amauroderma* sp.. Great interest is currently being expressed in white rot fungi and their ligninolytic enzymes due to recognized potential for degrading and detoxifying recalcitrant environmental pollutants such as dioxins. For practical application of white rot fungus to soil remediation, it is important that the fungus is resistant to contamination by autochthonous microorganisms in soil. Thus, we investigated whether AG-200 can degrade wood-lignin under highly acidic condition (pH 2.5) in which the grow of autochthonous microorganisms such as bacteria is inhibited. AG-200 had over 50% Klason lignin loss for 4 weeks of incubation under acidic and natural (pH 6) conditions, while the ligninolytic activities of *Phanerochaete sordida* YK-624 and IZU-154 were influenced by pH and markedly decreased under acidic condition. Therefore, it might be possible to use the acid-resistant fungus AG-200 for bioremediation of soil contaminated with aromatic compounds. Practical application of AG-200 to soil remediation should be the subject of a forthcoming study.

2005-210

リグニン分解酵素による 4-tert-オクチルフェノールのエストロゲン様活性除去

玉川祐基、平井浩文、河合真吾、西田友昭

静岡大学農学部

Removal of estrogenic activity of 4-tert-octylphenol by ligninolytic enzymes.

Yuuki Tamagawa, Hirofumi Hirai, Shingo Kawai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: 4-tert-Octylphenol (4-TOP) is widely used in a variety of industrial and residential applications, and is suspected of having estrogenic (endocrine-disrupting) activity. Thus, 4-TOP was treated with the white rot fungi, *Phanerochaete sordida* YK-624 and *Trametes versicolor*, under ligninolytic condition with low-nitrogen and high-carbon culture medium. 4-TOP decreased by over 90% within 6 days of treatments with the two fungi and the activities of ligninolytic enzymes, manganese peroxidase (MnP) and laccase, were detected during treatment, which suggested that the disappearance of 4-TOP is related to ligninolytic enzymes produced extracellularly by white rot fungi. Therefore, 4-TOP was treated with MnP and laccase prepared from the culture of white rot fungi. Using the yeast two-hybrid assay system, it was confirmed that both enzymatic treatments completely removed the estrogenic activity of 4-TOP after 2 h. This result strongly suggests that ligninolytic enzymes are effective in removing the estrogenic activity of 4-TOP.

2005-211

白色腐朽菌 *Phlebia brevispora* による PCB の代謝変換

亀井一郎<sup>\*1</sup>、其木茂則<sup>\*2</sup>、原口浩一<sup>\*3</sup>、近藤隆一郎<sup>\*4</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>麻布大学環境保健学部、<sup>\*3</sup>第一薬科大学、<sup>\*4</sup>九州大学大学院農学研究科

Fungal metabolism of polychlorinated biphenyls by white rot fungus *Phlebia brevispora*.

Ichiro Kamei<sup>\*1</sup>, Sigenori Sonoki<sup>\*2</sup>, Koichi Haraguchi<sup>\*3</sup>, Ryuichiro Kondo<sup>\*4</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>College of Environmental Health, Azabu University, <sup>\*3</sup>Daiichi College of Pharmaceutical Science, <sup>\*4</sup>Graduate School of Agriculture, Kyushu University

Abstract: The degradation of individual PCB congeners in the culture of *Phanerochaete sordida*, *Phlebia acerina*, and *Phlebia brevispora* are examined. These fungi showed the different traits of degradation of each compounds. *P. sordida* showed any degradation of tested PCBs. *P. acerina* showed the degradation of 3,3',4,4'-tetraCB, although more chlorinated PCBs were not degraded. On the other hand, in addition to 3,3',4,4'-tetraCB (#77), 2,3,3',4,4'-pentaCB (#105), 2,3',4,4',5-pentaCB (#118), 3,3',4,4',5-pentaCB (#126), and 2,3',4,4',5,5'-hexaCB (#167) were degraded by *P. brevispora*. By GC/MS analysis, methoxylated and dechlorinated metabolites were detected from the culture with these compounds. This is the first report on the biotransformation of toxic coplanar PCBs by fungal strains.

2005-212

木材腐朽菌による PVA フィルムの分解

魯風<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>、二階堂祐子<sup>\*3</sup>、岡 桂子<sup>\*3</sup>、檜垣達彦<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究科、<sup>\*3</sup>クラレ 暮らしき研究所

Biodegradation of PVA film by wood-rotting fungi.

Feng Lu<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>, Yuko Nikaido<sup>\*3</sup>, Keiko Oka<sup>\*3</sup>, Tatsuhiko Higaki<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Graduate School of Agriculture, Kyushu University, <sup>\*3</sup>Kurashiki Research Laboratories, Kuraray Co. Ltd.

Abstract: A polyvinyl alcohol (PVA) film is used for the packing for food and fats, because it is indissoluble in water. Degradation efficiency of solid polymer is important in the viewpoint of material recycle. The screening of wood-rotting fungi for the biodegradation of PVA film was examined. Although no white-rot fungi degraded PVA film, one fungus in *Gloeophyllum* genus, *G. trabeum* degraded PVA film extensively. The clarification of the degradation mechanism of PVA film by this fungus is now on progress.

2005-213

白色腐朽菌から抽出した酵素による Polychlorinated biphenyls (PCBs) 分解の試み

松尾保洋、藤井啓太、伊藤和貴、橘燦郎

愛媛大学農学部

Study on degradation of polychlorinated biphenyls with an enzymes from white rot fungi.

Yasuhiro Matsuo, Keita Fujii, Kazutaka Ito, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Degradation of 3,3',4,4'-Tetrachlorobiphenyl (TCB) with crude enzymes from PL1 and the enzymes isolated from the crude enzymes was investigated. About 40% of TCB was degraded by the crude enzymes in 48 hours in a liquid medium. Manganese peroxidase (MnP), Lignin peroxidase, Laccase and 1,2-Dioxygenase were isolated from the crude enzymes by ion-exchange and gel filtration chromatography. By the degradation of TCB with the isolated MnP in the liquid medium,

about 7% of TCB was degraded in 24 hours. On the contrary, about 2% of TCB was degraded when the degradation of TCB with the immobilized MnP was conducted for 24 hours in the liquid medium. From the results obtained here, it is suggested that MnP in the crude enzymes might not play an important role on the initial stage of degradation of TCB. Furthermore, a degradation pathway of TCB with the crude enzymes was proposed by confirmation of the intermediates.

#### 2005 パネルディスカッション「リグニン研究の過去・現在・未来」

パネリスト: 京都大学名誉教授 越島哲夫、名古屋大学名誉教授 寺島典二、京都大学名誉教授 樋口隆昌、北海道大学大学院農学研究科 浦木康光、九州大学大学院農学研究院 堤祐司、東京大学大学院農学生命科学研究科 横山朝哉  
コーディネーター: 名古屋大学大学院生命農学研究科 福島和彦

#### 2005-P01

##### 爆砕発酵処理バガスの抗酸化能と抗酸化性物質

大原誠資<sup>\*1</sup>、橋田光<sup>\*1</sup>、柏木豊<sup>\*2</sup>、藤野哲也<sup>\*3</sup>、稲福直<sup>\*3</sup>、稲福盛雄<sup>\*3</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 食品総合研究所、<sup>\*3</sup> 琉球バイオリソース開発株式会社

Antioxidant activity of steam-exploded, fermented bagasse and related antioxidant substances.

Seiji Ohara<sup>\*1</sup>, Koh Hashida<sup>\*1</sup>, Yutaka Kashiwagi<sup>\*2</sup>, Tetsuya Fujino<sup>\*3</sup>, Naoshi Inafuku<sup>\*3</sup>, Seiyu Inafuku<sup>\*3</sup>

<sup>\*1</sup> Forestry and Forest Products Research Institute, <sup>\*2</sup> National Food Research Institute, <sup>\*3</sup> Ryukyu Bio-Resource Development Co. Ltd.

Abstract: We have been studying for utilization of bagasse as foodstuffs. In this study, it has been found that steam explosion of bagasse followed by fermentation is an effective pretreatment not only on the formation of xylooligosaccharides, but also on increase in antioxidant activity. In addition, we examined steam explosion products of bagasse to elucidate the reaction mechanism causing the improvement of antioxidant activity. We concluded the following. 1) Antioxidant activity of steam-exploded bagasse is attributed to low molecular weight polyphenols formed during steam explosion. 2) Ferulic acid shows high antioxidant activity, while *p*-hydroxycinnamic acid and *p*-hydroxybenzoic acid don't. Ferulic acid is regarded as one of the compounds responsible for antioxidant activity of steam-exploded bagasse.

#### 2005-P02

##### ニセアカシアのシリングルリグニン生合成経路の探索

植田幸恵<sup>\*1</sup>、中坪朋文<sup>\*2</sup>、梅澤俊明<sup>\*2</sup>、堤祐司<sup>\*3</sup>、近藤隆一郎<sup>\*3</sup>

<sup>\*1</sup> 九州大学大学院生物資源環境科学研究科、京都大学生存圏研究所、<sup>\*2</sup> 九州大学大学院農学研究科、

Search of syringyl lignin biosynthesis in black locust (*Robinia pseudoacacia*).

Yukie Ueda<sup>\*1</sup>, Tomoyuki Nakatsubo<sup>\*2</sup>, Toshiaki Umezawa<sup>\*2</sup>, Yuji Tsutsumi<sup>\*3</sup>, Ryuichirou Kondo<sup>\*3</sup>

<sup>\*1</sup> Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup> Research Institute for Sustainable Humanosphere, Kyoto University, <sup>\*3</sup> Graduate School of Agriculture, Kyushu University

Abstract: It was reported that administered sinapate was incorporated into syringyl lignin of *Robinia pseudoacacia* and that 4CL isoenzyme in *Robinia* utilized sinapate unlike other plant 4CLs. These findings are indicative of an alternative route of syringyl lignin biosynthesis where sinapyl alcohol is biosynthesized passing through sinapate and sinapoyl CoA. We therefore examined 4CL, ALDH, F5H, and COMT enzyme reaction in lignifying xylem of *Robinia* to investigate the biosynthetic pathways of syringyl lignin in *Robinia*. All the enzymes possess a larger substrate preferences toward

syringyl substrates compared to the enzymes in other plant species ever reported. This result is an evidence for the presence of biosynthetic route of syringyl lignin via sinapate.

2005-P03

MWL 抽出残さ木粉に存在するリグニンの性状

藤本文<sup>\*1</sup>、高山雅人<sup>\*1</sup>、松本雄二<sup>\*1</sup>、飯塚堯介<sup>\*1</sup>、Hou-min Chang<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> ノースカロライナ州立大学

Characteristics of lignin structures in MWL isolation residue (MWLR)

Aya Fujimoto<sup>\*1</sup>, Masato Takayama<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>, Hou-min Chang<sup>\*2</sup>, Gyosuke Meshitsuka<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup> Department of Wood and Paper Science, North Carolina State University

Abstract: Beech (*Fagus crenata* Blume) milled woods were extracted with dioxane/water (96 : 4, v/v). The extracts were separated by centrifugation and the insoluble fraction was obtained as MWL isolation residue (MWLR). In this paper, the characterization of lignin in MWLR was tried out. The characteristics of lignin structures in MWLR were analyzed by the ozonation method and alkaline nitrobenzene oxidation method. The *erythro* and syringyl ratios of MWLRs were similar to or slightly higher than those of the corresponding milled woods and always higher than those of corresponding MWLs. These results and the lower *erythro* ratio of MWLR than the original wood meal indicated that lignin in MWLR was never free from structural changes during milling.

2005-P04

$\beta$ -O-4 型人工リグニンポリマーの合成 (4) -モノマー合成ルートの短縮-

岸本崇生、浦木康光、生方信

北海道大学大学院農学研究科

Synthesis of  $\beta$ -O-4 type artificial lignin polymer. (4). - Improved synthetic methods for monomer.

Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: The  $\beta$ -O-4 structure is one of the most important substructures in lignin. The first polymeric lignin mimic composed of only  $\beta$ -O-4 structure (DPw = 19.5-30.6) has been synthesized in our laboratory. In this investigation the synthetic method for the monomer was improved, where the starting material was changed from vanillin to acetovanillone.

2005-P05

DHP 調製における因子の検討

灰咲裕規<sup>\*1</sup>、芦谷竜矢<sup>\*2</sup>、藤田弘毅<sup>\*2</sup>、中川明子<sup>\*3</sup>、黒田健一<sup>\*2</sup>

<sup>\*1</sup> 九州大学大学院生物資源環境科学研究科、<sup>\*2</sup> 九州大学大学院農学研究院、<sup>\*3</sup> 筑波大学大学院生命環境科学研究科

Effect of DHP preparation factors on the chemical structures.

Hironori Haisaki<sup>\*1</sup>, Tastuya Ashitani<sup>\*2</sup>, Koki Fujita<sup>\*2</sup>, Akiko Nakagawa<sup>\*3</sup>, Kenichi Kuroda<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup> Graduate School of Agriculture, Kyushu University, <sup>\*3</sup> Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: DHP is made from *p*-hydroxycinnamyl alcohol by enzymatic polymerization, and it is used as a model compound for natural lignin. However the reaction conditions (pH, substrate additive rate, enzyme activity and so on) depend on each work and few people reported reproductivity of DHP preparation about yield and linkages. In this study, bulk DHP is enzymatically prepared from coniferyl alcohol under various pH conditions, and the chemical structures were examined by nuclear

magnetic resonance ( $^{13}\text{C}$ -NMR) and pyrolysis gas-chromatography (Py-GC/FID). DHP prepared under low pH condition has higher abundance of  $\beta$ -O-4 linkage, and that of  $\alpha$ -O-4 linkage was lower.

2005-P06

表面プラズモン共鳴を用いたモノリグノール類とヘミセルロースの相互作用(III)

中村淳、浦木康光、岸本崇生、生方信

北海道大学大学院農学研究科

Investigation on interaction between monolignols and hemicelluloses using surface plasmon resonance. (III).

Atsushi Nakamura, Yasumitsu Uraki, Takao Kishimoto, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University

Abstract: To clarify lignin biosynthesis, we investigated on the interactions of hemicelluloses (xylan and glucomannan) with monolignols (coniferyl alcohol and sinapyl alcohol) and its glucosides (coniferin and silyngin), and horseradish peroxidase by using surface plasmon resonance. The adsorption capacities of the oxidized hemicelluloses to monolignols were much larger than those to their glucosides. The interaction seems to be due to the hydrophobic interaction. The adsorption of HRP to xylan was likely to be specific, and its amount was larger than that to glucomannan. It is suggested from these results that substrate of lignin biopolymerization is supplied as monolignols from cytoplasm, and polymerized in xylan matrix.

2005-P07

リグニン前駆物質と多糖の相互作用に関する研究

藤加珠子、湯口宜明

産業技術総合研究所

Study on interaction of lignin precursor substances and polysaccharide.

Kazuko Toh, Yoshiaki Yuguchi

National Institute of Advanced Industrial Science and Technology

Abstract: Xyloglucan is a kind of hemicellulose, and exists in the cell wall or seed in the higher plants. We investigated that xyloglucan aqueous solution took place gelation by addition of precursors of lignin as coniferyl alcohol or sinapyl alcohol. Coniferyl alcohol needed for the formation of hydrogel was very low concentration of 0.75wt% with 0.5wt% xyloglucan at 5°C. The change in the line shape of the ESR spectrum was also observed during the sol-gel transition of these mixtures.

2005-P08

白色腐朽菌 *Phanerochaete sordida* YK-624 株の産生する新規リグニンペルオキシダーゼによる塩素化芳香族化合物の分解

平井浩文、政氏恵理、高橋昭裕、河合真吾、西田友昭

静岡大学農学部

Degradation of polychlorinated aromatic compounds by novel lignin peroxidase from white-rot fungus *Phanerochaete sordida* YK-624.

Hirofumi Hirai, Eri Masauji, Akihiro Takahashi, Shingo Kawai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University

Abstract: We tried to degrade various polychlorinated aromatic compounds by novel lignin peroxidase (YK-LiP) from *Phanerochaete sordida* YK-624. YK-LiP degraded 2,4,8-trichlorodibenzofuran and 2,7-dichlorodibenzo-*p*-dioxin although LiP (Pc-LiP) from *P. chrysosporium* could not degrade these dioxins, and the degradation rate of methoxychlor by YK-LiP was greater than that by

Pc-LiP. Moreover, YK-LiP degraded polychlorinated phenols more effectively than Pc-LiP. 2,4,6-Trichlorophenol (TCP) was converted to 2,6-dichloro-1,4-benzoquinone by YK-LiP. On the other hand, 2,6-dichloro-1,4-benzoquinone was not detected in MnP reaction mixture although the degradation of TCP by MnP was almost the same as that by YK-LiP.

2005-P09

白色腐朽菌から抽出した粗酵素によるダイオキシンの分解

佐々木良輝、伊藤和貴、橘燦郎

愛媛大学農学部

Biodegradation of dioxins with a crude enzyme from white-rot fungi.

Yoshiteru Sasaki, Kazutaka Ito, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: To obtain the basic information for bioremediation of dioxin-contaminated soil by a crude enzyme from white-rot fungi, biodegradation of 2,4,8-Trichlorodibenzofuran (2,4,8-TrCDF) was investigated. By biodegradation of 2,4,8-TrCDF with a crude enzyme from fungus PL1 in a liquid medium, about 50% of 2,4,8-TrCDF was degraded in 72 hours. Furthermore, the enzyme degraded about 20% of 2,4,8-TrCDF in soil when the slurry phase biodegradation was conducted for 72 hours. These results suggest that bioremediation of dioxin-contaminated soil by a crude enzyme from white-rot fungi is possible.

2005-P10

白色腐朽担子菌の系統解析とダイオキシン分解性

渡邊昌司<sup>\*1</sup>、亀井一郎<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究科

Phylogenetic analysis and characterization of degrading dioxin for white-rot fungi.

Masashi Watanabe<sup>\*1</sup>, Ichiro Kamei<sup>\*1</sup>, Ryuichirou Kondo<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Graduate School of Agriculture, Kyushu University

Abstract: In our previous study, we found that some *Phlebia* genera species were capable of degrading 2,7-dichlorodibenzo-*p*-dioxin (2,7-diCDD) as model dioxin compound. In the present paper, we focused on newly 42 *Phlebia* strains and screened them. As a result, only *Phlebia lindtneri* and *Phlebia acerina* could degrade 2,7-diCDD. In addition, most strains which belong to these three species were capable of degrading 2,7-diCDD. Therefore, we suggest that the ability of degrading chlorinated dioxin is conserved in the particular species of *Phlebia* genera.

2005-P11

白色腐朽菌による塩素系芳香族化合物の分解における 菌体内・菌体外酵素の役割について

丸吉美幸<sup>\*1</sup>、亀井一郎<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究科

Roles of intracellular and extracellular enzymes in degradation of chlorinated aromatic compounds by white rot fungi.

Miyuki Maruyoshi<sup>\*1</sup>, Ichiro Kamei<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Graduate School of Agriculture, Kyushu University

Abstract: Various white rot fungi (*Phanerochaete*, *Phlebia*, *Pleurotus* and *Trametes* sp.) were used in degradation experiment of 4,4'-dichlorobiphenyl (4,4'-DCB), 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD), 1,3,6,8-tetraCDD and dichlorodiphenyltrichloroethane (DDT). Although DDT and

4,4'-DCB were degraded by most fungi, dioxins were effectively degraded by only *Phlebia* species, Decolorization of poly R 478 which was thought to involve with ligninolytic enzyme was compared with degradation of pollutants. Decolorization rate seemed to correlate with degradation of DDT, but not dioxins. Furthermore, piperonyl butoxide (inhibitor of cytochrome P450) inhibited degradation of 2,7-DCDD, but not DDT. These results indicate that degradation mechanisms of dioxins and DDT were different.

2005-P12

白色腐朽菌によるダイオキシン汚染土壌の処理

原田和寿<sup>\*1</sup>、亀井一郎<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学研究科、<sup>\*2</sup>九州大学大学院農学研究科

Biodegradation of polychlorinated dioxin-polluted soil by white-rot fungi.

Kazuhisa Harada<sup>\*1</sup>, Ichiro Kamei<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, <sup>\*2</sup>Graduate School of Agriculture, Kyushu University

Abstract: 1,3,6,8-tetrachlorodibenzo-*p*-dioxin (1,3,6,8-tetraCDD) is a main contaminant of contaminated paddy soil. Therefore, the removal of 1,3,6,8-tetraCDD is the key component of decontamination. Recently, we showed that 1,3,6,8-tetraCDD was transformed by *Phlebia brevispora*, and 2-methoxy-1,3,6,8-tetraCDD and 3,5-dichlorocatechol were detected as metabolites<sup>1)</sup>. In this study, we attempted the degradation of 2,7-dichlorodibenzo-*p*-dioxin (2,7-diCDD) and 1,3,6,8-tetraCDD in soil. Forty six% of 1,3,6,8-tetraCDD in artificially contaminated soil were degraded by the treatment with *P. brevispora* for 14 days. And also, we identified the metabolites from 2,7-diCDD and 1,3,6,8-tetraCDD in artificially contaminated soil by treatment with *P. brevispora*.

2005-P13

アンモニウム残基を有するリグニン誘導体とクレーを原料とする複合体の調製

廣瀬重雄<sup>\*1</sup>、畠山兵衛<sup>\*2</sup>

<sup>\*1</sup>産業技術総合研究所、<sup>\*2</sup>福井工業大学工学部

Preparation of composites consisting of lignin derivative with ammonium residue and clay.

Shigeo Hirose<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Research Institute for Innovation in Sustainable Chemistry, <sup>\*2</sup>Fukui University of Technology

Abstract: Kraft lignin was allowed to react with glycidyltrimethylammonium chloride in polyethylene glycol 400 (molecular weight 400) in the presence of catalytic amount of dimethylbenzylamine at 100 °C for 12 h. The obtained reaction product was mixed with montmorillonite at room temperature. The obtained composites were allowed to stand for 1 day at 60 °C. The composites were studied by Fourier transfer infrared spectroscopy (FTIR). The thermal properties of the composites were also studied by differential scanning calorimetry (DSC) and thermogravimetry (TG).

## 第 51 回 (2006.10.26-27) 北海道大学 学術交流会館

2006-101

高分子リグニン酸化能力を有するペルオキシダーゼアイソザイム CWPO-C の機能解析

佐々木慎弥、野中大輔、割石博之、埴祐司、近藤隆一郎

九州大学大学院農学研究科

The role of the Tyr on the protein surface of cationic cell-wall-peroxidase.

Shinya Sasaki, Daisuke Nonaka, Hiroyuki Wariishi, Yuji Tsutsumi, Ryuichiro Kondo

Faculty of Agriculture, Kyushu University, 6-10-1, Fukuoka, 812-8581, Japan

**Abstract:** A unique peroxidase isoenzyme, cationic cell-wall-peroxidase (CWPO-C), from poplar callus oxidizes sinapyl alcohol, ferrocyanochrome *c* and synthetic lignin polymers, unlike other plant peroxidases. Here, the catalytic mechanism of CWPO-C was investigated using chemical modification and homology modeling. Tyr modification of CWPO-C strongly suppressed its oxidation activities toward syringaldazine and 2,6-DMP by 90%, and also suppressed its guaiacol oxidation activity to a lesser extent. Ferrocyanochrome *c* was not oxidized by TNM-modified CWPO-C. These results strongly suggest that Tyr residues in CWPO-C mediate its oxidation of syringyl compounds and high-molecular-weight substrates. Homology modeling indicated that Tyr-177 and Tyr-74 were located at the protein surface of CWPO-C and near the heme. These results suggest that Tyr residue on the protein surface is a key player in CWPO-C for its wide substrate oxidation spectrum.

2006-102

Characterization of *Carthamus tinctorius* cinnamyl alcohol dehydrogenases.

Safendri Komara Ragamustari<sup>\*1</sup>, Tomoyuki Nakatsubo<sup>\*1</sup>, Naoko Shiraiwa<sup>\*1</sup>,

Shiro Suzuki<sup>\*2</sup>, Takefumi Hattori<sup>\*1</sup>, Toshiaki Umezawa<sup>\*1</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto 611-0011, Japan

<sup>\*2</sup>Institute of Sustainability Science, Kyoto University, Uji, Kyoto 611-0011, Japan

**Abstract:** Characterization of three genes encoding cinnamyl alcohol dehydrogenase in *Carthamus*

*tinctorius* was carried out. Gas chromatography-mass spectrometry based enzyme analysis and substrate level enzyme kinetics show that two *Carthamus tinctorius* cinnamyl alcohol dehydrogenases (CtCADs), named CtCAD1 and CtCAD2, respectively, have a slightly different kinetic character. Lineweaver-Burk kinetic analysis shows that CtCAD1 and CtCAD2 have almost the same catalytic activity towards coniferaldehyde and sinapaldehyde. Inhibition assay of CtCAD1 shows that the reduction of coniferylaldehyde is inhibited by the presence of sinapaldehyde. In contrast, inhibition assay of CtCAD2 showed inhibition of both coniferaldehyde and sinapaldehyde reduction. The results show that CtCAD1 and CtCAD2 play an important role in the formation of both syringyl and guaiacyl monolignols. The characterization of another CtCAD (CtCAD3) is currently underway.

2006-103

イネをモデルとした植物細胞壁形成過程に関する研究 -Glycosylphosphatidylinositol はイネの細胞壁高次構造形成にどのように関わるのか?-2

鈴木瑠<sup>\*1</sup>、伊藤幸子<sup>\*1</sup>、佐藤かんな<sup>\*2</sup>、半智史<sup>\*3</sup>、北野英己<sup>\*2</sup>、船良<sup>\*3</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>名古屋大学大学院 BBC、<sup>\*3</sup>東京農工大学大学院農学研究科

Study of plant cell wall formation in *Oryza sativa* L. - How does glycosylphosphatidylinositol-anchored protein relate to cell wall conformation in rice plant (*Oryza sativa* L.)?-2.

Ryu Suzuki<sup>\*1</sup>, Sachiko Ito<sup>\*1</sup>, Kanna Sato<sup>\*2</sup>, Satoshi Nakaba<sup>\*3</sup>, Hidemi Kitano<sup>\*2</sup>, Ryo Funda<sup>\*3</sup>, Sinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

<sup>\*2</sup>Graduate school of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan

<sup>\*3</sup>Bioscience and Biotechnology Center, Nagoya University, Chikusaku, Nagoya, 464-8601 Japan

Abstract: There are many studies about cell wall formation using mutant. However, most of them are about biosynthesis of main cell wall component such as cellulose, hemicellulose, and lignin. Few information obtained about detailed mechanism and process of wall conformation. In this study, we used brittle culm mutant called 'cwa1', recessive mutant rice plant (*Oryza sativa* L.). Cwa1 has defective in plant mechanical strength. But there is a little distinction of amount of cell wall components. And it's revealed that cwa1 has defective cell wall thickness, and distribution of wall components by histological analysis. So cwa1 is predicted that it has defective in cell wall conformation after cell wall components are biosynthesized. By analyzing cwa1 and its' defective gene, *BC1*, we can discuss about mechanism and process of cell wall conformation in monocot..

2006-104

ポプラにおける細胞膜を介したモノリグノール輸送メカニズム

河合亮<sup>\*1</sup>、高部圭司<sup>\*1</sup>、藤田稔<sup>\*1</sup>、間藤徹<sup>\*1</sup>、研士反伸和<sup>\*2</sup>、矢崎一史<sup>\*2</sup>

<sup>\*1</sup> 京都大学大学院農学研究科、<sup>\*2</sup> 京都大学生存圏研究所

Mechanism of monolignol transportation through plasma membrane in poplar.

Ryo Kawai<sup>\*1</sup>, Keiji Takabe<sup>\*1</sup>, Minoru Fujita<sup>\*1</sup>, Toru Matoh<sup>\*2</sup>, Nobukazu Shitan<sup>\*2</sup>, Kazufumi Yazaki<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan, <sup>\*2</sup> Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji 611-0011, Japan

Abstract: The lignin biosynthesis consists of three parts, that is, biosynthesis, transportation, and polymerization of monolignols. Recent investigation shows that the enzymes, involved in conversion of the last step of monolignol biosynthesis, localize in cyto-sol. Therefore, monolignols probably exist in cytosol. They may be transported from cyto-sol to cell wall via plasma membrane and then polymerized within the cell wall. In this study, we analyzed the mechanism of monolignol transportation in lignifying tissues. The characterization of monolignol transport using microsomal fractions containing membrane vesicles showed that uptake of coniferin was stimulated by Mg/ATP, while that of coniferyl alcohol, sinapyl alcohol and syringin were little regardless of presence of ATP. Coniferin uptake was strongly inhibited with NH<sub>4</sub><sup>+</sup>, while vanadate, which was commonly used to inhibit ATP-binding cassette (ABC) transporters, had no effect. This suggests that coniferin uptake into membrane vesicles depends on the electrochemical gradient of H<sup>+</sup> across them.

2006-105

リグナン生合成経路におけるメチレンジオキシブリッジ形成と配糖化反応

小埜栄一郎<sup>\*1</sup>、中井正晃<sup>\*2</sup>、福井祐子<sup>\*2</sup>、富森菜美乃<sup>\*2</sup>、水谷正子<sup>\*1</sup>、佐竹炎<sup>\*3</sup>、斉藤雅之<sup>\*1</sup>、中尾正宏<sup>\*1</sup>、田中隆治<sup>\*3</sup>、勝田真澄<sup>\*4</sup>、梅津俊明<sup>\*5</sup>、田中良和<sup>\*1</sup>

<sup>\*1</sup> サントリー(株)先進コア技術研究所、<sup>\*2</sup> サントリー(株)健康科学研究所、<sup>\*3</sup> (財)サントリー生有研、<sup>\*4</sup> (独)作物研究所、<sup>\*5</sup> 京都大学生存圏研究所

Methylenedioxy bridge formation and glucosylation in lignan biosynthesis.

Eiichiro Ono<sup>\*1</sup>, Masaaki Nakai<sup>\*2</sup>, Yuko Fukui<sup>\*2</sup>, Namino Tomimori<sup>\*2</sup>, Masako Fukuchi-Mizutani<sup>\*1</sup>, Honoo Satake<sup>\*3</sup>, Masayuki Saito<sup>\*1</sup>, Masahiro Nakao<sup>\*1</sup>, Takaharu Tanaka<sup>\*3</sup>, Masumi Katsuta<sup>\*4</sup>, Toshiaki Umezawa<sup>\*5</sup>, Yoshikazu Tanaka<sup>\*1</sup>

<sup>\*1</sup> Institute for Advanced Core Technology, Suntory Ltd., Mishima, Osaka 618-8503, Japan, <sup>\*2</sup> Institute for Healthcare Science, Suntory Ltd., <sup>\*3</sup> Suntory Institute for Bioorganic Research, <sup>\*4</sup> Department of Field Crop Research National Institute of Crop Science, <sup>\*5</sup> Institute for Sustainable Humanosphere Kyoto University

Abstract: (+)-Sesamin, a furofuran class lignan, is widespread in vascular plants and represented by *Sesamum* spp. (+)-Sesamin has been of rapidly growing interest because of its beneficial biological effects in mammals, but its biosynthesis and physiological roles in plants remains

to be clarified. It is speculated to be synthesized from (+)-pinoresinol via (+)-piperitol by formation of two methylenedioxy bridges mediated by two distinct *Sesamum indicum* cytochrome P450 proteins. Here we report a novel *S. indicum* P450, CYP81Q1 that alone catalyzes (+)-sesamin biosynthesis from (+)-pinoresinol via (+)-piperitol by forming two methylenedioxy bridges. The CYP81Q1 gene expression profile was temporally consistent with the accumulation pattern of (+)-sesamin during seed development. The CYP81Q1-GFP chimera protein was co-localized with an endoplasmic reticulum (ER) targeting chimera protein, indicative that (+)-sesamin biosynthesis occurs on the ER cytoplasmic surface. Moreover, we isolated two CYP81Q1 homologs from other *Sesamum* spp. *S. radiatum* CYP81Q2 showed the dual (+)-piperitol/(+)-sesamin synthetic activity. CYP81Q2 as well as CYP81Q1, therefore corresponds to an (+)-piperitol/(+)-sesamin synthase (PSS) in lignan biosynthesis. In contrast, *S. alatum* CYP81Q3 showed no activity, in accord with (+)-sesamin being deficient in *S. alatum*. Our findings not only provide new insight into lignan biosynthesis but also unravel a novel mode of cytochrome P450 action.

2006-106

分化中木部における細胞壁成分の ToF-SIMS イメージング

齊藤香織、今井貴規、松下泰幸、福島和彦

名古屋大学大学院生命農学研究科

ToF-SIMS imaging of constituents in plant cell walls of differentiating xylem.

Kaori Saito, Takanori Imai, Yasuyuki Matsushita and Kazuhiko Fukushima

Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601

Abstract: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to visualize the distribution of lignin and polysaccharides in the differentiating xylem of *Pinus thunbergii*. A recent study using ToF-SIMS showed that lignin polymers can be characterized by specific secondary cations with a guaiacyl ring at  $m/z$  137 and 151. In this study, the specific monomeric ions of cellulose and xylan were also identified. ToF-SIMS imaging analysis showed that the image of deposition of cellulose and xylan disappeared after that the image of deposition of lignin started in the differentiating xylem.

2006-107

リグニン  $\beta$ -O-4 構造の細胞壁における絶対量と細胞壁「木質化」との関係

東京大学大学院農学生命科学研究科

中村裕貴、秋山拓也、Deded S. Nawawi、近藤憲哉、松本雄二

Absolute Amounts of  $\beta$ -O-4 structures in wood and non-wood cell walls.

Hirotaaka Nakamura, Takuya Akiyama, Deded S. Nawawi, Kenya Kondo, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of

Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: All higher vascular plants, whether they are wood species or not, contain lignin in the cell walls, but wood cell walls are much harder and stronger than non-wood cell walls such as leaves and grasses. The important key factor for cell walls to be hard and have enough strength is still unknown. The purpose of this investigation is to understand the difference between wood cell wall and non-wood cell wall such as of leaves and grasses from viewpoints of lignin structure and its content. As a measure to distinguish wood cell walls and non-wood cell walls, we examined the absolute amount of arylglycerol- $\beta$ -aryl ether ( $\beta$ -O-4) structure in cell wall, not in lignin, by ozonation method. It seems that a critical level is present for the amount of  $\beta$ -O-4 structures in wood cell wall and this level gradually increased depending on the syringyl ratio. Interestingly, this

amount found for all the leaves and most of the grass stems was lower than this critical level. We will hypothetically propose the importance of the absolute amount of  $\beta$ -O-4 structure in cell wall, not in lignin, to distinguish wood cell and non-wood cell.

2006-108

モノリグノール配糖体の HRP 触媒脱水素重合 Part 2.

飛松裕基、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

HRP catalyzed dehydrogenative polymerizations of monolignol glucosides. Part 2.

Yuki Tobimatsu, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University.

Sakyo-ku, Kyoto 606-8502, Japan

Abstract: Dehydrogenative polymerizations of monolignol  $\beta$ -D-glucosides (isokoniferin, **1a**; isosyringin, **1b**; triandrin, **1c**) using horseradish peroxidase (HRP)/  $H_2O_2$  as catalyst were carried out, resulting in the formations of water-soluble lignin-like polymers (DHPs): poly (**1a**)-(**1c**). The degrees of polymerization (DPs) of poly (**1a**) and poly (**1c**) were much higher than those of conventional DHPs, whereas DP of poly (**1b**) was low. Cyclic voltammetry analyses showed that the monomer **1b** had a lower oxidation potential than monomer **1a** and **1c**. HRP-catalyzed initial reaction rates of monomer **1b**, however, was extremely low and in the same range as that of sinapyl alcohol, while the oxidation rates of monomer **1a** and **1c** were significantly higher than those of corresponding monolignols. These results indicated that HRP had low specificity to monomer **1b** as well as to sinapyl alcohol and did not catalyze the formation of highly polymerized poly (**1b**) even in a homogeneous reaction system. Structural analyses confirmed that poly (**1a**)-(**1c**) were lignin-like polymers containing D-glucose units attached to the lignin sidechains.

2006-109

高速フローESR法を用いたリグニンモデル化合物に対するラジカル種の反応性に関する研究

大橋康典、宇野由紀子、渡邊崇人、本田与一、渡辺隆司

京都大学生存圏研究所

Studies on reactivity of radical species with lignin model compounds using a rapid flow-ESR method.

Yasunori Ohashi, Yukiko Uno, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Laboratory of Biomass Conversion, Research Institute for Sustainable Humansphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Abstract: It has been discussed that non-phenolic lignin model compounds (LMCs) are degraded by radical reactions. In the reactions with free radicals, it is suggested that extraction of electron or hydrogen atom from the LMCs are induced by the radicals. However, there has been no direct spectroscopic evidence demonstrating the production of initial radical intermediates from the LMCs by the free-radical-mediated degradation. Furthermore, it was not shown which radical species can degrade the LMCs. In the present study, we tried to detect the radicals derived from the LMCs produced by the reactions with alkoxyl, peroxy, hydroxyl and hydroperoxyl radicals using a rapid flow-ESR method. The results suggested that peroxy and hydroperoxyl radicals have no reactivity with the LMCs. On the other hand, hydroxyl radicals extract a hydrogen atom from the a position of veratryl alcohol (VA), a simplest monomeric LMC used. ESR spectrum of this radical was quite different from the radical produced by one electron extraction with  $Ce^{4+}$ .

2006-110

耐塩性白色腐朽菌 *Phlebia* sp. MG60 の産生するマンガンペルオキシダーゼの発現解析  
亀井一郎<sup>\*1</sup>、大黒千映子<sup>\*2</sup>、堤祐司<sup>\*2</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学 VBL、<sup>\*2</sup>九州大学大学院農学研究院

Expressional analysis of manganese peroxidases from saline-tolerant white rot fungus, *Phlebia* sp. MG60.

Ichiro Kamei<sup>\*1</sup>, Chieko Daikoku<sup>\*2</sup>, Yuji TsuTsumi<sup>\*2</sup>, Ryuichiro Rondo<sup>\*2</sup>

<sup>\*1</sup>VBL, Kyushu University, <sup>\*2</sup>Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: Expression pattern of manganese peroxidases (MnPs) which were produced by saline-tolerant white rot fungus, *Phlebia* sp. MG-60, was analyzed. When MG-60 was cultured in the Kirk medium containing 3% sea salts (salt medium), higher activity of MnPs was produced than that in the normal Kirk medium (0% sea salts). SDS-PAGE analysis demonstrated that two MnP isoenzymes were *de novo* synthesized during the culture in the salts medium. Three MnP encoding genes (*MG-mnp1*, *MG-mnp2*, and *MG-mnp3*) were isolated and these transcriptions in the Kirk medium with and without 2% NaCl were determined by real-time PCR technique. *MG-mnp2*, and *MG-mnp3* were highly expressed in the medium with NaCl.

2006-111

アカシアクラフトパルプのバイオブリーチングに向けた白色腐朽菌のスクリーニング  
アフリダ<sup>\*1</sup>、玉井 裕<sup>\*2</sup>、大崎 満<sup>\*1</sup>

<sup>\*1\*2</sup>北海道大学大学院農学研究科

Screening of white rot fungi and their potential application in biobleaching of acacia kraft pulp.

Afrida<sup>\*1</sup>, Yutaka Tamai<sup>\*2</sup>, Mitsuru Osaki<sup>\*1</sup>

<sup>\*1</sup>Laboratory of Plant Nutrition, <sup>\*2</sup>Laboratory of Forest Resource Biology, Graduate School of Agriculture, Hokkaido University, N-9, W-9, Kita-ku, Sapporo 060-8589, Japan

Abstract: To study the biobleaching to Acacia kraft pulp, over 600 strains of white rot fungi were collected from various natural sources such as fruiting bodies, rotten woods and trap piles at various locations in Indonesia such as West Java, Central Kalimantan, South Kalimantan, Jambi and North Sumatra. We succeeded to screen five strains of white rot fungi for application in Acacia kraft pulp bleaching.

2006-112

担子菌におけるヘム生合成の特異的制御機構

三浦大典<sup>\*1</sup>、志水元亨<sup>\*2</sup>、割石博之<sup>\*3</sup>

<sup>\*1</sup>九州大学大 VBL、<sup>\*2</sup>九州大学大学院農学研究院、<sup>\*3</sup>九州大学大学院農学研究院・KBAC

Molecular mechanisms involved in the regulation of heme biosynthesis in *Phanerochaete chrysosporium*.

Daisuke Miura, Moyoyuki Shimizu, Hiroyuki Wariishi

<sup>\*1</sup>Venture Business Laboratory, <sup>\*2</sup>Faculty of Agriculture, <sup>\*3</sup>Bio-Architecture Center, Kyushu University, Fukuoka, Japan

Abstract: Addition of exogenous aromatic compounds to *Phanerochaete chrysosporium* resulted in an immediate metabolic shift from a short-cut TCA/glyoxylate bicycle system into a general TCA cycle, which in turn resulted in the activation of the heme biosynthetic pathway branched at succinyl-CoA. On the other hand, a free heme is highly toxic to the cell. To reveal regulatory mechanisms involved in fungal heme biosynthesis, a comprehensive analysis for surveying heme-binding proteins produced by *P. chrysosporium* was performed. Biotinylated heme-streptavidin beads system was utilized for separating intracellular heme-binding proteins. From an

SDS-PAGE separation and MALDI/TOF-MS analysis on peptide mass fingerprinting of these proteins, mitochondrial citrate synthase (PcCS) and glyceraldehyde 3-phosphate dehydrogenase (PcGAPDH) were identified as putative heme-binding proteins. Recombinant PcCS and PcGAPDH were expressed as active forms in *E. coli* for further kinetic and spectroscopic characterization. Either PcCS or PcGAPDH was inhibited with a physiological concentration of hemin. Inhibitory mechanism was further characterized for PcCS using a homology modeling technique. These observations were the first evidence for a direct interaction of a heme molecule to metabolic enzymes to control a metabolic flux in the fungus.

2006-113

The oxidation of polyphenols by extracellular peroxidase from suspension cultured cells of liverwort *Heteroscyphus planus*.

Leily Tjandrawaskitasari<sup>\*1</sup>, Rie Hata<sup>\*1</sup>, Takashi Ohsasa<sup>\*2</sup>, Hanami Chiba<sup>\*2</sup>, Makoto Hashimoto<sup>\*2</sup>, Kosaku Takahashi<sup>\*1</sup>, Kensuke Nabeta<sup>\*1</sup>

<sup>\*1</sup>Laboratory of Bioorganic Chemistry, Division of Applied Bioscience, Research Faculty of Agriculture, Hokkaido University, <sup>\*2</sup>Department of Agriculture and Life Science, Obihiro University of Agriculture and Veterinary Medicine

**Abstract:** Suspension cultured cells of liverwort, *Heteroscyphus planus* excreted peroxidase in the culture medium. The peroxidase activities were induced by co-incubation of phenols such as *p*-cresol, 2,6-dimethoxyphenol, bisphenol-A (BPA) and lignin model compound (LMC, guaiacylglycerol- $\beta$ -guaiacyl ether). We observed the oxidation of BPA and LMC in the cultured cells of the liverwort. BPA was mainly polymerized to higher molecular compounds, while was partly biodegraded to small molecular compounds. The biodegraded compounds were identified as 4-isopropenyl and *p*-hydroxyacetophenone. The process to form these compounds was examined using deuterated-BPA. LMC was degraded to guaiacol, vanillin, coniferyl alcohol and ferulic acid, while a dimer of LMC, 1,1'-(4,4'-dihydroxy-3,3'-dimethoxy-5,5'-biphenylene)-bis [8-(2''-methoxyphenoxy)-7,9-propanediol] was also detected.

2006-特別講演 I

Invited Lecture, I

Biotechnology based wood quality research program for forest biorefinery.

H-m. Chang<sup>\*1</sup>, R. Sederoff<sup>\*2</sup>, B. Li<sup>\*2</sup>, B. Goldfarb<sup>\*2</sup>, J. F. Kadla<sup>\*3</sup>, V. L. Chiang<sup>\*1\*2</sup>

<sup>\*1</sup> Dept. of Wood and Paper Science, <sup>\*2</sup>Dept. of Forestry, College of Natural Resources, North Carolina State University, Raleigh, NC 27695-8005, USA, <sup>\*3</sup>University of British Columbia, Vancouver, B.C. V6T 1Z4, Canada

**Introduction:** The Southern U.S. is the major supplier of industrial wood and wood products to the world. North Carolina State University, in collaboration with industry and governmental agencies, has been undertaking an intensive breeding program for loblolly pine during the past fifty year, resulting in great increase in growth, straightness, wood density and disease resistance. In anticipation of ever increased demand for wood in the future, increasingly intensive plantation forestry is being used for wood supply. Great increases in the productivity of pine plantations in the southern US have been achieved due to genetic and silvicultural improvements in recent years. However, increased growth rates have resulted in trees with more juvenile wood, many properties of which are quite different from those of mature wood. We thus focus our efforts for the production of rapid growing short rotation juvenile loblolly pine with improved wood properties. To achieve this goal, we have been integrating research on wood properties, tree breeding, propagation and genomics during the past 8 years. Two approaches have been taken to achieve this goal: selection of the desired traits from the

genetically controlled natural variations in target properties and improvement through genetic profiling of the desired properties. On the other hand, recent sharp increase in the price of oil has greatly stimulated great interest in biofuel production. Several barriers still exist in converting lignocellulosic feed stock to biofuel. During the past two years, we have been undertaking study to overcome some of the barriers by lowering lignin content and increase syringylpropane to guaiacylpropane ratio (S/G) using transgenic approach. In this presentation, we attempt to briefly describe our efforts and summarize the results in these two areas of research.

2006-201

リグニンの立体化学と微生物代謝機能に関する研究(I) –guaiacylglycerol- $\beta$ -guaiacyl ether (GGE)の立体化学–

菱山正二郎<sup>\*1</sup>、中村雅哉<sup>\*1</sup>、大塚祐一郎<sup>\*1</sup>、大原誠資<sup>\*1</sup>、政井英司<sup>\*2</sup>、片山義博<sup>\*3</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 長岡技術科学大学・生物、<sup>\*3</sup> 東京農工大学大学院

Studies on stereochemistry of lignin and microbial metabolic functions. – Stereochemistry of lignin and microbial metabolic functions. –Stereochemistry of guaiacylglycerol- $\beta$ -guaiacyl ether (GGE)– Shojiro Hishiyama<sup>\*1</sup>, Masaya Nakamura<sup>\*1</sup>, Yuichiro Otsuka<sup>\*1</sup>, Seiji Ohara<sup>\*1</sup>, Eiji Masai<sup>\*2</sup>, Yoshihiro Katayama<sup>\*3</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan, <sup>\*2</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan, <sup>\*3</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: Four stereoisomers of guaiacylglycerol- $\beta$ -guaiacyl ether (GGE:1), which is important substrate for understanding the relationship between microbial metabolic functions and stereochemistry of lignin, were synthesized with enantiopure form. And two stereoisomers of  $\alpha$ -(2-methoxyphenyl)- $\beta$ -hydroxypropiophenone (MPHPV:2), which is important intermediate located in metabolic pathway of GGE microbial degradation, were also synthesized.

2006-202

リグニンの立体化学と微生物代謝機能に関する研究(II) –バクテリアの立体選択的グルタチオン-S-トランスフェラーゼによる $\beta$ -アリアルエーテル開裂機構–

政井英司<sup>\*1</sup>、市村篤史<sup>\*1</sup>、宮内啓介<sup>\*1</sup>、福田雅夫<sup>\*1</sup>、菱山正二郎<sup>\*2</sup>、中村雅哉<sup>\*2</sup>、片山義博<sup>\*3</sup>

<sup>\*1</sup> 長岡技術大学・生物機能工学、<sup>\*2</sup> 森林総合研研究所、<sup>\*3</sup> 東京農工大学大学院 BASE

Studies on stereochemistry of lignin and microbial metabolic functions (II): Cleavage of the  $\beta$ -aryl ether linkage catalyzed by bacterial enantioselective glutathione S-transferases.

Eiji Masai<sup>\*1</sup>, Atsushi Ichimura<sup>\*1</sup>, Keisuke Miyauchi<sup>\*1</sup>, Shojiro Hishiyama<sup>\*2</sup>, Masaya Nakamura<sup>\*2</sup>, Yoshihiro Katayama<sup>\*3</sup>, Masao Fukuda<sup>\*1</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, <sup>\*2</sup>Forestry and Forest Products Research Institute, Tsukuba, Ibaraki, 305-8687, <sup>\*3</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: Cleavage of the  $\beta$ -aryl ether linkage is the most important process in lignin degradation. In a previous study, we isolated the  $\beta$ -aryl ether degradation operon, *ligDFEG*, of *Sphingomonas paucimobilis* SYK-6. The *ligD* gene encodes Ca-dehydrogenase, which oxidizes guaiacylglycerol- $\beta$ -guaiacyl ether (GGE) to  $\alpha$ -(2-methoxyphenoxy)- $\beta$ -hydroxypropiovanillone (MPHPV). The *ligE*, *ligF*, and *ligG* genes showed similarity with glutathione S-transferases but only the gene products of *ligE* and *ligF* exhibited the  $\beta$ -etherase activity. In this study, we determined the actual roles of three GST genes. MPHPV was transformed by LigE and LigF to guaiacol and

$\alpha$ -glutathionyl- $\beta$ -hydroxy-propiovanillone (GS-HPV), suggesting that LigE and LigF catalyze the nucleophilic attack of glutathione on the carbon atom at the  $\beta$  position of MPHPV. HPLC-circular dichroism analysis indicated that LigE and LigF each attacked a different enantiomer of the racemic MPHPV preparation. LigG catalyzed the elimination of glutathione from GS-HPV generated by the action of LigF. Disruption of *ligE*, *ligF*, and *ligG* in SYK-6 showed that *ligF* is essential to the degradation of one of the MPHPV enantiomers. The alternative activities which metabolize the substrates of LigE and LigG are present in this strain.

2006-203

超臨界・亜臨界水条件での嘲 Björkman リグニンおよび微生物変性リグニンの反応  
金貞福<sup>\*1\*2</sup>、勝亦京子<sup>\*1</sup>、飯山賢治<sup>\*3</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 現: 中国浙江林業大学化学工程、<sup>\*3</sup> 東京大学アジア生物資源環境研究センター

Reaction of Björkman lignin and biologically modified lignin under supercritical and sub-critical water condition.

Zhenfu Jin<sup>\*1\*2</sup>, Kyoko S. Katsumata<sup>\*1</sup>, Kenji Iiyama<sup>\*3</sup>

<sup>\*1</sup> Graduate School of Agricultural & Life Sciences, the University of Tokyo, <sup>\*2</sup> Department of Chemical Engineering, Zhejiang Forestry University, China, <sup>\*3</sup> Asian Natural Environmental Science Center, the University of Tokyo

Abstract: Behavior of dissolved organic matters (DOM) in water, which was isolated from peat swamp water and characterised as biologically modified lignin, under condition at deep sea would be quite important for global carbon circulation. Reaction of DOM under supercritical water condition (650K, 22.4MPa) was investigated together with those of Björkman lignins isolated from *Abies firma* and *Fagus crenata*. Demethylation reaction was predominant, and major products were catechol derivatives.

2006-204

フェノール性  $\beta$ -エーテル型2量体モデル化合物の熱分解開裂機構に及ぼす C $\gamma$ -水酸基の影響  
河本晴雄、料理谷 正和、坂 志朗  
京都大学大学院エネルギー科学専攻科

Influence of C $\gamma$ -hydroxyl group on the mechanism of pyrolytic  $\beta$ -ether cleavage of phenolic model dimers.

Haruo Kawamoto, Masakazu Ryoritani, Shiro Saka

Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto, 606-8501, Japan

Abstract: We already reported that elimination of the C $\gamma$ -OH group substantially inhibited the pyrolytic cleavage of the  $\beta$ -ether bond of phenolic model dimers. The temperatures where model dimers became reactive in 1 min pyrolysis were different between C $\gamma$ -OH type (250°C) and C $\gamma$ -deoxy type (400°C). These previous findings indicate that cleavage mechanisms are different between these model dimers. In this paper, these cleavage mechanisms are discussed. Reactivity of the C $\gamma$ -deoxy type was very dependent on the pyrolysis conditions. C $\gamma$ -deoxy type was stable even at 400°C under the conditions which made the volatilization of low molecular weight (MW) products from the heated zone easy. On the other hand, the C $\gamma$ -deoxy type was completely decomposed at 400°C and even reactive at 300°C when model compound in a closed ampoule was heated in muffle furnace. These results indicate that radical chain reaction occurs in pyrolysis of the C $\gamma$ -deoxy type. To confirm this, influence of tetralin (a radical scavenger) was investigated for C $\gamma$ -deoxy and C $\gamma$ -OH types of model dimers. As a result, addition of tetralin substantially reduced the pyrolytic cleavage reactivity of the C $\gamma$ -deoxy type, whereas the reactivity of the C $\gamma$ -OH type

was not influenced by tetralin. Furthermore, reactivities of variously *p*-substituted model dimers (C  $\gamma$ -deoxy type) in sufficient amount of tetralin increased positively related to the order of ABDE of the substituent groups. These results suggest the radical chain mechanism starting from the direct homolytic C  $\beta$ -O bond cleavage for the C  $\gamma$ -deoxy type, although the  $\beta$ -ether bond of the C  $\gamma$ -OH type is cleaved through quinonemethide formation (an ionic reaction) at much lower temperature of 250°C. The role of the C  $\gamma$ -OH group is also proposed as stabilizing effect of the transition state in quinonemethide formation by hydrogen bonds between C  $\alpha$ - and C  $\gamma$ -OH groups. Under pyrolysis conditions, such intramolecular stabilization may play an important role in promoting the ionic type of reaction.

2006-205

酸素漂白条件下における活性酸素種による糖の被攻撃部位の特定(1)～アノマー位についての検討～

小西史子、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Specification of the site of carbohydrate attacked by active oxygen species under oxygen bleaching conditions (1). – Examination on the anomeric position –

Fumiko Konishi, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: It has still been the serious problem that oxygen delignification is accompanied by the depolymerization of carbohydrates. It is important to know the degradation mechanism of carbohydrates to protect them under oxygen bleaching conditions. In this study, the relative reactivity of active oxygen species (AOS) toward two carbohydrate model compounds, methyl  $\alpha$ -D-glucopyranoside (MGP  $\alpha$ ) and methyl  $\beta$ -D-glucopyranoside (MGP  $\beta$ ), was examined under practical oxygen bleaching conditions, where AOS were in situ generated by subjecting a phenolic compound, 2,4,6-trimethylphenol, to the oxygen oxidation. It was also examined whether or not the anomeric position is attacked by AOS by using a model compound, methyl  $\beta$ -D-[1-d]-glucopyranoside (MGP  $\beta$  [1-d]). As the degradation of MGP  $\beta$  was greater than MGP  $\alpha$  at pH 13.5, it is suggested that the stereo configurational difference in their anomeric positions has an influence on their reactions with AOS. And the result that the reactivity of AOS toward MGP  $\beta$  was higher than that toward MGP  $\beta$  [1-d], suggests a possible occurrence of the attack on the anomeric position.

2006-206

生命科学と有機材料科学を基盤としたリグニンの新しい高度利用に関する研究(I)

大塚祐一郎<sup>\*1</sup>、中村雅哉<sup>\*1</sup>、大原誠資<sup>\*1</sup>、重原淳孝<sup>\*2</sup>、梶田真也<sup>\*2</sup>、片山義博<sup>\*2</sup>、政井英司<sup>\*3</sup>、福田雅夫<sup>\*3</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 東京農工大学大学院 BASE、<sup>\*3</sup> 長岡技術科学大学

Studies on the novel advanced utilization system of lignin based on the life science and organic material chemistry (I).

Yuichiro Otsuka<sup>\*1</sup>, Masaya Nakamura<sup>\*1</sup>, Seiji Ohara<sup>\*1</sup>, Kiyotaka Shigehara<sup>\*2</sup>, Shinya Kajita<sup>\*2</sup>, Yoshihiro Katayama<sup>\*2</sup>, Eiji Masai<sup>\*3</sup>, Masao Fukuda<sup>\*3</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, Ibaraki, Japan, <sup>\*2</sup>Graduate School of Bio-Applications and Systems-Engineering, Tokyo University of Agriculture and Technology, Tokyo, Japan, <sup>\*3</sup>Nagaoka University of Technology, Niigata, Japan

Abstract: *Sphingomonas paucimobilis* SYK-6, which can degrade various low molecular weight

compounds derived from plant polyphenols such as lignin, lignan, and tannin, metabolizes these substances via 2-pyrone-4,6-dicarboxylic acid (PDC). We focused on this metabolic intermediate as a potential raw material for novel biopolymers. We cloned the *ligAB* and *ligC* genes of SYK-6, which respectively encode protocatechuate 4,5-dioxygenase and 4-carboxy-2-hydroxymuconate-6-semialdehyde dehydrogenase, into a broad host-range plasmid vector, pKT230MC. The resulting plasmid, pDVABC, was introduced into the PpY1100 strain of *Pseudomonas putida*, and we found that PDC could be stably produced from protocatechuate and accumulated. In addition, we examined the efficiency of production of PDC from protocatechuate on a 5-L scale in a LB-medium containing 100 mM glucose, and determined that PDC was stably produced from protocatechuate to yield 10g/L or more.

2006-207

生命科学と有機材料科学を基盤としたリグニンの新しい高度利用に関する研究(II)

近藤晋<sup>\*1</sup>、大塚博之<sup>\*1</sup>、重原淳孝<sup>\*1</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>、政井英司<sup>\*2</sup>、福田雅夫<sup>\*2</sup>、大塚祐一郎<sup>\*3</sup>、中村雅哉<sup>\*3</sup>、大原誠資<sup>\*3</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>長岡技術科学大学、<sup>\*3</sup>森林総合研究所

Studies on the novel advanced utilization system of lignin based on the life science and organic material chemistry (II).

Susumu Rondo<sup>\*1</sup>, Hiroyuki Otsuka<sup>\*1</sup>, Kiyotaka Shigehara<sup>\*1</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Eiji Masai<sup>\*2</sup>, Masao Fukuda<sup>\*2</sup>, Yuichiro Otsuka<sup>\*3</sup>, Masaya Nakamura<sup>\*3</sup>, Seiji Ohara<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei Tokyo, 184-8588, Japan, <sup>\*2</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka Niigata, 940-2188, Japan, <sup>\*3</sup>Forestry and Forest Products Research Institute, 1 Matsunosato Tsukuba, Ibaraki, 305-8687, Japan

Abstract: 2-Pyrone-4,6-dicarboxylic acid (PDC) is an intermediate metabolite of *Sphingomonas paucimobilis* SYK-6 which can degrade and assimilate low molecular lignin. PDC can be used as polymer materials. We decided to produce PDC using genetic engineering. For practical use, we tried to produce PDC from various kinds of low molecular lignin in large scale. We finally produced PDC in 5L scale from vanillin, vanillate, syringate and *p*-hydroxybenzoate which were provided from chemical treatment of lignin. In addition, we tried to produce PDC from terephthalate which can be obtained easily and cheaply. And now, we can produce PDC from 10g/l of terephthalate. It helps to develop PDC application.

2006-208

リグノスルホン酸系硬質ポリウレタンフォームの発泡速度制御と熱的・機械的性質

畠山兵衛<sup>\*1</sup>、塵垣亜耶<sup>\*1</sup>、畠山立子<sup>\*2</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>リグノセルリサーチ

Effect of reaction rate on thermal and mechanical properties of sodium lignosulfonate-based polyurethane foams.

Hyo Hatakeyama<sup>\*1</sup>, Aya Hirogaki<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui University of Technology, 3-6-1, Gakuen, Fukui 910-8505, <sup>\*2</sup>Lignocell Research, 2-6-16, Mejirodai, Bunkyo-ku, Tokyo 112-0015

Abstract: Sodium lignosulfonate (NaLS)-based polyurethane (PU) foams were prepared using three kinds of ethylene glycols, such as diethylene glycol, triethylene glycol or polyethylene glycol. Two kinds of NaLS, weak acid based NaLS(WA) and weak alkaline based NaLS (WB), were used in order to control the foaming reaction. Stirring time, cream time and rise time were used as an index of foaming reaction. Mixing time was defined as a time interval from adding MDI to detect evolved

heat under stirring, cream time as a time interval from termination of stirring to starting of foaming, and rise time as a time interval from starting to completion of foaming. The above reaction times increased with increasing the amount of NaLS (WA) content in polyols. Apparent density, compression strength and compression modulus of PU foams linearly increased with reaction times. At the same time, the molecular mass of ethylene glycols markedly affects the molecular motion of PU foams. It was found that mechanical and thermal properties of PU foams are controllable through foaming reaction rate.

2006-209

リグニンスルホン酸塩を原料とするエステル型エポキシ樹脂の合成と熱的性質

廣瀬重雄<sup>\*1</sup>、相楽壮志<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup>産業技術総合研究所・環境化学、<sup>\*2</sup>リグノセルリサーチ、<sup>\*3</sup>福井工業大学工学部

Synthesis and thermal properties of epoxy resins from ligninsulfonate.

Shigeo Hirose<sup>\*1</sup>, Soshi Sagara<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Research Institute for Innovation in Sustainable Chemistry, AIST, Central 5, 1-1-4, Higashi, Tsukuba, Ibaraki 305-8565, Japan, <sup>\*2</sup>Lignocel Research Ltd., 2-6-16 Mejirodai, Bunkyo-ku, Tokyo 112-0015, Japan, <sup>\*3</sup>Fukui University of Technology, 3-6-1 Gakuen, Fukui-City, Fukui 901-8505, Japan

Abstract: Sodium ligninsulfonate (LS) was dissolved in ethylene glycol (EG) and the obtained mixture was allowed to react with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (LS-EG polyacid, LSEGPA). EG-polyacid (EGPA) was also prepared from EG. The mixture of LSEGPA and EGPA was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratios, mol/mol) was maintained at 1.1. The contents of LSEGPA in the mixture of LSEGPA and EGPA (LSEGPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures ( $T_g$ 's) of epoxy resins increased with increasing LSEGPA contents suggesting that lignin acts as a hard segment in epoxy resin networks. Thermal decomposition temperatures ( $T_d$ 's) of epoxy resins were almost constant regardless of LSEGPA contents.

2006-210

リグノスルホン酸をベースとしたポリカプロラクトン誘導体の物性と生分解性について

島田 幹夫、山下寿々佳、大西 徹、畠山 兵衛

福井工業大学工学部

Effect of biodegradation on thermal and spectroscopic properties of lignosulfonate-based polycaprolactone derivatives.

Mikio Shimada, Szuka Yamashita, Toru Omishi, Hyoe Hatakeyama

Fukui University of Technology, 3-6-1, Gakuen, Fukui, 910-8505

Abstract: Lignosulfonate-based poly caprolactone (L-PCL) specimens were subjected to biodegradation in the field. Spectroscopic and thermal properties of the recovered samples were analyzed with FTIR and DSC. The results suggested that ester moieties in L-PCL were more rapidly degraded than lignin moieties. The alternative experiment with MODA (Microbial Oxidative Degradation Analyzer) recently developed indicated that sucrose linked with PCL was decomposed to CO<sub>2</sub> much faster than L-PCL and cellulose.

2006-211

環状カーボネート／グリコール系加溶媒分解で得られるリグニンの化学構造と熱特性

久保智史、山田竜彦、橋田光

森林総合研究所

Chemical structure and thermal properties of the Lignin fraction prepared by the solvolysis using cyclic carbonate/glycol systems.

Satoshi Kubo, Tatsuhiko Yamada, Koh Hashida

Forestry and Forest Products Research Institute, 1 Matsunosato, Department of Biomass Chemistry Tsukuba, 305-8687 Japan

Abstract: A new solvolysis system is being proposed for the bioconversion of lignocellulosics to valuable chemicals and materials in FFPRI. Using the solvolysis systems of cyclic carbonates/glycol, our system can convert lignocellulose into levulinates with high conversion rates, and moldable lignin fraction. During this process, glycol chains that have high thermal mobility are introduced into the lignin molecules by the reaction with both of cyclic carbonates and glycols. With extent of reaction period, average length of ethylene glycol chain is extended, and GPC average molecular weight is increased. The amount of introduced glycol chain can be estimated by quantitative  $^{13}\text{C}$ -NMR with relaxation reagent, UV and thermogravimetric analysis.

2006-212

オルガノソルブリグニン(アセテート)／セルロース親和性ポリマー複合体の分子間相互作用の評価と木材・紙用速乾性接着剤としての応用

寺本好邦、田中紀子、堺真奈美、遠藤黄土

産業技術総合研究所バイオマス研究センター

Interaction in organosolv lignin and its acetate with synthetic polymers comprising vinyl pyrrolidone unit.

Yoshikuni Teramoto, Noriko Tanaka, Manami Sakai, Takashi Endo

National Institute of Advanced Industrial Science and Technology (AIST), Biomass Technology Research Center (BTRC), Kure 737-0197, Japan

Abstract: Binary blends and pseudo complexes of organosolv lignin (OSL) and acetylated OSL with poly(N-vinyl pyrrolidone) (PVP) and poly(N-vinyl pyrrolidone-co-vinyl acetate) (PVPVAc) were prepared, respectively, by casting from mixed polymer solution in NN-dimethylformamide as good solvent and by spontaneous co-precipitation from solutions in tetrahydrofuran as comparatively poor solvent. Miscibility and intermolecular interaction of the blends were investigated by means of DSC and FT-IR. FT-IR spectra revealed the presence of hydrogen-bonding interactions between hydroxyl groups of OSL and carbonyl groups of N-vinyl pyrrolidone units. Thermal transition data obtained in the DSC analysis clarified that the blends of the two polymers exhibited decidedly a single and composition-dependant  $T_g$  between the  $T_g$ s of the individual components. This observation demonstrates that the blend system is miscible. The existences of both the hydroxyl group in OSL and VP unit in vinyl polymers were essential for the emergence of miscibility and the formation of pseudo-complexes.

2006-213

針葉樹パルプ製造とバイオエネルギー生産における国産カラマツ材の有効利用

高橋史帆、中川明子、金光汎、大井洋

筑波大学大学院生命環境科学研究科

Effective utilization of Japanese *Larix leptolepis* wood for production of softwood pulp and bio-energy.

Shiho Takahashi, Akiko Nakagawa-izumi, Guang-fan Jin, Hiroshi Ohi

Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Ibaraki  
305-8572 Japan

Abstract: Eighty seven percent of the afforestation area in Japan is coniferous forest. For the effective production of pulp and bio-energy, the kraft and soda pulp yields of Japanese major planted softwoods (*Larix leptolepis*, *Pinus densiflora*, *Cryptomeria japonica*) were investigated, and compared those of imported hardwoods (*Acacia*, *Eucalyptus*). The softwood pulp yields at a kraft pulp mill were estimated by a method based on the ratios of mannose to glucose from pulps. The organic elements components in the black liquors were estimated for their utilization as bio-energy.

2006-214

リグニンによる転写因子 NF- $\kappa$ B の活性化の抑制

三橋進也、岸本崇生、浦木康光、生方信

北海道大学大学院農学研究科

Lignin suppresses NF- $\kappa$ B activation in 293-T cells.

Shinya Mitsuhashi, Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata

Research Faculty of Agriculture, Hokkaido University

Abstract: Transcription factor NF- $\kappa$ B controls cell functions such as apoptosis, inflammation, the immune response, cell growth, differentiation, and chronic infection with human immunodeficiency virus type 1(HIV-1). Activation of NF- $\kappa$ B by external stimuli such as tumor necrosis factor  $\alpha$  (TNF  $\alpha$ ) and its binding to long terminal repeat (LTR) of HIV-1 triggers the initiation of transcription of viral genes. In this study, we use several lignins to show that lignins inhibit expression of NF- $\kappa$ B and LTR(HIV-1) reporter genes. Low molecular weight lignins (800<) were more effective rather than high molecular weight lignins. Furthermore, we exhibit that a  $\beta$ -5 lignin model compound shows stronger inhibitory activity than  $\beta$ -O-4 lignin model compounds. These results suggest that low molecular weight lignins (dimer or trimer?) suppress HIV-1 replication and NF- $\kappa$ B activation, and that lignin could be lead-compound for medical drugs.

2006-215

酢酸リグニンの工業利用に関する研究

宮田直紀<sup>\*1</sup>、荻野晋一<sup>\*1</sup>、浦木康光<sup>\*2</sup>、生方信<sup>\*2</sup>

<sup>\*1</sup> 関西ペイント株式会社、<sup>\*2</sup> 北海道大学大学院農学研究科

A study for industrial utilization of acetic acid lignin.

Naonori Miyata<sup>\*1</sup>, Sinichi Ogino<sup>\*1</sup>, Yasumitsu Uraki<sup>\*2</sup>, Makoto Ubukata<sup>\*2</sup>

<sup>\*1</sup>Kansai Paint Co., Ltd., Hiratsuka 254-8562, Japan, <sup>\*2</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

Abstract: Attempts were made to utilize palm oil residues with acetic acid pulping process under atmospheric pressure. Empty fruit bunch, herein after called EFB, of the oil palm was digested into pulp and acetic acid lignin, herein after called AL, through the process, since lignin reacted with and dissolved into acetic acid. Oil palm AL showed heat fusion characteristic and dissolved into organic solvents such as acetone and etc, as same manner as other ALs taken from ordinary woods. Board-shaped moldings were prepared from the pulp and the AL from EFB by proper pressurizing at around 170 degree C. Bending strength of the moldings was easily controlled by varying molding pressure and/or temperature or composition ratio between the pulp and the AL. Another attempt was made to prove termites repellent or termiticide of the AL. Cedar chips treated with diluted AL showed certain repellency and termiticide effect to suggest a new usage of the AL.

2006-特別講演 II

## 人工土壌マトリックスとしてのオガ屑 –リグニンの存在と意義–

寺沢 実

北海道大学大学院農学研究科、環境資源学部門、森林資源科学分野、森林化学研究室

Invited Lecture, II

Sawdust as an artificial soil matrix for bioconversion of biomass wastes into multifunctional recyclables, – Significance of the existence of lignin in sawdust–.

Minoru Terazawa

Research Group of Forest Resources Science, Environmental Resources Division, Graduate School of Agriculture, Hokkaido University, Sapporo 060–8589, Japan

Abstract: Biomass wastes such as garbage (food oriented wastes), excreta, and livestock manure are effectively bio-converted into multifunctional recyclables in the GADE (garbage automatic decomposer-extinguisher), BT (bio-toilet, dry toilet or composting toilet), and LMF (livestock manure fixer) systems, respectively, using sawdust as an artificial soil matrix in the systems. Mushroom cultivation beds, anti-fire fiberboard, nutrition containing planting pots, pellets, packing materials, etc. are the multi-functional recyclables. High porosity of sawdust is the main function of sawdust, offering the high air retention and moderate water retention. High surface ratio of sawdust contributes the effective evaporation of water from the sawdust matrix. These characteristics keep the matrix aerobic conditions. Aerobic biodegradation of the organic matters in the wastes is essential for the odorless operation of the systems. High bacterial tolerance and high abrasion tolerance are caused from the existence of lignin in the matrix. Because of the existence of lignin, sawdust can be used for long period as the artificial soil matrix. Practical uses of sawdust will be introduced.

2006–P01

### リグニンの $\alpha$ 位水酸基の生成と脱離に関する分子軌道解析

伊藤直人<sup>\*1</sup>、正本博士<sup>\*1</sup>、重松幹二<sup>\*1</sup>、岸本崇生<sup>\*2</sup>

<sup>\*1</sup> 福岡大学工学部、<sup>\*2</sup> 北海道大学大学院農学研究科

Molecular orbital analysis on the formation and cleavage of  $\alpha$ -hydroxyl group in lignin.

Naoto Ito<sup>\*1</sup>, Hiroshi Masamoto<sup>\*1</sup>, Mikiji Shigematsu<sup>\*1</sup>, Takao Kishimoto<sup>\*2</sup>

<sup>\*1</sup>Faculty of Engineering, Fukuoka University, Fukuoka 814–0180, Japan, <sup>\*2</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060–8589, Japan

Abstract: To investigate the formation of  $\alpha$ -hydroxyl group in lignin, the  $\beta$ -O-4 lignin model compounds were analyzed with an *ab initio* molecular orbital calculation using RB3LYP/6-31G\* method. The optimum conformations were varied with the existence of methoxyl groups in B-ring. The electrostatic charges at  $\alpha$ -carbon were negative value and similar in neutral quinonemethides. For cationic enol radicals of guaiacyl and syringyl models, the electrostatic charge at  $\alpha$ -carbon transferred to positive value by protonation of ketone in quinonemethides. Also the HOMO-LUMO gaps were independent with the methoxyl groups but much decreased with protonation.

2006–P02

### レジノール構造の生成に関する分子軌道解析

高口良輔, 正本博士, 重松幹二

福岡大学工学部

Molecular orbital analysis on the formation of resinol structure.

Ryosuke Kouguchi, Hiroshi Masamoto, Mikiji Sbigematsu

Faculty of Engineering, Fukuoka University, Fukuoka 814–0180, Japan

Abstract: The reaction mechanism in radical coupling reaction of lignin was analyzed with a

molecular orbital calculation. The charge density, the electrostatic potential and the spin density of monolignol radicals were determined with UB3LYP/6-31G\* basis set. For the simulation in acid solution, the spin density at C<sub>8</sub> was increased by protonation of O<sub>4</sub>. The transition states during radical coupling reaction were determined with semi-empirical molecular orbital calculation by using UPM3. The simulation on the reaction of cationic and neutral radicals of sinapyl alcohol demonstrated that β-O coupling dominantly produced compared with β-β coupling. This computational result agrees with the experimental result that the production of β-O dimer increases in acid solution.

2006-P03

木材抽出成分の着色に関する計算化学シミュレーション

宮脇圭司、正本博士、重松幹二

福岡大学工学部

Computer-chemical simulation on the coloration of woody extractives.

Keiji Miyawaki, Hiroshi Masamoto, Mikiji Shigematsu

Faculty of Engineering, Fukuoka University, Fukuoka 814-0180, Japan

Abstract: To predict the color change of norlignans, UV/VIS spectra were simulated with the molecular orbital energies determined by an *ab initio* molecular orbital calculation (RB3LYP/6-31G\*). Obtained spectra well expressed the coloration of sequirin-C involving the oxidation with enzyme, air or alkaline treatment; sequirin-C is the main component causing the blacking of sugi (*Cryptomeria japonica*) heartwood. We believe this simulation technique is useful for the prediction of UV/VIS spectrum of unknown or unpurified substances, and the chase of intermediates in various reaction pathways.

2006-P04

計算化学によるタンニン吸着機構の解析

荒木孝文<sup>\*1</sup>、正本博士<sup>\*1</sup>、重松幹二<sup>\*1</sup>、光永徹<sup>\*2</sup>

福岡大学工学部、岐阜大応生

Computer-chemical analysis on the adsorption mechanism of tannin.

Takafumi Araki<sup>\*1</sup>, Hiroshi Masamoto<sup>\*1</sup>, Mikiji Shigematsu<sup>\*1</sup>, Tohru Mitsunaga<sup>\*2</sup>

<sup>\*1</sup>Faculty of Engineering, Fukuoka University, Fukuoka 814-0180, Japan, <sup>\*2</sup>Faculty of Applied Biological Science, Gifu University, Gifu 501-1193, Japan

Abstract: The conformation, the dipole and the electrostatic potential of proanthocyanidins up to hexamer were computed with a semi-empirical molecular orbital calculation (RPM3). In the case of (4α-8)-catechins, the dipole increased with the degree of polymerization. This tendency was parallel to the experimental result in the precipitation of protein by fractionated bark tannin. For other proanthocyanidins, the dipoles of (4α-6)-catechins and (4β-8)-epicatechins were decreased at odd and even values, respectively, of the degree of polymerization.

2006-P05

リグニンの熱分解: β-O-4 構造単位由来の生成物

黒田健一<sup>\*1</sup>、岸本崇生<sup>\*2</sup>、中川明子<sup>\*3</sup>、芦谷竜矢<sup>\*4</sup>、藤田弘毅<sup>\*1</sup>

<sup>\*1</sup>九州大学大学院農学研究院、<sup>\*2</sup>北海道大学大学院農学研究科、<sup>\*3</sup>筑波大学大学院生命環境科学研究科、<sup>\*4</sup>秋田県立大学

Pyrolysis of lignin: Products stemming from β-O-4 subunits.

Ken-ichi Kuroda<sup>\*1</sup>, Takao Kishimoto<sup>\*2</sup>, Akiko Nakagawa-izumi<sup>\*3</sup>, Tatsuya Ashitami<sup>\*4</sup>, Koki Fujita<sup>\*1</sup>

<sup>\*1</sup>Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University,

6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan, \*<sup>2</sup>Graduate School of Agriculture, Hokkaido University, Sapporo, 060-85 89, Japa, \*<sup>3</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8572, Japan, \*<sup>4</sup>Institute of Wood Technology, Akita Prefectural University, 11-1, Kaiezaka, Noshiro, Akita 016-0876, Japan

Abstract: Sources of pyrolysis products of lignin were investigated in conventional pyrolysis and in pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) (TMAH thermochemolysis). To know the contribution of  $\beta$ -O-4 subunits to the pyrograms of lignins, a polymer (I, DPn 15.8), connected only by  $\beta$ -O-4 linkages, was subjected to both conventional pyrolysis (500°C/4s) and TMAH thermochemolysis (315°C/4s). Products were monitored by gas chromatography/mass spectrometry and compared with those of guaiacylglycerol- $\beta$ -guaiacyl ether (II) and lignins (bulk dehydrogenation polymer of coniferyl alcohol and Japanese cedar wood lignin). I produced most of monomeric products observed in conventional pyrolysis and TMAH thermochemolysis. The results show that  $\beta$ -O-4 subunits make a large contribution to the lignin pyrograms obtained in conventional pyrolysis and TMAH thermochemolysis.

2006-P06

白色腐朽担子菌による PCB 代謝に関与するメチルトランスフェラーゼ

岸本雅樹、亀井一郎、近藤隆一郎

九州大学大学院農学研究院

Methyltransferase involved in PCB metabolism by white-rot fungi.

Masaki Kishimoto, Ichiro Kamei, Ryuichiro Kondo

Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: Polychlorinated biphenyls (PCBs) are recalcitrant pollutants. Degradation experiment of model PCB compound, 4,4'-dichlorobiphenyl (4,4'-DCB) and its metabolites by white-rot fungus, *Phlebia brevispora* TMIC33929, which is capable of degrading a part of coplanar PCBs was carried out. The metabolic pathway of 4,4'-DCB was elucidated by the identification of metabolites upon addition of 4,4'-DCB and its metabolic intermediates. These results suggested the metabolic pathway was branched two pathways, a methylation pathway and a ring cleavage pathway, via initial metabolite, 3-hydroxy-4,4'-DCB. Of two pathways, the methylation pathway was predominantly compared to the ring cleavage pathway, and 3-methoxy-4,4'-DCB was decreased slowly. The conversion of 3-hydroxy-4,4'-DCB into 3-methoxy-4,4'-DCB was shown to occur by O methylation of 3-hydroxy-4,4'-DCB in a reaction catalyzed by S-adenosyl-L-methionine dependent O-methyltransferase.

2006-P07

白色腐朽菌からの微生物製剤作成の試み

佐々木良輝、古山健太、伊藤和貴、橘燦郎

愛媛大学農学部

Attempts to make a microbial preparation from a white-rot fungus.

Yoshiteru Sasaki, Kenta Furuyama, Kazutaka Itoh, Sanro Tachibana

Department of Applied Bioscience, Faculty of Agriculture, Ehime University, 3-5-7 Tarumi, Matsuyama, Ehime 790-8566, Japan

Abstract: In the present study, microbial preparation used several porous materials (zeolite, charcoal coated with ceramics, and wood) as basic materials were tried to prepare for bioremediation of dioxin-contaminated soil with white-rot fungi. The microbial preparations were made by adsorption of fungal biomass on the surface of porous materials. Furthermore, the microbial preparations were entrapped with calcium alginate gel. And the preparations were estimated by the

decolonization ability on the agar plate impregnated with the dye as well as degradation rate of 2,4,8-Trichlorodibenzofuran (2,4,8-TCDF) in the soil. The degradation rate of 2,4,8-TCDF in the soil was only 10% for 30 days when the treatment with non-entrapped microbial preparation (zeolite) was conducted for 30 days. In contrast, 20% of 2,4,8-TCDF was degraded when the treatment with entrapped microbial preparations (zeolite and charcoal) was conducted for 30 days. These results suggest that bioremediation of dioxin-contaminated soil by microbial preparations made from white-rot fungi is possible.

2006-P08

ダイオキシン分解菌からの酵素を用いた酵素製剤作成の試み

藤井啓太, 橘 燦郎, 栗田紘希, 柚本 聡, 伊藤和貴

愛媛大学農学部

Attempts to make an enzyme preparation by crude enzyme from fungus capable of dioxins.

Keita Fujii, Sanro Tachibana, Kouki Kurita, Satoshi Somamoto, Kazutaka Ito

Department of Applied Bioscience, Faculty of Agriculture, Ehime University, 3-5-7 Tarumi, Matsuyama, Ehime 790-8566, Japan

Abstract: Environmental pollution caused by endocrine disrupting chemicals (environmental hormones) such as DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane] has become a major social problem. Therefore, several methods of dealing with environmental pollution have been proposed. Bioremediation with microorganisms or enzymes from the microorganisms is considered a most effective method of dealing with widespread pollution involving a low concentration of pollutant. In the present report, biodegradation of environmental hormones [DDT, 2,4,8-TCDF (2,4,8-trichloro-dibenzofuran) and TCB (3,3',4,4'-tetrachlorobiphenyl)] in water with a double capsule (an enzyme preparation) prepared from crude enzyme from fungi capable of dioxins, HBT(1-hydroxybenzotriazole) and so on was conducted. The result showed that DDT, 2,4,8-TCDF and TCB could be degraded for 72 hours by the treatment. The rates of degradation were 50, 15 and 30%, respectively. In addition, environmental hormones (DDT, TCB) in soil were also degraded by the treatment.

2006-P09

ゴマの機能性リグナンの生合成、特にセサミノール配糖体等について

鈴木利貞<sup>\*1</sup>、片山健至<sup>\*1</sup>、大野素未<sup>\*1</sup>、小堀里恵<sup>\*1</sup>、並木満夫<sup>\*2</sup>、田代 亨<sup>\*3</sup>

<sup>\*1</sup>香川大学農学部、<sup>\*2</sup>おいしさの科学研究所、<sup>\*3</sup>千葉大学園芸学部

Biosynthesis of functional lignans, particularly sesaminol glycosides, in *Sesamum indicum* seeds

Toshisada Suzuki<sup>\*1</sup>, Takeshi Katayama<sup>\*1</sup>, Motomi Olmo<sup>\*1</sup>, Rie Kobori<sup>\*1</sup>, Mitsuo Namiki<sup>\*2</sup>, Toru Tashiro<sup>\*3</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795, <sup>\*2</sup>Institute of Oishisa Science, 2217-44 Hayashi, Takamatsu, Kagawa 761-0301, <sup>\*3</sup>Faculty of Horticulture, Chiba University, 648 Matsudo, Chiba 271-8510

Abstract: Sesame seeds contain phenolic and antioxidant lignans such as sesaminol and pinoresinol, as well as sesamin and sesamol. However, biosynthesis of the sesame lignans, particularly sesaminol and sesaminol glycosides was not clarified. In this study, feeding experiments of L-[U-<sup>14</sup>C]phenylalanine (Phe) were carried out. A solution of L-[U-<sup>14</sup>C]Phe (10 mM, 20 ml) was injected into unripe capsules of 11 week-old intact plants (*Sesame indicum* var. Mie-dai No.1 and *S. indicum* var. Chinese 36), and the plants were cultivated for a week at 26°C. The radioactivity was incorporated into free sesaminol and sesaminol triglucoside and sesaminol diglucoside. The percent incorporation into sesaminol and sesaminol glycosides in seeds was eight times larger than that in the pods. In addition, the radioactivity was incorporated into 7-carbonyl type lignan glycoside in seeds.

2006-P10

新規白色腐朽菌 *Phellinus* sp. SKM2102 株の脂肪酸不飽和化酵素遺伝子の単離・解析  
吉田太郎、矢野健太、津田冴子、渡邊崇人、本田与一、渡辺隆司  
京都大学生存圏研究所

Characterization of fatty acid desaturase genes from a white-rot fungus, *Phellinus* sp. SKM2102.  
Taro Yoshida, Kenta Yano, Saeko Tsuda, Takahito Watanabe, Yoichi Honda, Takashi Watanabe  
Laboratory of Biomass conversion, Research Institute for Sustainable Humansphere, Kyoto  
University, Gokasho, Uji, Kyoto 611-0011, Japan

Abstract: A new white-rot fungus, *Phellinus* sp. SKM2102, exhibits high pretreatment effects for enzymatic saccharification of wood similar to those of a selective lignin-degrading fungus, *Ceriporiopsis subvermispora*. However, profiles of their metabolites, such as fatty acids, are different, reflecting the differences of the gene expression involved in the fatty acid metabolism of these strains. We focus on the fatty acid metabolism, especially the biosynthesis of unsaturated fatty acids because unsaturated fatty acids are the precursors of lipid peroxidation in the selective lignin degradation by *C. subvermispora*. In order to investigate the unsaturation of fatty acids, we have already cloned fatty acid desaturase genes from *C. subvermispora*. In this report, we cloned fatty acid desaturase genes from SKM2102 by PCR-based method.

2006-P11

フェルラ酸ステアリルの酵素触媒二次元重合  
坂本昌平、上高原 浩、高野俊幸、中坪文明  
京都大学大学院農学研究科

Enzyme-catalyzed two-dimensional polymerization of stearylferulate.

Shohei Sakamoto, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo  
Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan

Abstract: Two-dimensional polymerization is a novel approach which can bring improved control of monomer reactivity and orientation in the resulting polymer compared to the polymer by conventional method. A good p-A isotherm of Stearylferulate (FA18) was obtained on phosphate buffer (pH=6.5) as well as on ultrapure water, so FA18 was spread at an air-water interface on buffer solution, and polymerized with horseradish peroxidase (HRP) and H<sub>2</sub>O<sub>2</sub> in dark. From the results of UV spectroscopic analysis, it was suggested that the two-dimensional polymerization afforded the polymer with different bond pattern from that of the conventional polymer.

2006-P12

リグニンモデル化合物の電気化学的酸化  
白石 匠、上高原 浩、高野俊幸、中坪文明  
京都大学大学院農学研究科

Electrooxidation of lignin model compounds.

Takumi Shiraishi, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo  
Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University,  
Sakyo-ku Kyoto, 606-8502, Japan

Abstract: The anodic oxidation of a lignin model compound, 1-(4'-ethoxy-3'-methoxyphenyl) ethanol (1G) was investigated to introduce carbonyl group at  $\alpha$ -position. Cyclic voltammetric measurements of 1G and other 1-phenyl ethanol derivatives, 1-(4'-ethoxy-3',5'-dimethoxyphenyl) ethanol (1S) and 1-(4'-ethoxyphenyl) ethanol (1P), were performed to determine their redox potentials and compare electronic properties of nonphenolic G, S, P substructures in lignins. The

compound 1G was oxidized by bulk electrolysis in acetonitrile. In electrolysis without base, various side reactions occurred, and  $\alpha$ -carbonyl product was obtained in low yield. Whereas, electrolysis with base or H<sub>2</sub>O gave  $\alpha$ -carbonyl derivative (2G) in high yield. The proposed electrooxidation mechanism of 1G is likely guideline for  $\alpha$ -carbonyl introduction to neutral lignin structures.

2006-P13

植物細胞壁木化過程のシュミレーション、 $\alpha$ -ポリエチレングリコールを用いたシリングルグリセロール- $\beta$ -シナピルアルコールエーテルの合成

小路裕美<sup>\*1</sup>、小林孝行<sup>\*1</sup>、棚橋光彦<sup>\*1</sup>、重松幹二<sup>\*2</sup>

<sup>\*1</sup> 岐阜大学大学院農学研究科、<sup>\*2</sup> 福岡大学工学部

Simulation of plant cell wall lignification process. - Dehydrogenative syringylglycerol- $\beta$ -sinapyl alcohol ether in the presence of polyethylene glycol-

Hiromi Koji<sup>\*1</sup>, Takayuki Kobayashi<sup>\*1</sup>, Mitsuhiko Tanahashi<sup>\*1</sup>, Mikiji Shigematsu<sup>\*2</sup>

<sup>\*1</sup>Laboratory of Biomass Conversion, Graduate School of Agriculture, Gifu University, 1-1 Yanagido, 501-1193 Gifu, Japan, <sup>\*2</sup>Faculty of Engineering, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

Abstract: DHPs (dehydrogenative polymer of monolignols, artificial lignins) have been used as model compounds to clarify the chemical structure and the formation mechanism of lignins in plant cell walls. DHP of the sinapyl alcohol is remarkably different from lignin in the hardwood cell wall. For example, syringaresinol is formed mainly from the sinapyl alcohol with a small amount of  $\beta$ -O-4 type on using the mixed method polymerization. Also, in relating to the drop-wised method polymerization, lower molecular weight S-DHP including mainly  $\beta$ - $\beta$  type linkage are formed. It is therefore important to examine the polymerization condition of DHP for clarifying the biosynthesis mechanism of lignin in cell wall. We have succeeded to synthesize lignin containing a large amount of  $\beta$ -O-4 unit under the hydrophobic condition using the polysaccharide gel. In the paper, enzymatic dehydrogenative polymerization of sinapyl alcohol is tried under the hydrophobic condition using polyethylene glycol (PEG).

2006-P14

広葉樹硫酸リグニンのフェノール化に関する研究

松下泰幸、佐野仁美、今井絡徳、今井貴規、福島和彦

名古屋大学大学院生命農学研究科

Study of phenolization of hardwood sulfuric acid lignin.

Yasuyuki Matsushita, Hitomi Sano, Masanori Imai, Takanori Imai, Kazuhiko Fukushima

Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601 Japan

Abstract: To study the behavior of hardwood sulfuric acid lignin (SAL) during phenolization, we compared the product yield, average molecular weight, methoxy content, and reactions of simple model compounds with those of softwood SAL, focusing on the difference between syringyl and guaiacyl units. The beech SAL reacted with phenol more readily than red pine SAL and yielded a greater soluble fraction of phenolized SAL. To investigate the difference in the phenolization activity of the syringyl and guaiacyl units in beech lignin, we prepared syringyl-nucleus-rich sulfuric acid lignin (S-rich-SAL) and guaiacyl-nucleus-rich sulfuric acid lignin (G-rich-SAL) from beech, which were subjected to phenolization. The results suggest that the syringyl unit in SAL had greater phenolization activity and its phenolized products were more soluble in acidic aqueous medium and introduced less phenol than the guaiacyl unit to solubilize. The study using model compounds also showed that the syringyl unit had higher phenolization reactivity than the guaiacyl unit.

2006-P15

リグノクレゾールを利用した環境適合型接着剤の開発

原田征<sup>\*1</sup>、石垣友三<sup>\*1</sup>、小田三都郎<sup>\*1</sup>、秋田重人<sup>\*1</sup>、平野幸治<sup>\*1</sup>、福田博行<sup>\*1</sup>、水野恭介<sup>\*2</sup>、岡部洋治<sup>\*2</sup>  
<sup>\*1</sup>名古屋市工業研究所、<sup>\*2</sup>東洋樹脂株式会社

Development of environmental-friendly lignocresol-based adhesive.

Masaki Harada<sup>\*1</sup>, Yuzo Ishigaki<sup>\*1</sup>, Mitsuo Od<sup>\*1</sup>, Shigendo Akita<sup>\*1</sup>, Koji Hirano<sup>\*1</sup>, Hiroyuki Fukuda<sup>\*1</sup>,  
Kyosuke Mizuno<sup>\*2</sup>, Yoji Okabe<sup>\*2</sup>

<sup>\*1</sup>Nagoya Municipal Industrial Research Institute, 3-4-41 Rokuban, Atsuta-ku, Nagoya 456-0058, Japan, <sup>\*2</sup>Toyo Jushi Co., 450, Hayashiazanohara, Komaki, Aichi 485-0805, Japan

Abstract: Biodegradable lignin-derivatives are gathering attention as a possible source for polymer materials. Lignocresol (LC) is produced through reactive extraction with *p*-cresol from lignin-containing wood, and is considered to be biomass-derived polyol since it has a number of phenolic and alcoholic hydroxyl groups. In this study, a polyurethane based adhesive was prepared from a ternary mixture of LC / polyethylene glycol (PEG) / Lysine triisocyanate (LTI) (2-Isocyanatethyl-2,6-diisocyanatecaproate), and was applied for the bonding of wood. Satisfactory tensile share strength of over 10 MPa was obtained with the adhesive, indicating a promising use of LC as an ingredient of environmentally-friendly adhesives.

2006-P16

白色腐朽菌 *Phanerochaete sordida* YK-624 株の産生する菌体外ペプチド様物質の機能特性  
平井浩文, 森田英弘, 河合真吾, 西田友昭

静岡大学農学部

Functional characterization of peptide-like compound produced by white-rot fungus *Phanerochaete sordida* YK-624.

Hirofumi Hirai, Hidehiro Morita, Shingo Kawai, Tomoaki Nishida

Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan

Abstract: White-rot fungus *Phanerochaete sordida* YK-624 produced a compound (YK-S) which inhibited the veratryl alcohol (VA) oxidation by novel lignin peroxidase (YK-LiP1) from this fungus. YK-S, which was produced under shaking culture, was purified to homogeneity by anion-exchange chromatography and gel permeation chromatography. By MALDI TOF-MS analysis, the molecular mass of YK-S was 1.822 Da, and YK-S contained 560 Da of peptide. Inhibitory effect of YK-S on VA oxidation by YK-LiP1 was investigated by Lineweaver-Burke plot in order to analyze the reaction mechanism of YK-S with YK-LiP1. YK-S inhibited VA oxidation by YK-LiP1 in a noncompetitive manner, and *K<sub>i</sub>* Value of YK-S for YK-LiP1 was 103 mM. Moreover, the inactivation of YK-LiP1 by hydrogen peroxide was repressed under the presence of YK-S. These results strongly suggest that the role of YK-S is same as that of VA which functions as the substrate of Lip from *P. chrysosporium*.

2006-P17

バクテリアによるリグニン由来化合物代謝に関与する新規脱メチルシステム

阿部友邦<sup>\*1</sup>、佐々木光雪<sup>\*1</sup>、宮内啓介<sup>\*1</sup>、政井英司<sup>\*1</sup>、福田雅夫<sup>\*1</sup>、片山義博<sup>\*2</sup>

<sup>\*1</sup>長岡技術科学大学・生物機能工学、<sup>\*2</sup>東京農工大学大学院 BASE

A novel tetrahydrofolate-dependent *O*-demethylation system in lignin metabolism by bacteria.

Tomokuni Abe<sup>\*1</sup>, Miyuki Sasaki<sup>\*1</sup>, Keisuke Miyauchi<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Eiji Masai<sup>\*1</sup>, Masao Fukuda<sup>\*1</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188,

<sup>\*2</sup>Graduate School of Bio Applications and Systems Engineering, Tokyo University of Agriculture and

Technology, Koganei, Tokyo 184-8588, Japan

**Abstract:** The catabolism of vanillate and syringate by bacteria is an important process of the microbial lignin degradation. In *Sphingomonas paucimobilis* SYK-6, vanillate and syringate are converted into protocatechuate (PCA) and 3-*O*-methylgallate (3MGA), respectively, by *O*-demethylases. In this study, we isolated the *ligM* gene that conferred on *Escherichia coli* the activity required for the conversion of vanillate and 3MGA to PCA and gallate, respectively, with similar specific activities. The LigM catalyzes the transfer of the methyl moiety of vanillate to tetrahydrofolate (H<sub>4</sub>folate), thereby forming PCA and 5-methyl-H<sub>4</sub>folate. We demonstrated that PCA is not a growth substrate for SYK-6 cells, but we also showed that this strain is able to grow well on PCA in the presence of methionine. This finding suggested that the 5-methyl-H<sub>4</sub>folate generated by the *O* demethylation of vanillate is essential for methionine biosynthesis. Downstream of *ligM*, two ORFs, which showed similarity with 5,10-methylene-H<sub>4</sub>folate reductase gene (*metF*) and 10-formyl-H<sub>4</sub>folate synthetase gene (*ligH*), were identified, and these genes were found to constitute an operon. These results indicated that the *O* demethylation of vanillate and the C<sub>1</sub> metabolism are simultaneously regulated in SYK-6. In conclusion, the *O* demethylation of vanillate catalyzed by LigM is important for SYK-6 cells, not only as a degradation step for vanillate, but also to supply the 5-methyl-H<sub>4</sub>folate required for methionine biosynthesis.

2006-P18

バクテリアによるシリング酸代謝に関するジオキシゲナーゼシステム

笠井大輔<sup>\*1</sup>、政井英司<sup>\*1</sup>、宮内啓介<sup>\*1</sup>、福田雅夫<sup>\*1</sup>、片山義博<sup>\*2</sup>

<sup>\*1</sup>長岡技術科学大学・生物機能工学、<sup>\*2</sup>東京農工大学大学院 BASE

The ring cleavage dioxygenase system involved in the syringate catabolic pathways in *Sphingomonas paucimobilis* SYK-6.

Daistike Kasai<sup>\*1</sup>, Eiji Masai<sup>\*1</sup>, Keisuke Miyauchi<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Masao Ftikuda<sup>\*1</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188,

<sup>\*2</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo Univswiy of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

**Abstract:** *Sphingomonas paucimobilis* SYK-6 converts vanillate and syringate, which are intermediate metabolites of lignin, to protochatechuate (PCA) and 3-*O*-methylgallate (3MGA), respectively. Previous studies have indicated that PCA is further degraded by the reaction catalyzed by PCA 4,5-dioxygenase (LigAB) in PCA 4,5-cleavage pathway. In order to determine die ring cleavage pathways for syringate metabolism, we isolated and characterized the ring cleavage dioxygenase genes, *desZ* and *desB*, which confer the 3MGA and gallate degradation activities on *Escherichia coli*, respectively. Based on the analysis of enzymatic properties of these gene products and various SYK-6 mutants lacking die genes involved in the syringate degradation, we concluded that (i) all three-ring cleavage dioxygenases are involved in syringate catabolism, (ii) DesB and LigAB are involved in the degradation of gallate, and (iii) the pathway involving DesB plays an especially important role in the growth of SYK-6 on syringate.

2006-P19

樹木の細胞分裂制御に関する研究

松井紀子<sup>\*1</sup>、本村菜荊子<sup>\*1</sup>、半智史<sup>\*2</sup>、西窪仲之<sup>\*3</sup>、篠崎祐介<sup>\*4</sup>、佐藤かな<sup>\*5</sup>、北野英己<sup>\*5</sup>、船田良<sup>\*2</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>東京農工大学大学院農学研究科、<sup>\*3</sup>理化学研究所植物科学研究センター、<sup>\*4</sup>名古屋大学大学院生命農学研究科、<sup>\*5</sup>名古屋大学・生物機能開発利用研究センター  
Research on cell division control of woody plant.

Noriko Matsui<sup>\*1</sup>, Mariko Motomura<sup>\*1</sup>, Satoshi Nakaba<sup>\*2</sup>, Nobuyuki Nishikubo<sup>\*3</sup>, Yusuke Shinozaki<sup>\*4</sup>, Kanna Sato<sup>\*5</sup>, Hidemi Kitano<sup>\*5</sup>, Ryo Funada<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan, <sup>\*2</sup>Graduate school of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo, 183-8509, Japan, <sup>\*3</sup>RIKEN Plant Science center, Yokohama, Kanagawa, 230-0045, Japan, <sup>\*4</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya, Aichi, 464-8601, Japan, <sup>\*5</sup>Bioscience and Biotechnology Center, Nagoya University, Nagoya, Aichi, 464-8601, Japan

**Abstract:** As the largest storage organ in woody plants, it is of economic significance because most forest products are derived from the stem and help alleviate global warming by sequestering and storing carbons in long-term storage. Thickening of stem occurs as a result of growth and differentiation of secondary tissues produced by the vascular cambium. Therefore, control of cell division in vascular cambium leads to the improvement of woody resource production. In this study, we generated transgenic tobacco and poplar overexpressing CycD, E2F and DP-core cell cycle related genes and examined their influences for cell division, cell expansion, cell wall biosynthesis and lignification in secondary xylem. Moreover, as another approach of the cell division control, we try to solve the mechanism of an increase of the number of cells by suppression of genes. Here, we screened and analyzed a rice mutant that has many cells though growth normally.

2006-P20

シキミ酸経路を経由したグルコースからの 2H-pyran-2-one-4,6-dicarboxylic acid (PDC) 生産系の開発

西野由香里<sup>\*1</sup>、田村真統<sup>\*1</sup>、大塚博之<sup>\*1</sup>、近藤晋<sup>\*1</sup>、政井英司<sup>\*2</sup>、片山義博<sup>\*1</sup>、梶田真也<sup>\*1</sup>  
東京農工大学大学院 BASE、長岡技術科学大学・生物機能工学

Biological conversion of glucose to 2H-pyran-2-one-4,6-dicarboxylic acid (PDC) by the bypassed shikimate pathways.

Yukari Nishino<sup>\*1</sup>, Masatsugu Tamura<sup>\*1</sup>, Hiroyuki Otsuka<sup>\*1</sup>, Susumu Kondo<sup>\*1</sup>, Eiji Masai<sup>\*2</sup>, Yoshihiro Katayama<sup>\*1</sup>, Shinya Kajita<sup>\*1</sup>

<sup>\*1</sup>Graduate school of Bio-Applications and Systems Engineering, <sup>\*2</sup>Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan, <sup>\*2</sup>Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

**Abstract:** PDC, 2H-pyran-2-one-4,6-dicarboxylic acid, is one of metabolic intermediates in *Sphingomonas paucimobilis* SYK-6 that is a degrader of lignin-derived compounds. This compound has been also characterized as a raw material for synthetic polymers such as polyester and polyamide. In the previous study, we have already constructed the system on which PDC was efficiently converted from the aromatic compounds such as vanillic acid and vanillin in the recombinant microorganisms. In order to develop alternative system for PDC production, we try to produce the compound from glucose, which is one of low-cost sugars expected to be converted from abundant cellulose wastes and biomass crops. In the present study, we constructed two types of recombinant bacteria with the bypasses in their own shikimate pathways. By HPLC analysis, a trace amount of PDC that derived from glucose could be detected in the culture medium of the recombinant bacterium with *ubiC*, *pobA* and *LigABC*. Our result suggests that the bypassed shikimate pathway provide an alternative option for PDC production.

2006-P21

カワラタケ由来のラッカーゼ遺伝子を導入した組換え植物に見られる雄性不稔の解析  
中村雄己<sup>\*1</sup>、園木和典<sup>\*2</sup>、飯村洋介<sup>\*2</sup>、片山義博<sup>\*1</sup>、梶田真也<sup>\*1</sup>

東京農工大学大学院 BASE、産業技術総合研究所

Analysis of male sterility in the transgenic plants with the chimeric gene construct derived from the *Trametes versicolor* laccase gene.

Yuki Nakamura<sup>\*1</sup>, Tomonori Sonoki<sup>\*2</sup>, Yosuke Iimura<sup>\*2</sup>, Yoshihiro Katayama<sup>\*1</sup>, Shinya Kajita<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan, <sup>\*2</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8569, Japan

Abstract: Laccase that require O<sub>2</sub> as secondary substrate can oxidize phenolic compounds. In the previous work, we have isolated a laccase cDNA, *CVL3*, from *Trametes versicolor* cDNA pool and generated transgenic tobacco plants in which a chimeric laccase gene was expressed under the control of cauliflower 35S promoter elements. Some of the transgenic plants overexpressing the gene could secret recombinant laccase protein from their roots. The secretory laccase activity in the plants was responsible for the transformation of phenolic compounds such as pentachlorophenol. Flowers of four transgenic lines, FL4, FL9, FL20 and FL22 with highly laccase activity exhibited male sterile due to inhibition of anther maturation and dehiscence. Levels of laccase activity in the anthers of these four transgenic plants have reached by over 6-fold increase as compared to that in wild-type plant. These results indicate that the laccase protein may play some physiological roles in anther development.

2006-P22

オゾン酸化を用いたリグニン系土壌改良剤の開発 II -オゾン酸化リグニンの酸化の程度と Al 毒性除去能との関係についての研究

相見 光、大村 知士、加藤 珠央、中原 知子、志水一允

日本大学生物資源科学部

Development of lignin soil conditioning agent by ozone treatment II. -Studies on relationship between degree of oxidation and reduction of aluminum toxicity for ozone treated lignin.

Hikaru Aimi, Satoshi Ohmura, Tamao Katoh, Tomoko Nakahara, Kazumasa Shimizu

Laboratory of Biomass Sciences, Department of Forest Sciences and Resources, College of Bioresource Sciences, the Nihon University, 1866 Kameino, Fujisawa, Kanagawa, 252-8510, Japan

Abstract: Relationship between degree of oxidation for oxidized lignin and its ability for the reduction of aluminum toxicity was examined in this study. The oxidized lignin samples were prepared by ozone or alkaline oxygen treatments. Degrees of oxidation for these samples were evaluated by permanganate consumption and methoxyl content after saponification. The lignin treated with ozone for 4h lost about 85% of methoxyl group, but the lignins treated by alkaline oxygen lost only about 4-14% of it. Both of them were, however, effective for reduction of aluminum toxicity. These facts were also confirmed by IR analysis. These results suggest that other factors, such as water-solubility or difference of reaction mechanism between ozone and alkaline oxygen, are more important than degree of oxidation for reduction of aluminum toxicity.

2006-P23

酸性下におけるリグニン  $\beta$ -O-4 結合開裂機構の再評価(3) - C<sub>6</sub>-C<sub>3</sub>リグニンモデル化合物を用いた解析-

伊藤宏昭、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Reevaluation of the mechanism for cleavage of lignin  $\beta$ -O-4 bond under acidic conditions (3) -Experiments using a C<sub>6</sub>-C<sub>3</sub> model compound -

Hiroaki Ito, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

**Abstract:** Acidolysis of lignin is a method used for structural analysis and isolation of lignin. The main reaction during acidolysis is the cleavage of  $\beta$ -O-4 bond. According to the mechanism proposed by Lundquist et al., the rate-determining step of the reaction is the abstraction of the  $\beta$ -proton from a benzyl cation substructure, resulting in the formation of an enol ether type substructure. Although other reports show the dependence of the cleavage rate on the kind of acid used, it is impossible to explain the dependence based on the mechanism proposed. Therefore, it is necessary to reinvestigate the reaction mechanism of acidolysis and analyze its kinetic. A dimeric non-phenolic lignin model compound, veratrylglycerol- $\beta$ -guaiacyl ether (VG), was treated with HBr in 82% aqueous dioxane. It was found that the elimination of  $\gamma$ -position as formaldehyde does not occur in the system. This result is contrast with the known fact that the elimination of formaldehyde is occurred when HCl is used as a catalyst. It is suggested that HBr is more suitable than HCl as a catalyst of acidolysis.

2006-P24

熱帯産樹アテ材のリグニン化学構造

Deded S. Nawawi, Wasrin Syafii, 秋山拓也、松本雄二、飯塚堯介  
東京大学大学院農学生命科学研究科

Chemical structure of lignin in reaction wood of tropical species.

Deded S. Nawawi, Wasrin Syafii, Takuya Akiyama, Yuji Matsumoto, Gyosuke Meshitsuka  
Wood Chemistry Laboratory, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

**Abstract:** Reaction woods were obtained from leaning wood stems or branches of several tropical wood species and the relationships between the type of reaction wood and lignin characteristics was surveyed. As lignin characteristics, stereo structure of  $\beta$ -O-4 linkage (*erythro* ratio), aromatic ring type (syringyl ratio), Klason lignin yield and acid soluble lignin content were determined. Tentatively, the relationships could be classified into 4 types. In all types, *erythro* ratio changed with clear tendency from the reaction wood part to opposite wood part, but the direction of the change was dependent on the type. In G-S lignin (guaiacyl-syringyl lignin) *erythro* ratio was highly correlated with syringyl ratio, and in G-lignin, it was correlated with p-hydroxyphenyl content.

2006-P26

アルカリ及びアルカリ酸素処理において  $\alpha$ -カルボニル基の存在が及ぼすリグニン分解反応への影響

今井愛子、横山朝哉、松本雄二、飯塚堯介  
東京大学大学院農学生命科学研究科

Effects of the presence of  $\alpha$ -carbonyl group on the degradation reactions of lignin during anaerobic and aerobic alkaline treatments.

Aiko Imai, Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka  
Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

**Abstract:** It is well known that the presence of  $\alpha$ -carbonyl group in lignin has a significant effect on its reactivity toward various chemical reactions. However in most of the researches, the effect has been studied when  $\alpha$ -carbonyl group is located at the lignin phenylpropane unit where

the target reactions are occurred (located at A-ring). In this study, the effect of  $\alpha$ -carbonyl group on the reactions occurred under anaerobic and aerobic alkaline conditions was examined when the group is located at the unit next to that where the reactions are operative (located at B-ring) using a dimeric lignin model compound, guaiacylglycerol- $\beta$ -ethylvanillin ether (GE). A significant amount of ethylvanillin was obtained in the nitrogen-alkali treatment of GE. This result indicates that the presence of  $\alpha$ -carbonyl group at the B-ring surprisingly accelerates the alkali promoted  $\beta$ -O-4 bond cleavage. A large amount of vanillin was obtained in the oxygen-alkali treatment of GE. This is quite contrast to the result observed when an analogous model compound of GE without the  $\alpha$ -carbonyl group was treated under the same conditions. These phenomena indicate that the rate of the C $\alpha$ -C $\beta$  bond cleavage exceeds that of the aromatic ring scission. It is suggested that the presence of  $\alpha$ -carbonyl group at the B-ring changes the reaction site of lignin where oxygen oxidation is occurred.

2006-P27

ケナフリグニンの化学構造について

中川明子<sup>\*1</sup>、土居修一<sup>\*1</sup>、黒田健一<sup>\*2</sup>

<sup>\*1</sup> 筑波大学大学院生命環境科学研究科、<sup>\*2</sup> 九州大学大学院農学研究院

Chemical structures of kenaf (*Hibiscus cannabinus*) lignin.

Akiko Nakagawa-izumi<sup>\*1</sup>, Ken-ichi Kuroda<sup>\*2</sup>, shuichi Doi<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8572 Japan, <sup>\*2</sup> Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: Kenaf (*Hibiscus cannabinus*), variety Everglades, bast native and isolated lignins were subjected to analytical pyrolysis to confirm unusual structures of kenaf lignin. Pyrolysis results showed that the kenaf sample employed in the present study contains no comiferyl and sinapyl alcohols with an acetyl group at the  $\gamma$ -position, and it has a paucity of 5-hydroxyguaiacyl units because the small abundance of 3-methoxycatechols was present in the pyrolyzates.

2006-P28

ケナフ靱皮クラフトパルプの酸素漂白特性

金光苑, 中川明子, 大井洋

筑波大学大学院生命環境科学研究科

Characteristic of kenaf bast kraft pulp for oxygen bleaching.

Guang-fan Jin, Akiko Nakagawa-izumi, Hiroshi Ohi

Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8572 Japan

Abstract: Kraft cooking efficiency of bast of *Hibiscus cannabinus* (kenaf) was compared with that of *Acacia mearnsii* and *Eucalyptus* spp. Although the lignin content of the bast was lower than that of *A. mearnsii* wood, the selectivity of delignification of the bast was not better than that of the hardwoods. The bast contained more uronic acids than the hardwoods. Then, it consumed more alkali during kraft cooking and did not show better delignification selectivity. However, the bast pulp was easily oxygen-bleached at a small alkali charge, resulting in a low kappa number.

2006-P29

リグニンの温度変調型 DSC 分析

久保智史<sup>\*1</sup>、山田竜彦<sup>\*1</sup>、橋田光<sup>\*1</sup>、浦木康光<sup>\*2</sup>、John F. Kadla<sup>\*3</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 北海道大学大学院農学研究院、<sup>\*3</sup> ブリティッシュコロンビア大学

Temperature modulated DSC analysis of isolated lignin.

Satoshi Kubo<sup>\*1</sup>, Tatsuhiko Yamada<sup>\*1</sup>, Koh Hashida<sup>\*1</sup>, Yasumitsu Uraki<sup>\*2</sup>, John F. Kadla<sup>\*3</sup>

<sup>\*1</sup>Department of Biomass Chemistry, Forestry and Forest Products Research Institute, Tsukuba, 305-8687 Japan, <sup>\*2</sup>Graduate School of Agriculture, Hokkaido University, Sapporo, 060-8589 Japan

<sup>\*3</sup>Department of Wood Science, University of British Columbia, Vancouver, B.C., V6T 1Z4 Canada

Abstract: DSC is commonly used to examine the thermal properties of lignin preparations. However, in many of the lignin preparations a large enthalpic relaxation peak overlaps the glass transition, T<sub>g</sub>, region in the DSC curve, which makes it difficult to identify the T<sub>g</sub>. This is typically addressed by applying a pre-heat treatment (first scan) to remove this endothermic peak. However, lignin preparations have thermosetting properties as well as thermo-plasticity; the chemical structure of lignin changes during the heat treatment. To avoid this problem, temperature modulated DSC (TMDSC) was examined for thermal analysis of lignin preparation. By use of TMDSC, an enthalpic relaxation peak can be removed from total heat flow, and T<sub>g</sub> of lignin preparation can be clearly seen without pre-treatment. In conventional DSC run, T<sub>g</sub> temperature of lignin preparations were only slightly increased by repeating heat treatment. However, T<sub>g</sub> temperature measured in 2nd heating run is remarkably higher than in 1st heating. This indicates that pre-heat treatment of DSC run affects the T<sub>g</sub> of the lignin preparation.

2006-P30

$\beta$ -O-4 型人工リグニンポリマーの合成とその性質 – シリングルタイプの合成 –

岸本崇生、浦木康光、生方信

北海道大学大学院農学研究科

Synthesis of  $\beta$ -O-4 type artificial lignin polymers and their properties. – Synthesis of syringyl type lignin polymer –.

Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata

Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589

Abstract: The  $\beta$ -O-4 structure is one of the most important substructures in lignin. Guaiacyl type artificial lignin polymer composed of only  $\beta$ -O-4 structure has been synthesized in our laboratory. In this investigation syringyl type monomer was treated with potassium carbonate and reduced with sodium borohydride to yield a polymer. The polymer was acetylated and fully analyzed by NMR spectroscopy.

2006-P31

オルガノソルブリグニンアルキルエステル/ポリ( $\epsilon$ -カプロラクトン)環境適合型ブレンドの相構造評価

寺本好邦<sup>\*1</sup>, 李承桓<sup>\*2</sup>, 田中紀子<sup>\*1</sup>, 堺真奈美<sup>\*1</sup>, 遠藤貴士<sup>\*1</sup>

<sup>\*1</sup>産業技術総合研究所バイオマス研究センター、<sup>\*2</sup>テネシー州立大学

Phase structure of biodegradable poly( $\epsilon$ -caprolactone) with organosolv lignin alkyl esters.

Yoshikuni Teramoto<sup>\*1</sup>, Seung-Hwan Lee<sup>\*2</sup>, Noriko Tanaka<sup>\*1</sup>, Manami Saka<sup>\*1</sup>, Takashi Endo<sup>\*1</sup>

<sup>\*1</sup>National Institute of Advanced Industrial Science and Technology (AIST), Biomass Technology Research Center (BTRC), Kure 737-0197, Japan, <sup>\*2</sup>Forest Products Center, The University of Tennessee, Knoxville, TN 37996, USA

Abstract: Organosolv lignin (OSL) alkyl esters (carbon number, 2-5) were synthesized by a homogeneous reaction with different acyl anhydrides/4-dimethylamino pyridine in pyridine solution. The miscibility of the esterified OSLs with poly( $\epsilon$ -caprolactone) (PCL) was investigated, mainly through thermal analysis by differential scanning calorimetry (DSC). DSC analysis revealed that a polymer pair OSL butyrate/PCL and valerate/PCL showed a compatibility. Atomic force microscopy

also indicated that no remarkable phase separation occurred in these two blends.

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2007-101

ゼラチン層を形成しない広葉樹あて材におけるリグニン分布

平岩季子、石栗 太、飯塚和也、横田信三、吉澤伸夫

宇都宮大学農学部

Lignin distribution in tension wood cell walls without gelatinous layer.

Tokiko Hiraiwa, Futoshi Ishiguri, Kazuya Iizuka, Shinso Yokota, Nobuo Yoshizawa

Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Japan

Abstract: The present study investigated affects of inclination angle on reaction wood formation in three angiosperm species (*Paulownia tomentosa*, *Liriodendron tulipifera*, and *Osmanthus fragrans*) which do not form typical gelatinous fibers. These sample trees were inclined artificially at angle of 30, 50, 70 degrees from the vertical. The amount of lignins was decreased by tension wood formation in the intercellular layer and wood fiber walls. It was found that inclination angle affects the amount of syringyl unit in lignins.

2007-102

ToF-SIMS による広葉樹木部におけるリグニン分布の解析

斉藤香織\*<sup>1</sup>、渡邊陽子\*<sup>2</sup>、勝山さやか\*<sup>1</sup>、松下泰幸\*<sup>1</sup>、今井貴規\*<sup>1</sup>、船田良\*<sup>3</sup>、小池孝良\*<sup>4</sup>、深澤和三\*<sup>4</sup>、福島和彦\*<sup>1</sup>

\*<sup>1</sup>名古屋大学大学院生命農学研究科、\*<sup>2</sup>北海道大学 FSC、\*<sup>3</sup>東京農工大学大学院農学研究科、

\*<sup>4</sup>北海道大学大学院農学研究科

Lignin distribution in the cell walls of angiosperm xylem determined by ToF-SIMS.

Kaori Saito\*<sup>1</sup>, Yoko Watanabe\*<sup>2</sup>, Sayaka Katsuyama\*<sup>1</sup>, Yasuyuki Matsushita\*<sup>1</sup>, Takanori Imai\*<sup>1</sup>, Ryo Funada\*<sup>3</sup>, Takayoshi Koike\*<sup>4</sup>, Kazumi Fukazawa\*<sup>4</sup>, Kazuhiko Fukushima\*<sup>1</sup>

\*<sup>1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, \*<sup>2</sup>Field Science Center for Northern Biosphere, Hokkaido University, Sapporo 060-0809, \*<sup>3</sup>Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Fuchu, 183-8509,

\*<sup>4</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589

Abstract: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to investigate the heterogeneous distribution of guaiacyl and syringyl lignin in the transverse section of the xylem of *Acer micranthum*. The lignin distribution was visualized by ToF-SIMS direct mapping of secondary ions with guaiacyl or syringyl rings at  $m/z$  137 and  $m/z$  167, respectively. The result supports the previous observation obtained by Mäule color reaction that the vessels are rich in guaiacyl lignin and the fibers are rich in syringyl lignin.

2007-103

ポプラペルオキシダーゼの遺伝子およびタンパク構造の多様性

江藤祐\*<sup>1</sup>、重松幹二\*<sup>2</sup>、堤祐司\*<sup>1</sup>、近藤隆一郎\*<sup>1</sup>

\*<sup>1</sup>九州大学大学院農学研究院、\*<sup>2</sup>福岡大学工学部

Structural diversity of poplar peroxidases.

Yu Eto\*<sup>1</sup>, Mikiji Shigematsu\*<sup>2</sup>, yuji Tsutsumi\*<sup>1</sup>, Ryuichiro Kondo\*<sup>1</sup>

\*<sup>1</sup>Faculty of Agriculture, Kyushu University, Fukuoka, 812-8581, Japan, \*<sup>2</sup>Department of Chemical Engineering, Fukuoka University, Fukuoka, 814-0180, Japan

Plant peroxidases form a numerous multigenic family in higher plants. We have surveyed peroxidase genes in the *Populus trichocarpa* database and found at least 79 sequences encode complete peroxidase protein with manual annotation, and diversity of peroxidase isoenzymes was investigated from genome structure and amino acid sequences. The coding sequence of the majority of the peroxidase genes are disrupted by three introns. The genes excluding this structure bring some light on the evolutionary steps encountered during the diversification of poplar peroxidase genes. Within the protein structure of 79 putative peroxidases, observed changes of highly conserved residue may cause significant change in enzyme kinetics and functions, and this observation suggest the diversification of plant peroxidases.

2007-104

改変型植物酸性 peroxidase の酵母での発現と精製

吉中喬慈, 平道哲理, 川合伸也

東京農工大学大学院農学研究院

Heterogeneous expression and purification of modified plant peroxidase.

T. Yoshinaka, T. Hiramichi, Shinya Kawai

The Graduate School of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509

Abstract: PrxA3a is an anionic peroxidase from hybrid aspen. A gene, *prxA3a*, was fused with sequence of His-tag. The construct was inserted into the downstream of FLAG sequence in a yeast expression vector, YE<sub>pr</sub>FLAG. Active peroxidase was secreted into the medium. The secreted peroxidase was purified by Ni-column. The peroxidase might be highly glycosylated. Other modified peroxidase is also analyzed.

2007-105

リグニン生合成を抑制した飼料用・エタノール変換用イネの分子育種

志波朋美、久保賢太郎、川合伸也

東京農工大学農学府

Down regulation of cinnamyl alcohol dehydrogenase (CAD) induces increase of cell wall digestibility in rice (*Oryza sativa*).

Tomomi Shiba, Kentaro Kubo, Shinya Kawai

Faculty of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

Abstract: Cinnamyl alcohol dehydrogenase (CAD) is the enzyme of the lignin-specific biosynthesis. Inverted repeats constructs of the DNA encoding CAD of *Oryza sativa* have been introduced into rice plants. CAD down-regulated plants did not displayed any abnormal phenotype compared with a wild type. Lignin content and cell wall digestibility measurement was performed on the transformants. Lignin content was not reduced, but cell wall digestibility increased. This suggested CAD down-regulation induced change in lignin composition. As a result, increasing of cell wall digestibility without weakening plant structure is realized.

2007-106

モノリグノール配糖体によるシリングル型 DHP の生成挙動の解析

飛松裕基, 上高原浩, 高野俊幸, 中坪文明

京都大学大学院農学研究科

*In-situ* UV spectroscopic study on the horseradish peroxidase-catalyzed polymerizations of monolignol glycosides.

Yuki Tobimatsu, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo  
Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University,  
Sakyo-ku, Kyoto 606-8502, Japan

Abstract: Horseradish peroxidase catalyzed homopolymerizations of syringyl-type (S-type) glycoside **1S** and copolymerizations of **1S** with guaiacyl-type (G-type) glycoside **1G** were monitored by *in situ* UV spectroscopy. In the former, new absorption peak at 325 nm ( $A_{325}$ ) from S-type quinone methide intermediates (S-QM) increased rapidly within 30 min, and then disappeared gradually, suggesting that the reactivities of the S-QM are significantly low. In the latter, the addition of **1G** promoted both of the increase and the following decrease of  $A_{325}$ , suggesting that **1G** acts not only as a radical mediator but also as a nucleophile for the S-QM during the copolymerizations.

2007-107

担子菌のラッカーゼ遺伝子を導入した組換え植物が示す雄性不稔の解析

Zannatul Nasrin<sup>\*1</sup>、園木和典<sup>\*2</sup>、飯村洋介<sup>\*12</sup>、片山義博<sup>\*1</sup>、梶田真也<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 産業技術総合研究所

Analysis of male sterility in transgenic plants with the chimeric gene for fungal laccase.

Zannatul Nasrin<sup>\*1</sup>, Tomonori Sonoki<sup>\*2</sup>, Yosuke Imura<sup>\*2</sup>, Yoshihiro Katayama<sup>\*1</sup>, Shinya Kajita<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan. <sup>\*2</sup> National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8569, Japan

2007-108

イネをモデル植物とした細胞壁形成過程に関する研究 -Glycosylphosphatidylinositol-anchored protein はイネの細胞壁高次構造形成にどのように関わるのか？ (3)-

伊藤幸子<sup>\*1</sup>、鈴木瑠<sup>\*1</sup>、佐藤かな<sup>\*2</sup>、半智史<sup>\*3</sup>、北野英己<sup>\*2</sup>、船由良<sup>\*3</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院 BASE、<sup>\*2</sup> 名古屋大学大学院 BBC <sup>\*3</sup> 東京農工大学大学院農学研究院

Study of plant cell wall formation in *Oryza sativa* L. -How does glycosylphosphatidylinositol-anchored protein relate to cell wall conformation in rice plant (*Oryza sativa* L.) ? (3)-

Sachiko Ito<sup>\*1</sup>, Ryu Suzuki<sup>\*1</sup>, Kanna Sato<sup>\*2</sup>, Satoshi Nakaba<sup>\*3</sup>, Hidemi Kitano<sup>\*2</sup>, Ryo Funada<sup>\*3</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan. <sup>\*2</sup> Bioscience and Biotechnology Center, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan, <sup>\*3</sup> Graduate School of Agriculture, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: To understand the mechanism that regulate the high-order conformation of plant cell wall, a mutant defective in stem strength had been isolated and characterized. A rice mutant *cell wall architecture 1 (cwa1)* exhibits the systemic brittle-culm phenotype with indistinguishable morphology from wild-type plant. Whereas abnormal depositions that contain much phenols were found at secondary cell wall in cortical fiber regions of *cwa1*. Thus *cwa1* is likely to be defective in control of cell wall architecture but not in biosynthesis of cell wall. We suggest that defective protein of *cwa1*;BC1 work as a scaffold for precise localization of each cell wall components.

2007-109

ヤマモモ抽出成分ミリカノールの生合成、 $\alpha$ -*p*-クマール酸および *p*-セドロキシフェニルプロパン酸の投与とその取り込み-

仲田京祐、河合真吾、西田友昭

静岡大学農学部

Myricanol biosynthesis in *Myrica rubra*. – Feeding experiments of *p*-coumaric acid and *p*-hydroxyphenylpropanoic acid –

Kyosuke Nakata, Shingo Kawai, Tomoaki Nishida

Department of Environment and Forest Resources Science, Faculty of Agriculture, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan

Abstract: Diarylheptanoids are one of the major wood extractives and have C<sub>6</sub>-C<sub>7</sub>-C<sub>6</sub> carbon skeleton. However, there is little evidence about the biosynthetic pathways for diarylheptanoids. We have investigated the biosynthesis of cyclic diarylheptanoid myricanol, which is the major extractive in *Myrica rubra*, and previously reported *in vivo* feeding experiments using [ $\beta$ ,  $\gamma$ -<sup>13</sup>C<sub>2</sub>]-*p*-coumaric acid. The results indicated that the involvement of two molecules of *p*-coumaric acid for myricanol biosynthesis in *M. rubra*. In the present study, we reports that the assignments of the incorporated positions of [ $\beta$ ,  $\gamma$ -<sup>13</sup>C<sub>2</sub>]-*p*-coumaric acid into myricanol with <sup>13</sup>C-NMR studies. Furthermore, to clarify whether *p*-hydroxyphenylpropanoic acid is a precursor for myricanol biosynthesis, <sup>13</sup>C-labeled *p*-hydroxyphenylpropanoic acid was prepared and administrated into *M. rubra*. The results reveal that [ $\gamma$ -<sup>13</sup>C]-*p*-hydroxyphenylpropanoic acid is incorporated into myricanol.

2007-110

Isolation of *Anthriscus sylvestris* *O*-methyltransferase cDNAs.

Safendri Komara Ragamustari\*<sup>1</sup>, Shiro Suzuki\*<sup>1</sup>, Yu Kitamura\*<sup>1</sup>, Masaomi Yamamura\*<sup>1</sup>, Eiichiro Ono\*<sup>2</sup>, Takefumi Hattori\*<sup>1</sup>, Toshiaki Umezawa\*<sup>1</sup>

\*<sup>1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto, 611-0011, Japan

\*<sup>2</sup>Institute for Healthcare Science, Suntory, 1-1-1 Wakayamadai, Shimamoto-cho, Mishima, Osaka 618-8503, Japan

Abstract: In order to further understand the role of *O*-methyltransferases (OMTs) in podophyllotoxin biosynthesis, we have isolated 7 OMT cDNAs from an *Anthriscus sylvestris* cDNA library. The isolation using digoxigenin (DIG) labeled probes resulted in 62 positives and further screening narrowed them down into 7 cDNA clones. Phylogenetic analysis showed that the 7 cDNA clones have high identity towards their respective probes. Among the isolated clones, we are particularly interested in clone #50 due to its close phylogenetic relationship with AEOMT. The clone is predicted to encode an AEOMT-like protein, which has a similar role in plant metabolism. Expression and characterization of the 7 clones are currently underway.

2007-111

白色腐朽菌 *Phanerochaete sordida* YK-624 株の形質転換系構築及び新規リグニンペルオキシダーゼの発現

杉浦立樹\*<sup>1</sup>、平井浩文\*<sup>1</sup>、西田友昭\*<sup>1</sup>、山岸賢治\*<sup>2</sup>、木村俊之\*<sup>2</sup>

\*<sup>1</sup> 静岡大学農学部、\*<sup>2</sup> 東北農業研究センター

Homologues expression of novel lignin peroxidases in *Phanerochaete sordida* YK-624.

Tatsuki Sugiura\*<sup>1</sup>, Hirofumi Hirai\*<sup>1</sup>, Tomoaki Nishida\*<sup>1</sup>, Kenji Yamagishi\*<sup>2</sup>, Toshiyuki Kimura\*<sup>2</sup>

\*<sup>1</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan, \*<sup>2</sup>National Agricultural Research Center for the Tohoku Region, National Agriculture and Food Research Organization, Fukushima 960-2156, Japan

Abstract] In our previous reports, the gene transformation system of white-rot fungus *Phanerochaete sordida* YK-624 has been developed, and we have cloned two cDNAs (*ylpA* and *ylpB*) and two genomic DNAs (*g-ylpA* and *g-ylpB*) encoding YK-Lips which are novel lignin peroxidases from this fungus. In the present study, we tried homologues expression of YK-Lips. The glyceraldehyde-3-phosphate dehydrogenase (GPD) promoter was used to drive the expression of

*g-y/pA* or *g-y/pB*, and plasmids (pGPD-*g-y/pA* and pGPD-*g-y/pB*) were constructed. Transformants were screened for YK-Lip activity in the liquid cultures (1.2 mM ammonium tartrate, pH 4.5), and A-11 and B-3 were selected as transformants which were high YK-Lips-expressing strains. Recombinant YK-Lips were secreted in active form by these transformants after 4 days of growth, whereas endogenous YK-Lips genes were not expressed in manganese-deficient liquid culture (40 mM ammonium tartrate, pH 6.5).

2007-112

シキミ酸経路を経由したグルコースからの 2-pyrone4, 6-dicarboxylic acid の発酵生産

中島正博<sup>\*1</sup>、西野由香里<sup>\*2</sup>、田村真統<sup>\*2</sup>、間瀬浩平<sup>\*3</sup>、政井英司<sup>\*4</sup>、大塚裕一郎<sup>\*5</sup>、中村雅哉<sup>\*5</sup>、大原誠資<sup>\*5</sup>、片山義博<sup>\*2</sup>、梶田真也<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学大学院農学研究院、<sup>\*2</sup> 東京農工大学大学院 BASE、<sup>\*3</sup> 豊田自動織機株式会社、

<sup>\*4</sup> 長岡技術科学大学・生物機能工学、<sup>\*5</sup> 森林総合研究所

Biological conversion of glucose to 2-pyrone-4, 6-dicarboxylic acid by the bypassed shikimate pathways.

Masahiro Nakajima<sup>\*1</sup>, Yukari Nishino<sup>\*2</sup>, Masatsugu Tamura<sup>\*2</sup>, Kohei Mase<sup>\*3</sup>, Eiji Masai<sup>\*4</sup>, Yuichiro Otsuka<sup>\*5</sup>, Masaya Nakamura<sup>\*5</sup>, Seiji Ohara<sup>\*5</sup>, Yoshihiro Katayama<sup>\*2</sup>, Shinya Kajita<sup>\*2</sup>

<sup>\*1</sup> Faculty of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan, <sup>\*2</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan, <sup>\*3</sup> Toyota Industries Corporation, Kariya, Aichi 448-8671, Japan, <sup>\*4</sup> Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan, <sup>\*5</sup> Forestry and Forest Products Research Institute, Tsukuba, Ibaraki 305-8687, Japan

Abstract: PDC, 2-pyrone-4, 6-dicarboxylic acid, is one of metabolic intermediates in *Sphingomonas paucimobilis* SYK-6 that is a degrader of lignin-derived compounds. PDC has been characterized as a material for synthetic polymers. In the previous study, we have already constructed the system on which PDC was efficiently converted from vanillic acid and vanillin. In order to develop alternative system for PDC production, we try to produce it from glucose, which is one of low-cost sugars expected to be converted from abundant cellulose wastes and biomass crops. In the present study, we generated six types of recombinant bacteria. PDC could be produced from glucose by all of the bacteria analyzed. Especially, the recombinant bacteria with *qutC* could produce PDC at high concentration than those with *ubiC* and *pobA*. Our results suggest that *qutC* is useful gene for the fermentative production of PDC.

2007-113

Biodegradation of chrysene in a soil by fungi screened from nature。

Tony Hadibarata, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: *Polyporus* sp. S133, a fungus collected from soil, was selected for its ability to grow on and degrade chrysene as a sole carbon source. The effect of adding several concentrations of tween 80 to increase degradation rate of chrysene was studied. Maximal degradation (86%) was obtained when *Polyporus* sp. S133 was incubated in a soil supplemented with 0.50% of tween 80. The mechanism for degradation of chrysene with the fungus through identification of the intermediates was found. Several enzymes (manganese peroxidase, lignin peroxidase, laccase, 1,2-dioxygenase and 2,3-dioxygenase) produced by *Polyporus* sp. S133 were detected in the culture. The highest enzyme activity was shown by 1,2-dioxygenase after 20 days of cultivation (237.5 UI<sup>-1</sup>). Those ligninolytic and dioxygenase enzymes played an important role to oxidize chrysene.

2007-114

Degradation of 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane (DDT) by brown rot fungus *Fomitopsis pinicola*.

Faculty of Agriculture, Kyushu University

Adi Setyo Purnomo, Ichiro Kamei and Ryuichiro Kondo

Abstract: *Fomitopsis pinicola* showed high ability to degrade DDT in PDB medium. To investigate the involvement of Fenton reaction, mineral salt medium with or without FeSO<sub>4</sub> was used. *F. pinicola* showed higher ability to degrade DDT in medium without FeSO<sub>4</sub> than that in medium with FeSO<sub>4</sub> either in vivo or in vitro experiment. It indicates that the extracellular iron-dependent reaction was not involved in DDT degradation by *F. pinicola*. DDD (1,1-dichloro-2,2-bis(4-chlorophenyl) ethane) was detected as metabolic product from DDT degradation. The transformation of DDT to DDD by *F. pinicola* might be involved extracellular enzymatic reaction.

2007-115

耐塩性白色腐朽菌 *Phlebia* sp. MG60 におけるペルオキシダーゼ転写制御

亀井一郎<sup>\*1</sup>、大黒千映子<sup>\*2</sup>、堤祐司<sup>\*2</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学 VBL、<sup>\*2</sup>九州大学大学院農学研究院

Transcriptional regulation of manganese peroxidases from saline-tolerant white rot fungus, *Phlebia* sp. MG60.

Ichiro Kamei<sup>\*1</sup>, Chieko Daikoku<sup>\*2</sup>, Yuji Tsutsumi<sup>\*2</sup>, Ryuichiro Kondo<sup>\*2</sup>

<sup>\*1</sup>Venture Business Laboratory, <sup>\*2</sup>Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: The expression pattern of manganese peroxidases (MnPs) in nitrogen-limited cultures of saline-tolerant fungus, *Phlebia* sp. MG-60, is differentially regulated under a hyper-saline condition at the transcriptional level. When MG-60 was cultured in the nitrogen limited medium containing 3% sea salts (LN-SSM), higher activity of MnPs was observed than that in the normal medium (LNM). SDS-PAGE analysis demonstrated that two MnP isoenzymes were de novo synthesized during the culture in LN-SSM. Three MnP encoding genes (*MG-mnp1*, *MG-mnp2*, and *MG-mnp3*) were isolated by RT-PCR and RACE-PCR techniques, and identification of each MnP protein was achieved by peptide mass fingerprinting (PMF) analysis of the tryptic fragments of each MnP isoenzyme observed on SDS-PAGE. Two MnP isoenzymes that were mainly observed in LN-SSM were encoded by *MG-mnp2* and *MG-mnp3*. Real-time PCR analysis revealed that *MG-mnp2* and *MG-mnp3* were highly transcribed in LN-SSM, and the transcription was induced 48 h after the addition of 2% NaCl. The induction of MnP production and gene transcription by saline was well correlated in the presence of Mn<sup>2+</sup>. However, in the absence of Mn<sup>2+</sup> there is no clear correlation between *mnp* transcription and MnP activity, suggesting the existence of a post-transcriptional regulation by Mn<sup>2+</sup>.

2007-116

*Phanerochaete chrysosporium* のリグニン分解能を支える代謝制御機構

割石博之<sup>\*1\*2\*3</sup>、石川真梨子<sup>\*4</sup>、志水元亨<sup>\*1</sup>、寺本寛<sup>\*4</sup>、三浦大典<sup>\*3</sup>、国武宣道<sup>\*4</sup>、中村朋史<sup>\*4</sup>、一瀬博文<sup>\*1</sup>

<sup>\*1</sup>九州大学大学院農学研究院、<sup>\*2</sup>九州大学バイオアーキテクチャーセンター、<sup>\*3</sup>九州大学先端融合医療レドックスナビ研究拠点、<sup>\*4</sup>九州大学大学院生物資源環境科学府

Systems biology of lignin biodegradation.

Hiroytiki Wariishi<sup>\*1\*2\*3</sup>, Mariko Ishikawa<sup>\*4</sup>, Motoyuki Shimizu<sup>\*1</sup>, Hiroshi Teramoto<sup>\*4</sup>, Daisuke Miura<sup>\*3</sup>,

Nohmichi Kunitake<sup>\*4</sup>, Tomofumi Nakamitani<sup>\*4</sup>, Hirofumi Ichinose<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, <sup>\*2</sup>Bio-Architecture Center, <sup>\*3</sup>Innovative Center for Medical Redox Navigation,

<sup>\*4</sup>Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, Fukuoka 812-8581, Japan

**Abstract:** Effect of exogenous vanillin on a cellular system in *Phanerochaete chrysosporium* was investigated utilizing integrative OMICS. Addition of vanillin caused an immediate flux shift at the TCA cycle, initiating a production of succinyl CoA. Transcriptomic data obtained from a 50-mer oligoDNA microarray system combined with proteomic data clearly indicated the activation of the heme biosynthetic pathway branched at succinyl CoA. Up-regulation of extracellular peroxidases and several cytochrome P450s was also observed. Addition of vanillin also brought about a down-regulation of extracellular oxalate dehydrogenase and intracellular formate dehydrogenase and an up-regulation of enzymes in mannitol cycle, suggesting the presence of unique regulation system for energy production in the fungus. These metabolic shifts seem to be required for optimizing its ligninolytic system.

2007-117

フリーラジカルによるリグニンモデル化合物の反応部位に関する研究

大橋康典、渡邊崇人、本田与一、渡辺隆司

Study on reactive position of lignin model compounds with free radicals.

Yasunori Ohashi, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Laboratory of Biomass Conversion, Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

**Abstract:** A white rot fungus, *Ceriporiopsis subvermispora* degrades lignin by radical reactions of low molecular mass metabolites at a site far from enzymes. As a possible ligninolytic system by the fungus, *in situ* radical reactions have been proposed. In the degradation of non-phenolic lignin model compounds (LMCs) by free radicals, it was proposed that the reaction was initiated by hydrogen abstraction from the benzyl position of LMCs. However, no concrete evidence has been presented. In the present study LMCs were reacted with *tert*-butoxyl radical generated by UV-photolysis of di-*tert*-butyl peroxide, and radical intermediates from the LMCs were analyzed by ESR. Reactivity of free radicals with the LMCs was also analyzed using *ab initio* MO calculation.

2007-特別講演 I

ブラシノステロイド研究の始まりと現在の進展

横田孝雄

帝京大学工学部バイオサイエンス学科

2007-201

リグニン熱分解物の気相における二次熱分解反応

細谷隆史、河本晴雄、坂 志朗

京都大学大学院エネルギー科学専攻科

Secondary reactions of lignin-derived pyrolysis vapor

Takashi Hosoya, Haruo Kawamoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

**Abstract:** Secondary reaction of lignin-derived primary tar (guaiacols with various side-chain) in vapor phase was studied with milled wood lignin (from Japanese cedar: *Cryptomeria japonica*) and various model compounds (conditions: N<sub>2</sub>/600 °C/ 50-120 s). The benzene-ring and side-chain

structures were found to change in the following pathways: benzene-ring: guaiacyl- → catechol-, *o*-cresol (2-methylphenol)- and phenol-types, side-chain: >C=C<, -CHO and >C=O → -H and saturated alkyl chain types. Secondary carbonization was also observed during these structural changes of the tar components, especially disappearing the -OCH<sub>3</sub> groups. These results indicate that the secondary carbonization is closely related to the formation of phenoxy and methyl radicals through the O-CH<sub>3</sub> bond homolysis. This is also supported by the experimental fact that only the model compounds with aromatic -OCH<sub>3</sub> formed secondary char.

2007-202

リグニンβ-エーテル構造の熱分解ラジカル連鎖開裂反応

渡辺敏弘, 河本晴雄, 坂 志朗

京都大学大学院エネルギー科学専攻科

Radical chain mechanisms in pyrolytic β-ether cleavage suggested from the products of lignin model dimers and trimer.

Toshihiro Watanabe, Haruo Kawamoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Abstract: Pyrolysis of lignin model dimers (phenolic and nonphenolic β-ether type) and trimer (nonphenolic α, β-ether type) in a closed ampule (N<sub>2</sub>) at 400°C for 2min gave Cα=O and isoeugenol (Cα=Cβ) types products as the β-ether-cleaved products. Formation of these products indicates that radical chain reactions proceed through H-abstraction of the Cα-H and phenolic-OH.

2007-203

全細胞壁の溶液 NMR 法によるイチヨウのプロトリグニンの <sup>13</sup>C 標識2D-NMR 示差スペクトル分析  
寺島典二\*<sup>1</sup>、秋山拓也\*<sup>2</sup>、John Ralph\*<sup>2</sup>

\*<sup>1</sup>名古屋大学、\*<sup>2</sup>DFRC, USA

2D-NMR difference spectra between specifically <sup>13</sup>C-enriched and unenriched ginkgo protolignin by solution-state whole-cell wall NMR.

Noritsugu Terashima\*<sup>1</sup>, Takuya Akiyama\*<sup>2</sup>, John Ralph\*<sup>2</sup>

\*<sup>1</sup> Prof. Emeritus, Nagoya University, 2-610 Udayama, Tenpaku, Nagoya, 468-0001 Japan, \*<sup>2</sup>US Dairy Forage Research Center, USDA-Agricultural Research Service, Madison, WI 53706-1108 USA

Abstract: Coniferins specifically <sup>13</sup>C-enriched at side chain carbons and unenriched coniferin were administered to growing stems of ginkgo. The whole newly formed xylems containing <sup>13</sup>C-enriched and unenriched lignins were milled and dissolved in a mixture of N-methylimidazole and DMSO, then acetylated. Solution-state 2D-NMR (HSQC) spectra of the dissolved whole xylem cell walls were determined in high resolution. Determination of difference spectra between the spectra of whole cell walls containing <sup>13</sup>C-enriched and unenriched lignins afforded simplified 2D spectra in which all signals were assigned exclusively to the specifically enriched carbons. The present novel NMR technique provides a useful nondestructive tool for elucidation of the structure and behavior of entire lignin in the cell wall (protolignin) not only in ginkgo but also in most common conifers.

2007-204

構造を制御した人工リグニンの化学合成

岸本崇生\*<sup>1</sup>、浦木康光\*<sup>2</sup>、生方信\*<sup>2</sup>

\*<sup>1</sup>富山県立大学工学部、\*<sup>2</sup>北海道大学大学院農学研究科

Synthesis of β-O-4 type artificial lignin polymers.

Takao Kishimoto<sup>\*1</sup>, Yasumitsu Uraki<sup>\*2</sup>, Makoto Ubukata<sup>\*2</sup>

<sup>\*1</sup>Faculty of Engineering, Toyama Prefectural University, Imizu-shi, Toyama 939-0398, Japan

<sup>4</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

Abstract: The  $\beta$ -O-4 structure is one of the most important substructures in lignin. Artificial lignin polymer composed of only  $\beta$ -O-4 structure has been synthesized in our laboratory.

Brominated acetophenone derivatives were treated with potassium carbonate and reduced with sodium borohydride to yield polymers. The polymers were acetylated and fully analyzed by NMR spectroscopy. The spectra of guaiacyl-type homopolymer and guaiacyl/syringyl-type heteropolymer with three-carbon side chain were well consistent with  $\beta$ -O-4 substructure in milled wood lignin from Japanese tdo fir wood and Japanese white birch wood, respectively.

2007-205

$\beta$ -O-4 結合定量法としてのチオアシドリシス法の評価、 $\beta$ -O-4 型人工リグニンポリマーの反応の定量性から

金津香枝<sup>\*1</sup>、浦木康光<sup>\*2</sup>、生方信<sup>\*2</sup>、岸本崇生<sup>\*3</sup>

<sup>\*1\*2</sup> 北海道大学大学院農学研究科、<sup>\*3</sup> 富山県立大学工学部

Thioacidolysis as quantitative determination of  $\beta$ -O-4 bond. -Quantifiability of the reaction of  $\beta$ -O-4 type artificial lignin polymer-

Yoshie Kanazawa<sup>\*1</sup>, Uraki yasumitu<sup>\*1</sup>, Ubukata Makoto<sup>\*1</sup>, Takao Kishimoto<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

<sup>\*2</sup>Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

<sup>\*3</sup>Faculty of Engineering, Toyama Prefectural University, Toyama 939-0398, Japan

Abstract: Thioacidolysis is a method for quantitative determination of  $\beta$ -O-4 bond in lignin. We established the synthetic route to artificial lignin polymer comprised of only  $\beta$ -O-4 linkage. In this study, we evaluated thioacidolysis reactivity to  $\beta$ -O-4 bond by using this lignin polymer. The monomer yield for the artificial lignin polymer was less than 100% (about 70%) under the conventional thioacidolysis conditions, whereas approximately 100% yield for the dimer model compound under the same conditions. No enhancement of monomer yield was observed, by prolonging reaction time. These results suggest that thioacidolysis was not a stoichiometrical decomposition method for  $\beta$ -O-4 macromolecule.

2007-206

リグニンおよび微生物変性水可溶リグニンの超臨界水・亜臨界水条件下での反応：原油生成機構  
Zhenfu Jin<sup>\*1</sup>、勝亦京子<sup>\*1\*2</sup>、飯山賢治<sup>\*3</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*3</sup> 東京大学アジア生物資源環境研究センター

Reaction of lignin and biologically modified lignin under supercritical and subcritical water conditions: Presumptive production mechanism of petroleum.

Zhenfu Jin<sup>\*1\*2</sup>, Kyoko S. Katsumata<sup>\*1</sup>, Kenji Iiyama<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Present address: Department of Engineering, Zhejiang Forestry University, China, <sup>\*3</sup>Japan International Research Center for Agricultural Sciences, the University of Tokyo

Abstract: The annual discharge of dissolved organic mater (DOM) and particulate organic matter (POM) from rivers to ocean is estimated as  $\sim 0.4 \times 10^9$  ton, which are primarily composed of biologically modified remains of terrestrial vegetation. The DOM in the ocean could form insoluble sediments by chelating with metal ions and considered to be precursor of kerogen. Kerogen is defined as the sedimentary organic matter generating petroleum, which is an insoluble matter, in contrast petroleum soluble in usual organic solvents. Reaction of model compounds, Björkman

lignins and DOM were examined under supercritical water condition to confirm the formation mechanism of petroleum at deep sea, where is subcritical condition. It was confirmed that demethylation and demethoxylation reactions were the major reactions of lignins and DOM. These reactions also were confirmed by phenol, guaiacol and 2,6-dimethoxyphenol (syringol) as model compounds.

2007-207

ハード酸とソフト塩基の組み合わせによるリグニンエーテル結合の新規開裂方法の検討

湯川邦彦、幸田圭一、小島康夫

北海道大学大学院農学研究科

A novel ethereal bond cleavage of lignin interunit linkage by a combination of hard acid and soft base. Kunihiro Yukawa<sup>\*1</sup>, Keiichi Koda<sup>\*2</sup>, Yasuo Kojima<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, Kita 9, Nishi 9, Kita-ku, Sapporo, 060-8589 Hokkaido, Japan, <sup>\*2</sup>Research Faculty of Agriculture, Hokkaido University, Kita 9, Nishi 9, Kita-ku, Sapporo, 060-8589 Hokkaido, Japan

Abstract: Ethereal bond cleavage of wood meal, isolated lignin, and lignin model compound (guaiacylglycerol- $\beta$ -guaiacyl ether) by aluminium (III) iodide, known as a hard Lewis acid as well as a soft nucleophile, were investigated to explore a new procedure to delignify woody preparations effectively under relatively mild reaction conditions. The lignin model compound was successfully degraded even when treated at room temperature for 4.5 hours, suggesting AlI<sub>3</sub> can cleave ethereal bond of lignin structural units under some mild reaction conditions. Enhanced delignification of wood meal by AlI<sub>3</sub> treatment at refluxing temperature was also observed, but optimized conditions were yet to be established.

2007-208

炭水化物のアノマー位に対する活性酸素種の反応性の評価

小西史子、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Evaluation of the reactivity of active oxygen species toward the anomeric position of carbohydrate. Fumiko Konishi, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: The reactivity of active oxygen species (AOS) toward two different anomeric types of carbohydrate was examined using methyl  $\alpha$ -D-glucopyranoside (MGP  $\alpha$ ) and methyl  $\beta$ -D-glucopyranoside (MGP  $\beta$ ). In this study, AOS were in situ generated by subjecting a phenolic compound, 2,4,6-trimethylphenol (TMPH), to the oxygen oxidation. As the degradation of MGP  $\beta$  was greater than MGP  $\alpha$ , it was suggested that the stereo configurational difference in their anomeric positions has an influence on their reactions with AOS. It was also examined whether or not the anomeric position is certainly attacked by AOS subjecting TMPH, MGP $\beta$ , and methyl  $\beta$ -D-[1-d]-glucopyranoside (MGP  $\beta$  [1-d]) to the oxygen oxidation. The result obtained by the GC-MS analysis showed that the degradation of MGP  $\beta$  [1-d] is slower than MGP  $\beta$  suggesting a possible occurrence of the certain abstraction of the anomeric hydrogen.

2007-209

酸性下におけるリグニン  $\beta$ -O-4 結合開裂機構の再評価 (4) 一酸の種類の影響について

伊藤宏昭、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Reevaluation of the mechanism for the cleavage of lignin  $\beta$ -O-4 bond under acidic conditions (4).  
—On the effect of kind of acid—

Hiroaki Ito, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: A dimeric non-phenolic lignin model compound, veratrylglycerol- $\beta$ -guaiacyl ether (VG), was treated with HBr in 82% aqueous dioxane. It was found that the elimination of  $\gamma$ -position as formaldehyde does not occur in the system. Because the C<sub>6</sub>-C<sub>3</sub> type enol ether afforded from VG by the water elimination was not detected at all, it could not be clarified whether or not the enol ether is produced during the VG acidolysis. The results obtained by the use of VG with the deuterium at the  $\beta$ -position (VG<sub>bd</sub>) indicated that the abstraction of the  $\beta$ -proton from the benzyl cation structure resulting in the formation of the C<sub>6</sub>-C<sub>3</sub> type enol ether (referred to reaction (I) in the following) probably relates to the rate-determining step in the disappearance of VG. However, because the difference in the  $\beta$ -O-4 bond cleavage rate between kind of acids cannot be explained from the rate difference in the reaction (I), there seems to be another step with a similar rate to the reaction (I), where kind of acids affects its rate.

2007-210

国産針葉樹材アルカリパルプのヘキセンウロン酸含有量と無塩素漂白特性

高橋史帆, 中川明子, 金光箔, 大井洋

筑波大学大学院生命環境科学研究科

Hexenuronic acid contents of various alkali pulps from Japanese softwood and their non-chlorine bleaching response.

Shiho Takahashi, Akiko Nakagawa-izumi, Guang-fan Jin, Hiroshi Ohi

Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba. Ibaraki 305-8572 Japan

Abstract: We estimated hexenuronic acid (HexA) contents and lignin contents of various alkali pulps given by kraft, kraft-anthraquinone (kraft-AQ), and polysulfide-anthraquinone (PS-AQ) cookings based on some cooking factors such as cooking time, active alkali charge, AQ charge, and sulfur charge. HexA contents of PS-AQ and kraft-AQ pulps with kappa number 25 at H-factor 1200 from Japanese softwood were higher than that of the conventional kraft pulp. Various alkali pulps were bleached using the O-A-Z-E-Ep sequence. We discussed that their non-chlorine bleaching response from the standpoint of brightness and residual HexA contents.

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南アフリカ産ユーカリ材のクラフト・アントラキノン蒸解および無塩素漂白特性

本間光子<sup>\*1</sup>, 中川明子<sup>\*1</sup>, 大井洋<sup>\*1</sup>, 中俣恵一<sup>\*2</sup>

<sup>\*1</sup>筑波大学大学院生命環境科学研究科、<sup>\*2</sup>北越製紙株式会社

Characteristics of various eucalyptus woods from South Africa for kraft-AQ cooking and TCF bleaching.

Mitsuko Honma<sup>\*1</sup>, Akiko Nakagawa-izumi<sup>\*1</sup>, Hiroshi Ohi<sup>\*1</sup>, Keiichi Nakamata<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, 305-8572 Ibaraki, Japan. <sup>\*2</sup>Technical & Development Division, Hokuetsu Paper Mills, Ltd., 3-2-2 Hongoku-cho, Nihonbashi, Chuo-ku, 103-0021 Tokyo, Japan

Abstract: *Eucalyptus nitens*, *E. grandis*, *E. smithii* and *E. macarthurii* woods grown in South

Africa, which have been used in Japanese pulp mills, were investigated to clarify their characteristics for kraft-anthraquinone (AQ) cooking and totally chlorine-free (TCF) bleaching. They had various densities from 0.477 to 0.751 g/cm<sup>3</sup>. Lower lignin contents on original wood resulted in higher pulp yields. Higher ratios of syringaldehyde to vanillin by alkaline nitrobenzene oxidation of lignin brought higher brightness after cooking. After oxygen bleaching, the kappa number decrease of *E. grandis* pulp was quite low because of its high hexenuronic acid content which contributed kappa number. Pulp sheet were made under neutral conditions after TCF bleaching and the accelerated yellowing tests were performed. Each pulp showed little brightness reversion, and there are no clear relationship between the hexenuronic acid (HexA) contents and the brightness reversion. All TCF bleached pulps except *E. grandis* showed high brightness around 85% ISO and *E. smithii* is the highest (86.7% ISO).

2007-212

アルカリ処理オゾン酸化リグニンのアルミニウム毒性除去能についての研究

相見 光、大村 知士、加藤 珠央、中原 知子、志水一允

日本大学生物資源科学部

Studies on elimination of aluminum toxicity with modified kraft lignin.

Hikaru Aimi, Satoshi Ohmura, Tamao Katoh, Tomoko Nakahara, Kazumasa Shimizu

Laboratory of Biomass Sciences, Department of Forest Sciences and Resources, College of Bioresource Sciences, the Nihon University, 1866 Kameino, Fujisawa, Kanagawa, 252-8510, Japan

Abstract: Ozone treated kraft lignins were subjected to alkaline treatment and the effect of these modified kraft lignins on elimination of aluminum toxicity was assayed by planting experiment. Modified kraft lignins with ozone followed by alkaline treatments were more effective on elimination of aluminum toxicity and acceleration of root growth than that with only ozone. It is, furthermore, observed that the kraft lignin which was subjected to alkaline treatment was also effective on elimination of aluminum toxicity and acceleration of root growth in this experiment. This fact suggests that kraft lignin itself has chemical structure which is effective on above favorable effects.

2007-213

リグノスルホン酸塩-糖蜜系木質充填型バイオコンポジットの熱的・機械的性質

畠山兵衛<sup>\*1</sup>、大菅忠秀<sup>\*1</sup>、島田幹夫<sup>\*1</sup>、広瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>産業技術総合研究所、<sup>\*3</sup>リグノセルリサーチ

Thermal and mechanical properties of sodium lignosulfonate and molasses-based polyurethane biocomposites.

Hyo Hatakeyama<sup>\*1</sup>, Tadahide Ohsuga<sup>\*1</sup>, Mikio Shimada<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Fukui University of Technology, 3-6-1, Gakuen, Fukui 910-8505, <sup>\*2</sup>AIST, 1-1-1, Higashi, Tsukuba, 305-8565, <sup>\*3</sup>Lignocell Research, 2-6-16, Mejirodai, Bunkyo-ku, Tokyo 112-0015

Abstract: Molasses ( ML ) is obtained as a by-product of the sugar industry. Sodium lignosulfonate (LS) is obtained as a by-product of the pulping industry. ML polyol (MLD) and LS polyo1 (LSD) are obtained by dissolving ML and LS in diethyleneglycol (DEG). In this study, MLD and LSD were reacted with poly(phenylene methylene) polyisocyanate (MDI) that was used for the preparation of molasses- and lignin-based polyurethane (PU) composites using wood meal as fillers. In the above biocomposites, wood meal contents were changed from 50 to 90 %. MLD and LSD mixing ratios were changed as follows, 0:100, 20:80, 40:60, 50:50, 60:40, 80:20, 100:0. Apparent density, compression and thermal properties of the PU composites were examined. Apparent density and compression strength showed the optimum point at MLD and LSD the mixing ratio 60:40. Thermal degradations ( $T_d$ ) of composites were observed as two steps, low temperature side ( $T_{d1}$ ) and

high temperature side of thermal degradation ( $T_{d2}$ ). The  $T_{d1}$  at ca. 290°C is attributed to the degradation of MLP and LSPU matrix. The  $T_{d2}$  observed at 310–360°C is attributed to the degradation of wood meal. It was found that mechanical and thermal properties of composites are controllable through reaction conditions.

2007-214

リグニンスルホン酸塩を原料とする飽和及び不飽和エステル型エポキシ樹脂の合成と熱的性質  
広瀬重雄<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup> 福井工業大学工学部、産業技術総合研究所、<sup>\*2</sup>リグノセルリサーチ、<sup>\*3</sup>福井工業大学工学部

Synthesis and thermal properties of epoxy resins with saturated and unsaturated ester chains from ligninsulfonate salt.

Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Research Institute for Innovation in Sustainable Chemistry, AIST, Central 5,1-1-4 Higashi, Tsukuba, Ibaraki 305-8565, Japan, <sup>\*2</sup>Lignocel Research Ltd., 2-6-16 Mejirodai, Bunkyo-ku, Tokyo 112-0015, Japan, <sup>\*3</sup>Fukui University of Technology, 3-6-1 Gakuen, Fukui-City, Fukui 901-8505, Japan

Abstract: Sodium ligninsulfonate (LS) was dissolved in ethylene glycol (EG) and the obtained mixture was allowed to react with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (LS-EG polyacid, LSEGPA). EG-polyacid (EGPA) was also prepared from EG. The mixture of LSEGPA and EGPA was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ( $[EPOXY]/[AA]$  ratios, mol/mol) was maintained at 1.1. The contents of LSEGPA in the mixture of LSEGPA and EGPA (LSEGPA content) were varied from 0 to 100%. A mixture of ester-carboxylic acid derivatives (LS-EGM polyacid, LSEGMPA) and EGM-polyacid (EGMPA) were also synthesized using maleic anhydride. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures ( $T_g$ 's) of epoxy resins increased with increasing LSEGPA and LSEGMPA contents suggesting that lignin acts as a hard segment in epoxy resin networks. Thermal decomposition temperatures ( $T_d$ 's) of epoxy resins were almost constant regardless of LSEGPA and LSEGMPA contents.

2007-215

オルガノソルブリグニンアルキルエステル/ポリ( $\epsilon$ -カプロラクトン)相溶ブレンドの相構造評価と結晶化挙動

寺本好邦 李承桓, 遠藤貴土

産業技術総合研究所バイオマス研究センター

Phase structure and crystallization behavior of biodegradable blends of poly( $\epsilon$ -caprolactone) with organosolv lignin alkyl esters.

Yoshikuni Teramoto, Seung-Hwan Lee, Takashi Endo

National Institute of Advanced Industrial Science and Technology (AIST), Biomass Technology Research Center (BTRC), 2-2-2, Hirosuehiro, Kure, Hiroshima, 737-0197, Japan

Abstract: Organosolv lignin (OSL) alkyl esters (carbon number, 2-5) were synthesized by a homogeneous reaction with different acyl anhydrides/4-dimethylamino pyridine in pyridine solution. The miscibility of the esterified OSLs with poly( $\epsilon$ -caprolactone) (PCL) was investigated, mainly through the evaluation of the glass transition temperature ( $T_g$ ) using differential scanning calorimetry (DSC). DSC analysis revealed that the blends of OSL esters with  $n=3-5$  with PCL showed a composition-dependent shift in  $T_g$ . Therefore, the blend systems can be regarded as miscible ones in a scale of  $T_g$ -detection, usually assumed to be less than a couple of tens of nanometers. Atomic

force microscopy also indicated that no remarkable phase separation occurred in these blends. On the other hand, it was noted that the crystallinity of PCL vanished for PCL-rich compositions of the miscible pairs. This observation also supports that the blends show the higher degree of miscibility with PCL. In order to obtain further details of the crystalline development, isothermal crystallization experiments were conducted by means of polarized optical microscopy.

2007-216

イオン液体への木材の溶解性とリグニンモデル化合物の安定性

久保智史<sup>\*1</sup>、橋田 光<sup>\*1</sup>、細谷修二<sup>\*1</sup>、眞柄謙吾<sup>\*1</sup>、山田竜彦<sup>\*1\*2</sup>、岸野正典<sup>\*3</sup>、大野弘幸<sup>\*4</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*1</sup> 農林水産省農林水産技術会議事務局、<sup>\*3</sup> 北海道林産試験場、<sup>\*4</sup> 東京農工大学大学院共生科学技術研究院

Solubility of wood and stability of lignin model compounds in ionic liquid.

Satoshi Kubo<sup>\*1</sup>, Tatsuhiko Yamada<sup>\*1\*2</sup>, Koh Hashida<sup>\*1</sup>, Shuji Hosoya<sup>\*1</sup>, Kengo Magara<sup>\*1</sup>, Masanori Kishino<sup>\*3</sup>, Hiroyuki Ohno<sup>\*4</sup>

<sup>\*1</sup>Department of Biomass Chemistry, Forestry and Forest Products Research Institute, Tsukuba, Ibaraki, Japan, <sup>\*2</sup>Agriculture, Forestry and Fisheries Research Council, Tokyo, Japan, <sup>\*3</sup>Wood Utilization Division, Hokkaido Forest Products Research Institute, Asahikawa, Hokkaido,

<sup>\*4</sup>Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Japan,

Abstract: Structure stability of lignin model compounds in ionic liquids was studied to develop the novel isolation methods of lignin and LCC from wood. Four imidazolium based ionic liquids, and two phenolic lignin model compounds, Guaiacylglycerol- $\beta$ -guaiacyl ether and its  $\alpha$ -ethoxy model compound, were examined in this study. Under the temperature condition of 120 °C, cellulose component in wood meal were decrystallized by more than 48 hs treatment. However, lignin model compounds were gradually decomposed under this temperature condition with extending the processing time. Depending on the ionic liquid used, more than 40% of loaded model compound were decomposed for 48 hs treatment. Under the lower temperature condition (100 °C), those model compounds were relatively stable. Decomposition degree after 48 hs treatment was less than 20% in chlorinated ionic liquid, 1-Butyl-3-methylimidazolium and 1-Allyl-3-methylimidazolium chloride, although significant decomposition was estimated in other ionic liquids.

2007-特別講演 II

熱分解ガスクロマトグラフィーによるリグニンの分析

黒田 健一

九州大学大学院農学研究院

Invited Lecture, II: Analysis of lignin by pyrolysis-gas chromatography.

Ken-ichi Kuroda

Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University, 6-10-1, Higashi-ku, Hakozaki, Fukuoka 812-8581, Japan

Abstract: Emergence of analytical pyrolysis combined with modern instruments such as gas chromatography and/or mass spectrometry has provided new possibilities to analyze the lignin owing to its high sensitivity, lesser sample-preparation steps and a short analysis time. Under controlled pyrolysis conditions, lignin is reproducibly broken to give products retaining structural attributes. This paper examines several recent advances in analytical pyrolysis. Selected aspects are exemplified using original results.

2007-P01

イネ稈及び葉鞘の組織構造とリグニン分布

三瓶広幸、平岩季子、石栗 太、飯塚和也、横田信三、吉澤伸夫

Anatomy and lignin distribution of stem and leaf tissues in *Oryza sativa*.

Hiroyuki Sanpe, Tokiko Hiraiwa, Futoshi Ishiguri, Kazuya Iizuka, Shinso Yokota, Nobuo Yoshizawa  
Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Japan

Abstract: For utilization of biomass resources, anatomy and lignin distribution of stem and leaf tissues in *Oryza sativa*, which is one of the popular crops in Japan, were investigated. Tracheid wall and vessel walls in vascular bundles in cortex and parenchyma tissues showed pinkish color after Wiesner reaction. Spectrophotometry analysis showed a distinct absorption peak around 570 nm in these walls after Wiesner reaction, suggesting that substances with coniferyl aldehyde structure exist in these tissues. On the other hand, fiber walls in cortex were weakly stained with Wiesner reagent and did not show any distinct peak in visible-light absorption microspectra. These results indicate that the amount and type of lignin in cell walls of *O. sativa* vary among cell types.

2007-P02

Lignin deposition and peroxidase activity in Japanese birch plantlets (Tohoku) infected with *Inonotus obliquus* IO-U1 strain.

Md. Mahabubur Rahman<sup>\*1\*2</sup>, Futoshi Ishiguri<sup>\*2</sup>, Yuya Takashima<sup>\*2</sup>, Mariko Satoh<sup>\*2</sup>, Mustafa Abul Kalam Azad<sup>\*2</sup>, Kazuya Iizuka<sup>\*2</sup>, Nobuo Yoshizawa<sup>\*2</sup>, Shinso Yokota<sup>\*2</sup>

<sup>\*1</sup>United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan, <sup>\*2</sup>Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Japan

Abstract: Histochemical studies were undertaken on defensive reactions of *Betula platyphylla* var. *japonica* Tohoku clone after infection with *Inonotus obliquus* IO-U1 strain. As a defensive reaction, phenolics deposition was found rapidly within 2 hrs of infection and reached extensive by 10 days. The peroxidase activities were observed in phenolics-deposited cell walls. Cell walls of vessels and wood fibers were rich in lignin at the infection site in 10 days of treatment. These histochemical changes are considered to occur as defense reactions in the infected Tohoku birch plantlets.

2007-P03

モノリグノール類の電解重合

関口卓也、松下泰幸、今井貴規、福島和彦  
名古屋大学大学院生命農学研究科

Electropolymerization of monolignols.

Takuya Sekiguchi, Yasuyuki Matsushita, Takanori Imai, Kazuhiko Fukushima

Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan

Abstract: We carried out anodic oxidation of monolignols, especially coniferyl alcohol, by galvanostatic (constant-current) method. Using dichloromethane/methanol as a mixed solvent, a yellow filmy product was deposited on Pt anode during the electrolysis reaction. Although the yield of this electropolymerized product was very low, thioacidolysis analysis suggests that it has high  $\beta$ -O-4 linkage content. Probably, the electropolymerization of monolignols could produce the characteristic polymer that we have not obtained from conventional DHP preparation method.

2007-P04

リグニン重合機構の解明 –モノリグノールのラジカル重合の可能性–

鈴木啓介<sup>\*1</sup>、浦木康光<sup>\*2</sup>、生方 信<sup>\*2</sup>

<sup>\*1</sup>北海道大学大学院生命科学院、<sup>\*2</sup>北海道大学大学院農学研究科

Elucidation of the lignin polymerization mechanism. –Possibility of radical polymerization of monolignol– .

Keisuke Suzuki<sup>\*1</sup>, Yasumitsu Uraki<sup>\*2</sup>, Makoto Ubukata<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Life Science, Hokkaido University, Sapporo 060–8589, Japan. <sup>\*2</sup>Research Faculty of Agriculture, Hokkaido University, Sapporo 060–8589, Japan.

Abstract: We investigated possibility of radical polymerization of coniferyl alcohol as a monolignol. The monolignol was found to be polymerized under the solution polymerization conditions with and without initiators. The resultant polymeric materials contain aliphatic alcohols having only a few double bonds. These results suggest that the polymer was formed by radical polymerization together with dehydration.

2007–P05

ポプラペルオキシダーゼアイソザイム CWPO–C の機能解析

清永裕子<sup>\*1</sup>, 佐々木慎弥<sup>\*1</sup>, 堤 祐司<sup>\*2</sup>, 近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学府、<sup>\*2</sup>九州大学大学院農学研究院

Function of cationic cell–wall–peroxidase (CWPO–C) from poplar.

Yuko Kiyonaga<sup>\*1</sup>, Shinya Sasaki<sup>\*1</sup>, Yuji Tsutsumi<sup>\*2</sup>, Ryuichiro Kondo<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioresource and Bioenvironmental Sciences, <sup>\*2</sup>Faculty of Agriculture, Kyushu University, Fukuoka, 812–8581, Japan

Abstract: A unique peroxidase isoenzyme, cationic cell–wall–peroxidase (CWPO–C), from poplar oxidizes sinapyl alcohol, ferrocyanide and synthetic lignin polymers, unlike other plant peroxidase. Recently, catalytic mechanism of CWPO–C was investigated using chemical modification and homology modeling. It was suggested that Tyr residues on the protein surface, such as Tyr–177 and Tyr–74, are considered to be important for the oxidation activities of CWPO–C with a wide range of substrates. In this study, we focused on CWPO–C homolog genes of *Arabidopsis thaliana*, and these T–DNA mutant lines were analyzed. The point–mutated recombinant CWPO–C was also generated to determine the oxidation sites of CWPO–C.

2007–P06

ポプラ分化中木部における 4–coumarate:CoA ligase 免疫局在

山下恭平、高部圭司、藤田稔

京都大学大学院農学研究科

Immunolocalization of 4CL in differentiating xylem of poplar.

Kyohei Yamashita, Keiji Takabe, Minoru Fujita

Laboratory of Tree Cell Biology, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kitashirakawaoiwake–cho, Sakyo–ku, Kyoto 606–8502, Japan

Abstract: Anti–4–coumarate:CoA ligase (4CL) antiserum were raised using artificially synthesized peptides. They were injected several times into mouse, and then the mouse anti–4CL serum was obtained. Specificity of the anti–serum was confirmed by western blotting and immunoprecipitation techniques. Immunolocalization of 4CL was observed in differentiating xylem cells of *Populus sieboldii* X *P. grandidentata*.

2007–P07

Stereochemistry on the formation of syringylglycerol–8–O–4'–(sinapyl alcohol) ether from sinapyl alcohol with enzyme preparations of *Eucommia ulmoides*.

Md. Shameul Alam, Takeshi Katayama, Toshisada Suzuki

Faculty of Agriculture, Kagawa University, Miki–cho, Kagawa 761–0795

Abstracts: Incubation of a soluble enzyme preparation with [8-<sup>14</sup>C]sinapyl alcohol (SA) in the presence of H<sub>2</sub>O<sub>2</sub> gave [<sup>14</sup>C]syringylglycerol-8-O-4'-(sinapyl alcohol) ether (SGSE). The *erythro* isomer was more favored than the *threo* isomer with 63.2 percentage of diastereomeric excess (% d.e.) at 30min and 26.7% d.e. at 60min, respectively. The *erythro* and *threo* isomers at 60min were levorotatory with 47.4% and 21.6% enantiomeric excess (% e.e.), respectively. Incubation of an insoluble enzyme preparation with [8-<sup>14</sup>C]SA also gave [<sup>14</sup>C]SGSE. The *erythro* isomer was more favored than *threo* isomer with 60.8% d.e. at 2min and 11.4% d.e. at 60min, respectively. At 60min (+)-*erythro* and (-)-*threo* isomers were formed with 24.8 and 14.6 enantiomeric excess (% e.e.), respectively. Interestingly, the soluble preparation catalyzed the formation of (-)-*erythro* SGSE, whereas the insoluble preparation did (+)-*erythro* SGSE.

2007-P08

カテキン類の熱変性に対する計算化学解析

徳満圭祐<sup>\*1</sup>、石井 圭<sup>\*1</sup>、正本博士<sup>\*1</sup>、重松幹二<sup>\*1</sup>、光永 徹<sup>\*2</sup>

福岡大学工学部、岐阜大学応用生物科学部

Computer chemistry analysis of thermal transformation of catechins.

Keisuke Tokumitsu<sup>\*1</sup>, Kei Ishii<sup>\*1</sup>, Hiroshi Masamoto<sup>\*1</sup>, Mikiji Shigematsu<sup>\*1</sup>, Tohru Mitsunaga<sup>\*2</sup>

<sup>\*1</sup>Faculty of Engineering, Fukuoka University, Fukuoka 814-0180, JAPAN, <sup>\*2</sup>Faculty of Applied Biological Science, Gifu University, Gifu 501-1193, JAPAN

Abstract: (+)-Catechin transforms to (+)-epicatechin at high temperature, and they reach to thermodynamically equilibrium state expressible with the equilibrium constant, K. This report deals with the equilibrium constants calculated by several methods of computer chemistry, K<sub>Calc</sub>, and the comparison of them to experimental value, K<sub>Expt</sub>. The K<sub>Calc</sub> by a molecular orbital calculation (RB3LYP/6-31G\*) designated qualitatively agreement with K<sub>Expt</sub>. Which denotes superior of (+)-catechin to (+)-epicatechin and decreases with temperature. However, K<sub>Calc</sub> quantitatively disagrees with K<sub>Expt</sub>.

2007-P09

高圧水蒸気蒸留による桐材成分の抽出

金原弥生、西谷耕三、棚橋光彦

岐阜大学大学院連合農学研究科

Extraction of constituents from paulownia wood by high-pressure steam distillation.

Yayoi Kimpara, Kouzou Yoshitani, Mitsuhiko Tanahashi

Laboratory of Biomass Conversion, United Graduate School of Agriculture, Gifu University, Gifu 501-1193, Japan

Abstract: Paulownia (*Pauloumia tomentosa*) wood contains sesamin and paulownin which have a repellent action against insects. In this study, steam distillation of paulownia wood was conducted at two different pressures (1.5 and 2.1MPa) and the distilled oil was analyzed by GC-MS. During high-pressure steaming for paulownia wood, sesamin and paulownin were epimerized. The combined yield based on the dry wood weight under 2.1MPa of sesamin and episesamin was 0.098%, and that of paulownin and epipaulownin was 0.82%. Meanwhile, those of total extraction with alcohol-benzene refluxed for 24 hr were 0.49% and 1.1%, respectively.

2007-P10

白色腐朽菌 *Phanerochaete crassa* WD1694 由来のグリオキサールオキシダーゼの生産と精製

高野麻理子、中村雅哉、山口宗義、渋谷源

## 森林総合研究所

Production and purification of glyoxal oxidase from a white-rot fungus *Phanerochaete crassa* WD1694.

Mariko Takano, Masaya Nakamura, Muneyoshi Yamaguchi, Hajime Shibuya  
Forestry and Forest Products Research Institute, Matsunosato 1, Tsukuba 305-8687

Abstract: As a preliminary step to analyze localization mechanism of peroxidase reaction at hyphal tips of *P. crassa* WD1694, production and purification of glyoxal oxidase from *P. crassa* WD1694 was studied. The maximum activity of glyoxal oxidase was produced in cultures containing 100 mg/l MnSO<sub>4</sub> and 0.05% Tween 80 on day 4 of growth. The harvested culture was filtrated, concentrated, and further purified with DEAE-Sepharose. The purified GLOX was detected as a single band by the analysis of SDS-PAGE.

2007-P11

フラクトメータを用いた腐朽測定値とリグニン分解過程の相互関係

松本かほる、石栗太、飯塚和也、横田信三、吉澤伸夫

森林総合研究所

Relationship between compression strength of decayed wood measured by Fractometer and lignin degradation process.

Kahoru Matsumoto, Futoshi Ishiguri, Kazuya Iizuka, Shinso Yokota, Nobuo Yoshizawa  
Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Japan

Abstract: To obtain basic knowledge for detecting the degree of wood decay using Fractometer, relationship between compression strength of decayed wood measured by Fractometer and lignin degradation process was investigated. Sapwood cores of *Cryptomeria japonica*, *Prunus jamasakura*, and *Magnolia obovata* were decayed for 60 days by a brown-rot fungus (*Corirolellus palustri*, FFPRI 0507), a white-rot fungus (*Coriolus versicolor*, FFPRI 1030), and a soft-rot fungus (*Chaetomium globosum*, NBRC 6347). When *C. japonica* and *P. jamasakura* cores were decayed, compression strength of each core was decreased. These results suggest that degree of decay in wood can be evaluated using compression strength measured by Fractometer.

2007-P12

*Sphingomonas paucimobilis* SYK-6 株の  $\beta$ -アリールエーテル代謝に関与する 4 種の脱水素酵素の機能と立体選択性

政井英司<sup>\*1</sup>、森内英輝<sup>\*1</sup>、佐藤裕介<sup>\*1</sup>、福田雅夫<sup>\*1</sup>、菱山正二郎<sup>\*2</sup>、中村雅哉<sup>\*2</sup>、片山義博<sup>\*3</sup>

<sup>\*1</sup>長岡技術科学大学・生物機能工学、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>東京農工大学大学院 BASE

Stereoselectivity and roles of four distinct guaiacylglycerol- $\beta$ -guaiacyl ether dehydrogenases from *Sphingomonas paucimobilis* SYK-6.

Eiji Masai<sup>\*1</sup>, Hideki Moriuchi<sup>\*1</sup>, Yusuke Sato<sup>\*1</sup>, Shojiro Hishiyama<sup>\*2</sup>, Masaya Nakamura<sup>\*2</sup>, Yoshihiro Katayama<sup>\*3</sup>, Masao Fukuda<sup>\*1</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188,

<sup>\*2</sup>Forestry and Forest Products Research Institute, Tsukuba, Ibaraki 305-8687, <sup>\*3</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: Degradation of arylglycerol- $\beta$ -aryl ether is the most important process of bacterial lignin catabolism. *S. paucimobilis* SYK-6 oxidizes guaiacylglycerol- $\beta$ -guaiacyl ether (GGE) to  $\alpha$ -(2-methoxyphenoxy)- $\beta$ -hydroxypropiovanillone (MPHPV), and then the ether linkage of MPHPV is cleaved to generate  $\alpha$ -glutathionyl- $\beta$ -hydroxypropiovanillone and guaiacol. We have characterized enantioselective glutathione S-transferases, which are involved in the ether cleavage

of different enantiomers of MPHPV. In this study, we found that three GGE dehydrogenases of SYK-6 are involved in the transformation of GGE into MPHPV. LigD1 is essential for the transformation of

( $\alpha$  R,  $\beta$  S)-GGE and ( $\alpha$  R,  $\beta$  R)-GGE. Both LigD2 and LigD4 participate in the conversion of ( $\alpha$  S,  $\beta$  R)-GGE and ( $\alpha$  S,  $\beta$  S)-GGE.

2007-P13

*Sphingomonas paucimobilis* SYK-6 株のプロトカテク酸ジオキシゲナーゼが関与する 3-O-メチルガリツク酸解裂経路

笠井大輔<sup>\*1</sup>、政井英司<sup>\*1</sup>、福田雅夫<sup>\*1</sup>、片山義博<sup>\*2</sup>

<sup>\*1</sup>長岡技術科学大学・生物工学、<sup>\*2</sup>東京農工大学大学院 BASE

Degradation of 3-O-methylgallate in *Sphingomonas paucimobilis* SYK-6 by pathways involving protocatechuate 4,5-dioxygenase.

Daisuke Kasai<sup>\*1</sup>, Eiji Masai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Masa. Fukuda<sup>\*2</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata, 940-2188,

<sup>\*2</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: *Sphingomonas paucimobilis* SYK-6 converts vanillate and syringate to protocatechuate (PCA) and 3-O-methylgallate (3MGA), respectively. 3MGA is metabolized via multiple pathways involving 3MGA 3,4-dioxygenase, PCA 4,5-dioxygenase (LigAB), and gallate dioxygenase. In this study, we investigated the role of LigAB in syringate metabolism. The reaction product of 3MGA catalyzed by His-tagged LigAB was identified as 4-carboxy-2-hydroxy-6-methoxy-6-oxohexa-2,4-dienoate (CHMOD) and 2-pyrone-4,6-dicarboxylate (PDC), indicating that 3MGA is transformed to CHMOD and PDC by the reaction catalyzed by LigAB. Mutant analysis revealed that the 3MGA catabolic pathways involving LigAB are functional in SYK-6.

2007-P14

リグニン下流代謝系プロトカテク酸 4, 5-解裂経路遺伝子群の転写制御機構

上村直史<sup>\*1</sup>、高村一寛<sup>\*1</sup>、原啓文<sup>\*1</sup>、政井英司<sup>\*1</sup>、福田雅夫<sup>\*1</sup>、片山義博<sup>\*2</sup>

<sup>\*1</sup>長岡技術科学大学・生物工学、<sup>\*2</sup>東京農工大学大学院 BASE

Transcriptional regulation of the genes involved in the protocatechuate 4,5-cleavage pathway.

Naofumi Kamimura<sup>\*1</sup>, Kazuhiro Takamura<sup>\*1</sup>, Hirofumi Hara<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Eiji Masai<sup>\*1</sup>, Masao Fukuda<sup>\*1</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata, 940-2188,

<sup>\*2</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: The protocatechuate (PCA) 4,5-cleavage pathway is the essential metabolic route for lignin catabolism in *Sphingomonas paucimobilis* SYK-6. Here we examined the operon structure of the PCA 4,5-cleavage pathway genes and investigated the transcriptional regulation of the genes. Reverse transcription-PCR analysis indicated that the PCA 4,5-cleavage pathway genes of SYK-6 consist of three transcriptional units, including the *ligK-orf1-ligI-lsdA* operon, the *ligJ-ligA-ligB-ligC* operon, and the monocistronic *ligR*. Transcription of *ligK* and *ligJ* operons are directly up-regulated by LigR, and this transcriptional activation requires PCA as an inducer.

2007-P15

リグニンモデル化合物の電気化学的酸化(2)、— 1-phenylethanol 誘導体の酸化反応—  
白石 匠、上高原 浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Electrooxidation of lignin model compounds (2). – Oxidation of 1-phenylethanol derivatives –.

Takumi Shiraishi, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

The Chemistry of Biomaterials, Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: The anodic oxidation of 1-phenylethanol derivatives, 1-(4'-ethoxy-3'methoxyphenyl) ethanol (1G), 1-(4'-ethoxy-3', 5'-dimethoxyphenyl) ethanol (1S) and 1-(4'-ethoxyphenyl) ethanol (1P) were investigated for the application to the pretreatment of kraft pulping. The oxidation with 2,6-lutidine, gave the corresponding  $\alpha$ -carbonyl derivatives (4-O-ethylacetovanilone : 2G, 4-O-ethylacetosyringone : 2S, 4-ethoxyacetophenone : 2P) in 40-70%. The electrooxidation mechanism of 1-phenylethanols is also proposed.

2007-P16

非木質試料におけるリグニン定量値の評価

中村裕貴, 秋山拓也, Zhenfu Jin, Deded S. Nawawi, 横山朝哉, 松本雄二

東京大学大学院農学生命科学研究科

Evaluation of lignin content in non-wood plants.

Hirota Nakamura, Takuya Akiyama, Zhenfu Jin, Deded S. Nawawi, Tomoya Yokoyama, Yuji Matsumoto

Wood Chemistry Laboratory, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: To evaluate the lignin content in non-wood cell walls, leaves and grass stems of various vascular plants were subjected to different kind of wet chemical analyses and these results were compared with the apparent lignin content obtained by Klason procedure. As a method of wet chemical analysis, nitrobenzene oxidation and ozonation were applied. Infrared spectroscopy was also used to estimate the amount of aromatic structures. The comparison of apparent lignin content and the yields of specific degradation products obtained by wet chemical methods suggested that the Klason procedure cannot give the correct lignin content in the case of non-wood cell walls. The amount of aromatic structures estimated by FT-IR was correlated very well with the yield of nitrobenzene oxidation products, which strongly supported the idea that lignin content in non-wood cell walls can be more reasonably expressed by the yields of these specific degradation products rather than Klason procedure.

2007-P17

リグニンの熱分解による機能性炭素への物質変換

肥留川孝治、木島正志

筑波大学大学院数理物質科学研究科

Conversion of lignin to functional carbon materials by pyrolysis.

Takaharu Hirukawa, Masashi Kijima

Institute of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba

Abstract: It is attempted that nano-structured and porous carbon materials were synthesized by pyrolysis of lignin. Under anaerobic conditions of a slow heating rate, lignin (alkaline) was converted to a porous carbonaceous material showing 738 m<sup>2</sup>/g of BET surface area. Under the same heating conditions, a freeze-dried reverse micelle of lignin converted to a high porous carbonaceous material showing 1003 m<sup>2</sup>/g of surface area.

2007-P18

$\beta$ -5 型リグニンモデル化合物の熱分解—メチル化

黒田健一<sup>\*1</sup>、中川明子<sup>\*2</sup>、芦谷竜矢<sup>\*3</sup>、藤田弘毅<sup>\*1</sup>

<sup>\*1</sup>九州大学大学院農学研究科、<sup>\*2</sup>筑波大学大学院生命環境科学研究科、<sup>\*3</sup>山形大学農学部

Tetramethylammonium hydroxide (TMAH) thermochemolysis of lignin: Behavior of  $\beta$ -5-type lignin model compounds.

Ken-ichi Kuroda<sup>\*1</sup>, Akiko Nakagawa<sup>\*2</sup>, Tatsuya Ashitani<sup>\*3</sup>, Koki Fujita<sup>\*1</sup>

<sup>\*1</sup>Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan, <sup>\*2</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8572, Japan <sup>\*3</sup>Faculty of Agriculture, Yamagata University, 1-23 Wakaba, Tsuruoka, Yamagata 997-8555, Japan

Abstract: Phenolic 2-aryl coumarans **1-6** were subjected to tetramethylammonium hydroxide (TMAH) thermochemolysis (500 °C/4 s) to investigate reactions occurring in lignin specifically under these conditions. Products were monitored by gas chromatography/mass spectrometry (GC/MS). GC/MS signals corresponding to dimers overwhelmed all GC/MS traces. (2-Phenyl-2,3-dioxane-3-yl) methan-1-ols (**1** and **6**) predominantly gave 2,3,3',4'-tetramethoxystilbenes involving in a loss of the  $\gamma$ -CH<sub>2</sub>OH substituent. 3-Methyl-2-phenyl-2,3-dihydrobenzofurans (**2-5**) gave a mixture of 1-(3,4-dimethoxyphenyl)-2-(2,3-dimethoxyphenyl)-1-methoxypropanes and 2,3,3',4'-tetramethoxy-stilbenes having the  $\gamma$ -methyl group. Side chains -CH=CHCH<sub>2</sub>OH and -COOH on ring B were simply methylated to produce the corresponding methyl ether and ester, respectively. A -CH=CHCH<sub>3</sub> side chain was preserved intact, whereas a -CH=CHCHO side chain changed to a -CHO side chain. This was confirmed by isolating 5-formyl-2,3,3',4'-tetramethoxystilbene as an off-line TMAH thermochemolysis product from 3-[2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxy-2,3-dihydrobenzofuran-5-yl] propenal.

2007-P19

DSC で検出されるリグニンのガラス転移温度に対する加熱前処理の影響—針葉樹と広葉樹の違いおよびメトキシ基量の影響

山田竜彦<sup>\*1\*2</sup>、久保智史<sup>\*1</sup>、橋田 光<sup>\*1</sup>、John F. Kadla<sup>\*3</sup>、Hou-min Chang<sup>\*4</sup>、Vincent Chang<sup>\*4</sup>

<sup>\*1</sup>森林総合研究所、<sup>\*2</sup>農林水産省農林水産技術会議事務局、<sup>\*3</sup>ブリティッシュコロンビア大学、<sup>\*4</sup>ノースカロライナ州立大学

Effects of DSC pre-heat treatment on the glass-transition temperature of lignin. -Difference between softwood and hardwood lignin, and effect of methoxy contents.

Satoshi Kubo<sup>\*1</sup>, Tatsuhiko Yamada<sup>\*1\*2</sup>, Koh Hashida<sup>\*1</sup>, John F. Kadla<sup>\*3</sup>, Hou-min Chang<sup>\*4</sup>, Vincent Chiang<sup>\*4</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, Tsukuba, Japan, <sup>\*2</sup>Agriculture, Forestry and Fisheries Research Council, Tokyo, Japan, <sup>\*3</sup>The University of British Columbia, Vancouver, B.C., Canada, <sup>\*4</sup>North Carolina State University, Raleigh, NC, USA

Abstract: In the DSC analysis of lignin, thermal treatment "pre-heat treatment" is usually required to remove thermal history before measurement. However, glass transition temperature of softwood kraft lignin was significantly affected by this pre-heat treatment. By contrast, such T<sub>g</sub> increase was not observed for hardwood kraft lignin. Typical structural difference between softwood and hardwood lignin can be found in the aromatic ring structure. Therefore, DSC analysis was also performed for various lignins which have different S/G. However, clear correlation could not be detected between S/G and T<sub>g</sub> increases. S/G would be not solo factor to such T<sub>g</sub> increase of lignin.

2007-P20

リグニンを基盤とした新規ポリマーの創製  
井上宗亮、松下泰幸、今井貴規、福島和彦  
名古屋大学大学院生命農学研究科

Development of novel polymer based on lignin.

Sosuke Inoue, Yasuyuki Matsushita, Takanori Imai, Kazuhiko Fukushima

Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601

Abstract: In Japan, lignosulfonate is mainly used for water reducing agent of cement and dye dispersant. In order to expand in application, we tried to produce a novel polymer based on the lignosulfonate. We obtained ion-conducting polymers from sodium lignosulfonate by substitution of sodium ion to imidazole compound. The polymers showed higher conductivity with longer the side chain of imidazole compound. Purification of sodium lignosulfonate led low ion conductivity. It is suggested that impurity contained in the sodium lignosulfonate, such as sugars, induced the ion conductivity.

2007-P21

イオン性相互作用によるリグノスルホン酸の生体関連物質吸着能

長谷川大輔<sup>\*1</sup>、寺本好邦<sup>\*2</sup>、西尾嘉之<sup>\*1</sup>

<sup>\*1</sup>京都大学大学院農学研究科、<sup>\*2</sup>産業技術総合研究所バイオマス研究センター

Functionalization of lignosulfonic acid: Its adsorption property to catch bio-related substances by ionic interactions.

Daisuke Hasegawa<sup>\*1</sup>, Yoshikuni Teramoto<sup>\*2</sup>, Yoshiyuki Nishio<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, <sup>\*2</sup>National Institute of Advanced Industrial Science and Technology (AIST), Biomass Technology Research Center, 2-2-2, Hirosuehiro, Kure, Hiroshima, 737-0197, Japan

Abstract: Poly-ion complexes of anionic lignosulfonic acid (LSA) with cationic poly(L-lysine) (PLL) were prepared by spontaneous precipitation from mixed aqueous solutions adjusted at different pHs. Fourier transform infrared (FTIR) measurements and elementary analysis for the complexes revealed the presence of strong ionic interactions between the sulfonic anion of LSA and the  $\epsilon$ -aminocation of PLL. Circular dichroism measurements revealed that an  $\alpha$ -helix conformation of PLL changed to a random coil conformation when the complexes were formed. An adsorption property of LSA to catch nicotine compounds was also examined by FTIR measurements and high performance liquid chromatography.

2007-P22

高圧水蒸気蒸留による竹からのチロシンの効率的な抽出

烏日郷<sup>\*1</sup>・道家真一<sup>\*2</sup>・村手宏隆<sup>\*2</sup>・棚橋光彦<sup>\*1\*2</sup>

<sup>\*1</sup>岐阜大学農学部、<sup>\*2</sup>岐阜大学工学部

Development of the efficient extraction of tyrosine from grown bamboo shoot by high-pressure steam distillation.

Wurina<sup>\*1</sup>, Shinichi Doke<sup>\*2</sup>, Hiroataka Murate<sup>\*2</sup>, Mitsuhiro Tanahashi<sup>\*1\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan, <sup>\*2</sup>Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

Abstract: It was confirmed that large quantities of tyrosine is contained in grown bamboo shoot by solid state CPMAS <sup>13</sup>C-NMR analysis. Because of its chemical structure, tyrosine is not distillable with common steam distillation method. Therefore, a new high-pressure steam distillation method was evaluated for efficient extraction of tyrosine from bamboo shoot. From the distilled essential oil of madake bamboo shoot, 4-hydroxy styrene and 3-methoxy-4-styrene derivatives were isolated

and identified.

## 第 53 回 (2008.10.30-31) 東京大学農学部 弥生講堂

2008-101

イネのケイヒ酸モノリグノール経路遺伝子の検索と遺伝子発現解析

山本直樹<sup>\*1</sup>、鈴木史朗<sup>\*2</sup>、村上真也<sup>\*1</sup>、坂本正弘<sup>\*3</sup>、服部武文<sup>\*1</sup>、梅澤俊明<sup>\*1\*2</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> 京都大学生存圏研究所基盤ユニット、<sup>\*3</sup> 京都大学大学院農学研究科  
Computational identification and expression analysis of monolignol biosynthesis pathway genes in rice.

Naoki Yamamoto<sup>\*1</sup>, Shiro Suzuki<sup>\*2</sup>, Shinya Murakami<sup>\*1</sup>, Masahiro Sakamoto<sup>\*3</sup>, Takefumi Hattori<sup>\*1</sup>, Toshiaki Umezawa<sup>\*1\*2</sup>

<sup>\*1</sup> Research Institute for Sustainable Humanosphere, Kyoto university. Gokasho, Uji, Kyoto 611-0011, Japan, <sup>\*2</sup> Institute of Sustainability Science, Kyoto university. Gokasho, Uji, Kyoto 611-0011, Japan, <sup>\*3</sup> Faculty/Graduate School of Agriculture, Kyoto university, Kitashirakawa Oiwakecho, Sakyo-ku, Kyoto, Kyoto 606-8502, Japan..

Abstract: It is still unknown which gene set works in monolignol biosynthesis in rice. Here, we surveyed computationally the genes encoding enzymes of the cinnamate/monolignol pathway in all rice protein sequences. Expression analysis of the rice genes showed diversification of the qualitative and quantitative expression patterns among the gene family members. The most part of the genes were classified into 5 groups with the organ-specific expression pattern using Self Organizing Maps method. The fact that all the groups have plural enzyme genes of the monolignol biosynthesis pathway implies role and responsibility of the gene sets for monolignol synthesis in each organ.

2008-102

TDNA 挿入変異体を用いたシロイヌナズナ 4CL 遺伝子の機能解析

吉村奈穂、佐藤かんな、片山義博、梶田真也

東京農工大学大学院 BASE

The functional analysis of 4-coumarate:CoA ligase genes in *Arabidopsis thaliana* by using T-DNA tagged mutants.

Naho Yoshimura, Kanna Sato, Yoshihiro Katayama, Shinya Kajita

Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: 4-Coumarate:CoA ligase is one of key enzymes in biosynthesis of monolignols in many plants. *Arabidopsis thaliana* has five 4CL genes (*At4CL1-At4CL5*) in its genome. To understand the function of the genes for 4CL in the lignin biosynthesis, the phenotypes of two T-DNA inserted mutants (*At4cl1/At4cl1* and *At4cl2/At4cl2*) were analyzed in this study. We have measured 4CL activity of the mutants with crude enzymes from their stems. The activities of *At4cl1/At4cl1* and *At4cl2/At4cl2* lines were 12.5% and 43.7% of that in control line, respectively. As the results of lignin specific staining, decrease in lignin content and composition of syringyl residue in *At4cl1/At4cl1* line were revealed, whereas those in *At4cl2/At4cl2* line were nearly identical to the control plant. The mutant and control lines showed similar development pattern except for a *At4cl1/At4cl1* line, SALK142526, which exhibited dwarf phenotype. These results suggest that *At4CL1* plays crucial roles in lignin biosynthesis in *A. thaliana*.

2008-103

改変型植物酸性 peroxidase の酵母での発現と精製(2)

吉中喬慈、川合伸也

東京農工大学大学院

Heterogeneous expression and purification of modified plant peroxidase. (2)

Kyoji Yoshinaka, Shinya Kawai

Faculty of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8, Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

Abstract: Lignin peroxidase of *Phanerochaete chrysosporium* can oxidize the environmental pollutants and lignin by assuming Trp-171 near the surface of the protein to be a catalyst site. CWPO-C that is a kind of poplar peroxidases can oxidize sinapyl alcohol, and is presumed that Tyr-74 and Tyr-177 exposed to the surface of the protein are the catalyst sites. We introduced the mutations into *prxA3a*, a POX gene of *Populus kitakamiensis*, changed the amino acid residues at the corresponding positions to Trp and Tyr residues, and examined the changes in the substrate specificities.

2008-104

選択的リグニン分解菌が産生する菌体外脂質関連代謝物の構造解析

西村裕志、村山京子、渡連崇人、本田与一、渡辺隆司

京都大学生存圏研究所

Structural analyses of extracellular lipid-related metabolites produced by a selective lignin degrading fungus.

Hiroshi Nishimura, Kyoko Murayama, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Laboratory of Biomass Conversion, Research Institute for Sustainable Humanosphere (RISH), Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

Abstract: Wood-rot fungus, *Ceriporiopsis subvermispora* can degrade lignin without intensive damage of cellulose. We have been focusing on extracellular metabolites participating in the selective ligninolysis, and characterized a series of unique metabolites, ceriporic acids. Important function of ceriporic acid is inhibition of cellulose degradation by hydroxyl radicals (HO $\cdot$ ) produced by the Fenton reaction system. Here, we investigate extracellular lipid-related metabolites using liquid chromatography, mass spectrometry and nuclear magnetic resonance spectrometry. New metabolites including a series of ceriporic acids were found and analyzed.

2008-105

抗炎症剤であるジクロフェナクおよびメフェナム酸の白色腐朽菌による毒性除去

畑 貴之<sup>\*1</sup>、河合真吾<sup>\*1</sup>、西田友昭<sup>\*1</sup>、岡村秀雄<sup>\*2</sup>

<sup>\*1</sup> 静岡大学農学部、<sup>\*2</sup> 神戸大学大学院海事科学研究科

Removal of toxicities of anti-inflammatory drugs, diclofenac and mefenamic acid, by white rot fungus *Phanerochaete sordida* YK-624.

Takayuki Hata<sup>\*1</sup>, Shingo Kawai<sup>\*1</sup>, Tomoaki Nishida<sup>\*1</sup>, Hideo Okamura<sup>\*2</sup>

<sup>\*1</sup>Department of Environment and Forest Resources Science, Faculty of Agriculture, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan, <sup>\*2</sup>Faculty of Maritime Sciences, Kobe University Graduate school of Maritime Sciences, 5-1-1 Fukaeminamicho, Higashinada-ku, Kobe 658-0022, Japan

Abstract: At present, there is an increasing concern on the presence of pharmaceutical compounds in the environment mainly due to their potential risk to the aquatic environment. In this study, diclofenac (Dic) and mefenamic acid (Mef), which are used widely as non-steroidal anti-

inflammatory drugs and are ubiquitously found in the water sample, were treated with white rot fungus *Phanerochaete sordida* YK-624 under ligninolytic condition with low-nitrogen and high-carbon culture medium. After 6 days of fungal treatment, Dic completely disappeared and Met decreased by about 90%. During the treatment of Dic, two major metabolites, 4'-hydroxydiclofenac and 5-hydroxydiclofenac, were found in the cultures. On the other hand, a major metabolite of Mef was 3'-hydroxymefenamic acid. Toxicities of Dic and Mef before and after fungal treatment were evaluated by acute lethal toxicity test using freshwater crustacean *Thamnocephalus platyurus*. The profiles for removal of toxicities of Dic and Mef and decrease in concentrations of both drugs during treatment were very similar. These results suggested that hydroxylation of Dic and Mef is mainly involved in detoxification of these drugs.

2008-106

冬虫夏草 (*Cordyceps*) 菌による多環式芳香族炭化水素および塩素化ダイオキシン分解の試み  
久野祐功<sup>\*1</sup>、渡辺昌司<sup>\*1</sup>、亀井一郎<sup>\*1\*2</sup>、近藤隆一郎<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学府、<sup>\*2</sup>福岡大学工学部、<sup>\*3</sup>九州大学農学研究院

Attempts to degrade polycyclic aromatic hydrocarbons (PAHS) and chlorinated dioxins by *Cordyceps* species.

Tasuku Kuno, Ichiro Kamei, Masashi Watanabe, Ryuichiro Kondo

Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University, 6-10-1, Hako2aki, Higashi-ku, Fukuoka, 812-8581, Japan

Abstract: Degradation experiments of chlorinated dioxins using *Cordyceps* species were carried out. As chlorinated dioxins, 2,7-dichloro-, 2,3,7-trichloro-, 1,3,6,8-, 1,3,7,8-, and 1,3,7,9-tetrachloro-dibenzo-p-dioxin and 2,4,8-trichlorodibenzofuran were used. *Cordyceps brongniartii* and *Cordyceps militaris*, were selected based on the ability of 2,7-dichlorodibenzo-p-dioxin (2,7-diCDD) degradation. 2,7-DCDD, 2,3,7-triCDD and 2,4,8-triCDF were biotransformed to hydroxyl compounds by *C. militaris*. PAHs were degraded rapidly in medium containing chitin or chitosan by *C. militaris* and *C. brongniartii*. Phenanthrene and pyrene were completely disappeared in these medium. In addition, benzo [a] pyrene and indeno [1,2,3-c,d] pyrene also were degraded extensively.

2008-107

Biodegradation of phenanthrene, an aromatic hydrocarbon by *Polyporus* sp. S133 in liquid medium.

Tony Hadibarata, Sanro Tachibana, Kazutaka Itoh

Department of Applied Bioscience, Faculty of Agriculture, Ehime University, 3-5-7 Tarumi, Matsuyama, Ehime 790-8566, Japan

Abstract: The effect of adding several concentrations of tween 80 and agitation rate to increase degradation rate of phenanthrene by using *Polyporus* sp. S133 collected from contaminated soil was studied. A maximal degradation rate (92%) was obtained when *Polyporus* sp. S133 was cultured under agitation of 120 rpm for 30 days, as compared to just 44% degradation in non-agitated cultures. The degradation rate increased as the amount of tween 80 added increased. The rate in agitated cultures was about 2 times that in non-agitated cultures. The mechanism for degradation of phenanthrene with the fungus through identification of the metabolites was found.

2008-108

微生物機能を用いた植物バイオマス資源(リグニン)の新規ポリマー原料への変換技術と新しい機能性材料の製造 III

岡村祐里子<sup>\*1</sup>、大塚博之<sup>\*1</sup>、間瀬浩平<sup>\*1</sup>、阿部友邦<sup>\*1</sup>、笠井大輔<sup>\*2</sup>、政井英司<sup>\*2</sup>、福田雅夫<sup>\*2</sup>、大塚祐一郎<sup>\*3</sup>、中村雅哉<sup>\*3</sup>、大原誠資<sup>\*3</sup>、重原淳孝<sup>\*4</sup>、佐藤かな<sup>\*1</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>

\*<sup>1</sup> 東京農工大学大学院 BASE、\*<sup>2</sup> 長岡技術科学大学・生物機能工学、\*<sup>3</sup> 森林総合研究所、\*<sup>4</sup> 東京農工大学工学部

Studies of technology that converts plant biomass (lignin) into new polymer materials using bacterial function and products novel functionality materials. III.

Yuriko Okamura<sup>\*1</sup>, Hiroyuki Otsuka<sup>\*1</sup>, Kohei Mase<sup>\*1</sup>, Tomokuni Abe<sup>\*1</sup>, Daisuke Kasai<sup>\*2</sup>, Eiji Masai<sup>\*2</sup>, Masao Fukuda<sup>\*2</sup>, Yuichiro Otsuka<sup>\*3</sup>, Masaya Nakamura<sup>\*3</sup>, Seiji Ohara<sup>\*3</sup>, Kiyotaka Shigehara<sup>\*4</sup>, Kanna Sato<sup>\*1</sup>, Shinya Kajita<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>

\*<sup>1</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei Tokyo, 184-8588, Japan, \*<sup>2</sup>Department of BioEngineering, Nagaoka University of Technology, Nagaoka Niigata, 940-2188, Japan, \*<sup>3</sup>Forestry and Forest Products Research Institute, Matsunosato Tsukuba Ibaraki, 305-8687, Japan, \*<sup>4</sup>Graduate School of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: *Sphingomonas paucimobilis* SYK-6 is able to grow on various lignin-derived biaryls, and 2-pyrone-4,6-dicarboxylic acid (PDC), an intermediate of these compounds, can be used as the polymer materials. In a previous study, we built a bioreactor to produce PDC with genetic technique, and succeeded in producing PDC from protocatechuate, vanillin, vanillate, and *p*-hydroxybenzoate. In this study, we examined the feasibility of industrial PDC production by using liginosulfonic acid, one of the actual lignin resolvent. The existence of resolvent of liginosulfonic acid did not inhibit PDC production from 5 g/L vanillin. This result raise the possibility of industrial PDC production built into the paper-forming process.

2008-109

単離リグニンの両親媒性化とその機能評価

本間春海<sup>\*1</sup>、浦木康光<sup>\*1</sup>、久保智史<sup>\*2</sup>、山田竜彦<sup>\*2</sup>、松下泰幸<sup>\*3</sup>、福島和彦<sup>\*3</sup>

\*<sup>1</sup> 北海道大学大学院農学研究科、\*<sup>2</sup> 森林総合研究所、\*<sup>3</sup> 名古屋大学大学院生命農学研究科

Conversion of lignin to amphiphilic compounds and their characterization.

Harumi Homma<sup>\*1</sup>, Satoshi Kubo<sup>\*2</sup>, Tatsuhiko Yamada<sup>\*2</sup>, Yasuyuki Matsushita<sup>\*3</sup>, Kazuhiko Fukushima<sup>\*3</sup>, Yasumitsu Uraki<sup>\*4</sup>

\*<sup>1</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, Japan, \*<sup>2</sup>Department of Biomass Chemistry, Forestry and Forest Products Research Institute, Tsukuba 305-8687, Japan, \*<sup>3</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan, \*<sup>4</sup>Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

Abstract: The acetic acid lignin (AL) was converted to an amphiphilic polymer by derivatization of AL with several polyethylene glycol diglycidylethers (PEGDE) to make use of them as a nonionic surfactant. The derivatives revealed significant surface activity, such as reduction of water surface tension and critical micelle concentrations (CMC), although both PEGDE and PEG showed very weak. The surface activity of AL derivative was improved by the reaction with monoepoxide compound, ethoxy-(2-hydroxy)-propoxy-polyethylene glycol glycidylether (PEGGE). The hydrophile-lipophile balance (HLB) suggested these derivatives were suitable to use as emulsifiers and detergents. In addition, these derivatives were found to have higher biodegradability than lignin. Consequently, these derivatives are promising as environmentally-friendly surfactants.

2008-110

バイオエタノール生産副産物加水分解リグニンを原料とするポリウレタンの調製と物性

畠山兵衛<sup>\*1</sup>、辻本泰人<sup>\*1</sup>、廣瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>

\*<sup>1</sup> 福井工業大学・工学部、\*<sup>2</sup> 産業技術総合研究所、\*<sup>3</sup> リグノセルリサーチ

Preparation and properties of polyurethane derived from hydrolysis lignin obtained as byproduct of

bioethanol.

Hyoe Hatakeyama<sup>\*1</sup>, T. Ohsuga<sup>\*1</sup>, M. Shimada<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Fukui University of Technology, 3-6-1, Gakuen, Fukui 910-8505, AIST, 1-1-4 Higashi, Tsukuba, 305-8565, Lignocell Research, 73-8, Yatsumata, Fukui 910-3558

Abstract: Polyurethane (PU) foams were prepared using hydrolysis lignin (HL) obtained as a by-product of bioethanol industry. Four kinds of HL's from Russia and New Zealand were utilized. Sodium lignosulfonate (LS) obtained as a by-product of the pulping industry was also used as a reference. HL and LS polyols were obtained by dissolving HL and LS in diethyleneglycol (DEG) and polyethyleneglycol (PEG200). In this study, PU foams were obtained by reacting the above polyols with poly(phenylene methylene) polyisocyanate (MDI) using a small amount of water as foaming reagent. Apparent density of PU foams was in a range from 0.04 to 0.08 g/cm<sup>3</sup>. Compression strength ( $\delta$  10) was in a range from 0.1 to 0.4MPa. Thermal degradation was ca. 300 °C and mass residue at 500 °C was ca. 35 %. Glass transition temperature (T<sub>g</sub>) of PU foams from DEG was ca. 100 °C regardless of kinds of lignin. In contrast, T<sub>g</sub> of PU foams from PEG was ca. 50 °C. Thermal conductivity was ca. 0.03 W/mK which indicates that PU foams show excellent insulation effect. It is concluded that PU foams derived from HL can be applicable for housing materials as an insulator.

2008-111

リグニンスルホン酸塩、エチレングリコール及びグリセリンを原料とするエポキシ樹脂の合成と熱的性質

廣瀬重雄<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup>産業技術総合研究所、<sup>\*2</sup>リグノセルリサーチ、<sup>\*3</sup>福井工業大学工学部、

Synthesis and thermal properties of epoxy resins from ligninsulfonate, ethylene glycol and glycerol. Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Research Institute for Innovation in Sustainable Chemistry, AIST, Central 5, 1-1-4 Higashi, Tsukuba, Ibaraki 305-8565, Japan, <sup>\*2</sup>Lignocel Research Ltd., Yatsumata, Fukui 910-3558, Japan,

<sup>\*3</sup>Fukui University of Technology, 3-6-1 Gakuen, Fukui-City, Fukui 910-8505, Japan

Abstract: Sodium ligninsulfonate (LS) was dissolved in glycerol (GLY) and the obtained mixture was allowed to react with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (LS-GLY polyacid, LSGLYPA). LS-ethylene glycol (EG)-polyacid (LSEGPA) was also prepared from EG. The mixture of LSGLYPA and LSEGPA was reacted with glycerol diglycidyl ether (GLYDGE) in the presence of catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratio, mol/mol) was maintained at 1.1. The contents of LSGLYPA in the mixture of LSGLYPA and LSEGPA (LSEGPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (T<sub>g</sub>'s) of epoxy resins increased with increasing LSGLYPA contents suggesting that glycerol act as a cross-linking forming agent in epoxy resin networks. Thermal decomposition temperatures (T<sub>d</sub>'s) of epoxy resins were almost constant regardless of LSGLYPA contents.

2008-特別講演

有機合成化学的アプローチによる木質バイオマス成分研究 ー木材の総合研究と総合利用ー  
中坪文明

京都大学大学院農学研究科

Studies on the woody biomass constituents by organic synthetic approach. -Toward total utilization of woody biomass by interdisciplinary research-

Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Abstract: Studies on the woody biomass constituents by organic synthetic approach toward total utilization of woody biomass by interdisciplinary research are reported: general synthetic method for oligo- and polyphenols and novel selective cleavage method for  $\beta$ -O-4 in the lignin chemistry; chemical synthesis of cellulose and its extended research to the preparation and characterization of Langmuir-Blogett films, cellulosic photocurrent generation thin films in the cellulose chemistry, and syntheses of hydrolysable and condensed tannins and their properties in tannin chemistry.

2008-201

クラフト-アントラキノン蒸解におけるアントラキノン浸透処理の効果

田中潤治<sup>\*1</sup>、大井 洋<sup>\*2</sup>、横山朝哉<sup>\*3</sup>、松本雄二<sup>\*3</sup>

<sup>\*1</sup>川崎化成工業株式会社技術研究所、<sup>\*2</sup>筑波大学生命環境科学研究科、<sup>\*3</sup>東京大学農学生命科学研究科

Effects of anthraquinone compounds impregnation in kraft cooking.

Junji Tanaka<sup>\*1\*3</sup>, Hiroshi Ohi<sup>\*2</sup>, Tomoya Yokoyama<sup>\*3</sup>, Yuji Matsumoto<sup>\*3</sup>

<sup>\*1</sup>Kawasaki Kasei Chemicals Ltd., <sup>\*2</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, <sup>\*3</sup>Graduate School of Agricultural and Life Sciences, The University of Tokyo

Abstract: In order to increase the pulp yield by anthraquinone compounds, it is very important to impregnate anthraquinone compounds efficiently into wood chips. In this report, the effect of impregnation treatment before kraft cooking process was investigated using the laboratory cooking equipments. By measuring 9,10-anthraquinone in the liquor after the impregnation treatment, the impregnation conditions (temperature, time, active alkali charge, and liquor/wood ratio) were optimized. By the employment of the optimized impregnation condition, the pulp yield was improved by about 0.4% when compared at kappa 16.

2008-202

Analysis of lignin by the use of whole wood solution consisting of DMSO-LiCl.

Zhiguo Wang, Tomoya Yokoyama, Yuji Matsumoto

Department of Biomaterials Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo

Abstract: The whole lignin in wood was analyzed by the use of whole wood solution consisting DMSO/LiCl. The wood solution formed gel after standing one day at room temperature.

Concentration of milled wood required for gel formation was dependent on the milling time. The gram absorptivity of lignin at 280nm was obtained by the use of this whole wood solution. The <sup>1</sup>H-NMR spectrum of whole wood solution clearly shows the lignin aromatic part without any interfering overlapping peak. This is the first time to obtain information of aromatic part in whole lignin directly without any kind of isolation treatment.

2008-203

イオン液体処理過程における木材成分の溶出挙動とリグニンの変化

蓮見愛<sup>\*1</sup>、中川明子<sup>\*1</sup>、大井洋<sup>\*1</sup>、岸野正典<sup>\*2</sup>

<sup>\*1</sup>筑波大学大学院生命環境科学研究科、<sup>\*2</sup>北海道立林産試験場

Structural change of lignin during a process of wood components dissolution into ionic liquid.

Ai Hasumi<sup>\*1</sup>, Akiko Nakagawa-izumi<sup>\*1</sup>, Masanori Kishino<sup>\*2</sup>, Hiroshi Ohi<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai,

Tsukuba, Ibaraki 305-8572, Japan, <sup>\*2</sup>Hokkaido Forest Products Research Institute, 1-10 Nishikagura, Asahikawa, Hokkaido 071-0198, Japan

Abstract: Wood meals of *Abies sachalinensis* and three eucalyptus were treated with one of the ionic liquids: 1-n-butyl-3-methylimidazolium chloride ([bmim]Cl). The contents of lignin and carbohydrates in the insoluble fractions were determined. The insoluble fractions were applied to analytical pyrolysis for lignin characterization. The results showed that cellulose dissolved significantly during the [bmim]Cl treatment. The pyrograms of insoluble fraction were quite similar to that of untreated wood. Moreover, the amount of  $\beta$ -O-4 linkage in lignin were slightly decreased by this treatment. Therefore, it showed that chemical characteristics of lignin were hardly changed by the [bmim]Cl treatment.

2008-204

イオン液体中での  $\beta$ -O-4 型リグニンモデル化合物の反応性  
久保智史、山田竜彦、橋田光、菱山正二郎、眞柄謙吾、細谷修二  
森林総合研究所

Reactivity of  $\beta$ -O-4 type lignin model compounds in ionic liquids.

Satoshi Kubo, Tatsuhiko Yamada, Koh Hashida, Shojiro Hishiyama, Kengo Magara, Shuji Hosoya  
Forestry and Forest Products Research Institute. 1 Matsunosato, Tsukuba, Ibaraki

Abstract: Structural stabilities and reactivity of lignin in ionic liquids (ILs) have been examined using lignin model compounds. *Threo* type guaiacylglycerol- $\beta$ -guaiacyl ether (T-GG) was decomposed similarly to [Z] isomer of enol-ether, [Z]-3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol (Z-EE), as *erythro*GG (E-GG), although decomposition rates of E-GG were faster than TLGG. Hardwood type  $\beta$ -O-4 lignin model compounds, *threo*-guaiacylglycerol- $\beta$ -syringyl ether (T-GS) was decomposed rather faster than softwood type  $\beta$ -O-4 lignin model compounds, and nonphenolic model compounds were relatively stable in ILs. These results could be comparable with the structural stability of  $\beta$ -O-4 type lignin model compounds in alkaline conditions, although the reaction mechanisms in ionic liquids have not been elucidated.

2008-205

イオン液体中での木材の反応挙動 - 針葉樹と広葉樹の比較 -  
中村篤史<sup>\*1</sup>、宮藤久士<sup>\*1</sup>、坂志朗<sup>\*1</sup>、植田文雄<sup>\*2</sup>、森みどり<sup>\*2</sup>

<sup>\*1</sup>京都大学大学院エネルギー科学専攻科、<sup>\*2</sup>トヨタ自動車株式会社

Reaction behavior of wood in an ionic liquid - Comparisons between softwood and hardwood -  
Atsushi Nakamura<sup>\*1</sup>, Hisashi Miyafuji<sup>\*1</sup>, Shiro Saka<sup>\*1</sup>, Fumio Ueda<sup>\*2</sup>, Midori Mori<sup>\*2</sup>

<sup>\*1</sup>Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan, <sup>\*2</sup>Vehicle Engineering Group, Toyota Motor Corporation, 1, Toyota-cho, Toyota, Aichi, 471-8572, Japan

Abstract: Reaction behavior of western red cedar (*Thuja plicata*) and beech (*Fagus crenata*) as treated in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) which can dissolve cellulose was investigated. Much residue after [C2mim][Cl] treatment can be obtained from western red cedar, compared to beech. Lignin content in the residues from western red cedar is higher than in that from beech. It is also found that the degradation of lignin occurs by the cleavage of the ether linkage with [C2mim][Cl] treatment.

2008-206

$\beta$ -エーテル型リグニン 2 主体モデル化合物の熱分解における同位体効果  
渡辺敏弘、河本晴雄、坂 志朗

京都大学大学院エネルギー科学専攻科

Kinetic isotope effects in pyrolysis of lignin  $\beta$ -ether model dimers.

Toshihiro Watanabe, Haruo Kawamoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Abstract: From the comparison of the reactivities and the pyrolysis products of lignin  $\beta$ -ether-type dimers between an open-top and a closed ampoule reactors, We have proposed some radical chain reactions starting from the H-abstraction reactions. In this paper, kinetic isotope effects observed in the deuterated dimers are described. Based on the results, possibilities of radical chain reactions in lignin pyrolysis are discussed.

2008-207

木材ガス化におけるセルロース-リグニン間の相互作用

細谷隆史, 河本晴雄, 坂 志朗

京都大学大学院エネルギー科学専攻科

Interactions between cellulose- and lignin-derived pyrolysis products in gasification.

Takashi Hosoya, Haruo Kawamoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Abstract: Interactions between cellulose- and lignin-derived pyrolysis products were studied under gasification conditions ( $N_2/600^\circ C/40-80s$ ). A dual-space closed ampoule reactor was used to eliminate the solid-phase interactions, and careful comparison of the resulting data with those of the pyrolysis of the mixed samples gave some insights into the solid- and vapor-phase interactions separately. As a result, significant interactions were observed which include acceleration of the gasification of cellulose-derived volatiles and the formation of methane and catechols from lignin. These influences are explained with a proposed mechanism, in which the cellulose-derived volatiles act as H-donors while the lignin-derived volatiles (radicals) as H-acceptors.

2008-208

$^{13}C$  標識テトラメチルアンモニウムヒドロキシドを用いた熱分解-メチル化法によるリグニン中の  $\beta$ -O-4 型構造およびシンナミルアルコール末端基の検討

中川明子<sup>\*1</sup>、Timothy R. Filley<sup>\*2</sup>、黒田健一<sup>\*3</sup>

<sup>\*1</sup>筑波大学大学院生命環境科学研究科、<sup>\*2</sup>Purdue 大学、<sup>\*3</sup>九州大学大学院農学研究院

Characterization of  $\beta$ -O-4 and cinnamyl alcohol end units in lignin by  $^{13}C$ -labeled TMAH thermochemolysis.

Akiko Nakagawa-izumi<sup>\*1</sup>, Timothy R. Filley<sup>\*2</sup>, Ken-ichi Kuroda<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennoudai, Tsukuba, Ibaraki, 305-8572, Japan, <sup>\*2</sup>Department of Earth and Atmospheric Sciences, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana 47907, USA, <sup>\*3</sup>Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: To estimate the origins of pyrolysis-methylation products from lignin,  $^{13}C$ -labeled tetramethylammonium hydroxide ( $^{13}C$ -TMAH) thermochemolysis was applied to lignins pre-methylated with diazomethane. Products were monitored by gas chromatography/mass spectrometry. The number of  $^{13}C$  atom incorporated in the products showed that in guaiacyl synthetic lignin (DHP) coniferyl alcohol end units are present in a 7/3 of 4-O-/ $\gamma$ -O-etherified forms, while in Japanese cedar wood they are present in roughly 6/4 ratio. In both lignins,

guaiacylglycerol moieties involving in  $\beta$ -O-4 linkage provided the same amount of 1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane consisting of two isomers (*erythro*- and *threo*-forms) from end units and core units. Although G-DHP provided many dimer products, the cedar provided those in a trace amount.

2008-209

リグニンモデル化合物の間接電解酸化反応

白石匠、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Indirect electrooxidation of lignin model compounds.

Takumi Shiraishi, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: Indirect electrooxidation of lignin model compounds using N-hydroxyphthalimide (NHPI) as a mediator was studied to introduce carbonyl group at  $\alpha$ -position. Monomeric lignin models, 1-(4'-ethoxy-3'-methoxyphenyl)ethanol (1G), 1-(4'-ethoxy-3',5'-dimethoxyphenyl)ethanol (1S) were oxidized to the corresponding carbonyl compounds (2G, 2S) in high yields (over 90%) and high current efficiencies (ca. 90%). In the indirect electrooxidation of dimeric lignin model (4-ethoxy-3-methoxyphenylglycerol- $\beta$ -guaiacyloether (3)),  $\alpha$ -carbonyl dimer (3-hydroxy-1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-propan-1-one (4)) was formed, while 4-O-ethylvanillin was formed in the direct oxidation. These results suggest that NHPI-mediated indirect electrooxidation is an effective method for  $\alpha$ -carbonyl introduction to natural lignin structures.

2008-210

モノリグノール配糖体によるシリングル型 DHP の生成挙動の解析(II) -pH の影響-

飛松裕基、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Mechanistic study of the dehydrogenative polymerization using  $\gamma$ -glycosylated monolignols. II.

-The effect of pH on the formation of syringyl dehydrogenation polymers.

Yuki Tobimatsu, Hiroshi Kamitakahara, Toshiyuki Thkano, Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Abstract: Horseradish peroxidase (HRP)-catalyzed polymerization of syringyl-type monolignol glycoside (iso-S) was carried out in homogeneous aqueous media of different acidity and was monitored by UV spectroscopic and GPC techniques, in order to determine the effect of pH on the formation of syringyl dehydrogenation polymers (S-DHPs). It was found that at lower pH, the S-type quinone methide intermediates (S-QM) were quenched more rapidly to result in more efficient formation of S-DHP. The results for the polymerization of S-alc also support this view. Structural analyses on the S-DHPs demonstrated that the reaction of S-QM with water was promoted at low pH, indicating its higher reactivity than that in neutral media.

2008-211

TOF-SIMS によるリグニン S/G 比顕微分析法の開発

齊藤香織<sup>\*1</sup>、渡連陽子<sup>\*2</sup>、岸本崇生<sup>\*3</sup>、家田真理子<sup>\*1</sup>、勝山さやか<sup>\*1</sup>、松下泰幸<sup>\*1</sup>、今井貴規<sup>\*1</sup>、船田良<sup>\*4</sup>、小池孝良<sup>\*5</sup>、深澤和三<sup>\*5</sup>、福島和彦<sup>\*1</sup>

<sup>\*1</sup> 名古屋大学大学院生命農学研究科、<sup>\*2</sup> 北海道大学北方生物圏フィールド科学センター、<sup>\*3</sup> 富山大学工学部、<sup>\*4</sup> 東京農工大学大学院農学研究科、<sup>\*5</sup> 北海道大学大学院農学研究科

The syringyl/guaiacyl (S/G) ratio of lignin estimated by TOF-SIMS.

Kaori Saito<sup>\*1</sup>, Yoko Watanabe<sup>\*2</sup>, Takao Kishimoto<sup>\*3</sup>, Mariko Ieda<sup>\*1</sup>, Sayaka Katsuyama<sup>\*1</sup>, Yasuyuki Matsushita<sup>\*1</sup>, Takanori Imai<sup>\*1</sup>, Ryo Funada<sup>\*4</sup>, Takayoshi Koike<sup>\*5</sup>, Kazumi Fukazawa<sup>\*5</sup>, Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, <sup>\*2</sup>Field Science Center for Northern Biosphere, Hokkaido University, Sapporo 060-0809, <sup>\*3</sup>Faculty of Engineering, Toyama Prefectural University, Imizu 939-0398, <sup>\*4</sup>Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Fuchu, 183-8509, <sup>\*5</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589

Abstract: The syringyl/guaiacyl (S/G) ratios were estimated by time-of-flight secondary ion mass spectrometry (TOF-SIMS) using lignin model compounds and the transverse section of the xylem of *Acer micranthum*. The result showed that the value of S/G ratios detected by TOF-SIMS and the molar S/G ratios were similar in the spectra of 8-O-4' polymers. In other hands, the S/G ratios calculated in the spectra of monomer and dimer model compounds were much higher than the molar S/G ratios. This result suggests that the estimation of S/G ratio by TOF-SIMS is reliable in lignin polymers. Further experiments were needed to estimate the reliability of S/G ratio calculated in TOF-SIMS spectra.

2008-212

リグニン中の枝分かれ構造の探索 - 非フェノール性ダイベンゾダイオキソシン構造の <sup>1</sup>H-および <sup>13</sup>C-NMR 化学シフトの特徴 -

秋山拓也<sup>\*1</sup>、John Ralph<sup>\*1\*2</sup>

<sup>\*1</sup>US DFRC, <sup>\*2</sup>Univ. Wisconsin

Characteristics in <sup>1</sup>H- and <sup>13</sup>C-NMR chemical shifts of non-phenolic dibenzodioxocin model compounds as branch-points in lignin.

Takuya Akiyama<sup>\*1</sup>, John Ralph<sup>\*1\*2</sup>

<sup>\*1</sup>US Dairy Forage Research Center, USDA-ARS, Dairy Forage Research Center, 1925 Linden Drive West, Madison, WI 53706, USA, <sup>\*2</sup>University of Wisconsin-Madison, Department of Biochemistry, Enzyme Institute, 1710 University Ave., Madison, WI 53726, USA

Abstract: Non-phenolic dibenzodioxocin compounds modelling the 4-O-β-ethers that would be generated following radical coupling with a monolignol were synthesized to explore branch-points in lignin. NMR measurements on acetylated models revealed that the aromatic carbons (C1) attached to the side chain of a dibenzodioxocin had significantly different chemical shifts between phenolic and non-phenolic models ( $\Delta\delta \sim 3.6$  ppm) while the other side chain proton and carbon shifts ( $\alpha$ - and  $\beta$ -positions) were similar. It is suggested that phenolic and non-phenolic dibenzodioxocin models can be distinguished from each other by NMR, particularly via long-range correlation (HMBC) NMR experiments.

2008-213

オイルパーム材のバイオエタノール製造原料としての特性

村井宏輔<sup>\*1</sup>、内田隆一郎<sup>\*1</sup>、大久保篤史<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学府、<sup>\*2</sup>九州大学大学院農学研究院

The characterization of oil palm trunk as a material of bio-ethanol production.

Kousuke Murai<sup>\*1</sup>, Ryuichiro Uchida<sup>\*1</sup>, Atsusi Okubo<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>

Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581 Japan

Abstract: Using some samples cut out vertically and radially from 25 years old *Elaeis guineensis*

(oil palm) trunks, chemical composition was determined. As a result, as higher and innerer the oil palm trunk, the more hot water extractable glucose were observed. The hot water extractable glucose, fructose and sucrose contents of oil palm trunk were roughly estimated as 63, 13 and 11 kg, respectively. Estimated ethanol production per cultivated area was 7.4 kL/ha. The ethanol yields of fermentation of sugar liquors from oil palm wood meals by *Zymomonas mobilis* were almost same as that from glucose solution, so it would appear that there was no fermentation inhibitor in oil palm wood meal.

2008-214

高圧下におけるツヤ酸の水蒸気蒸留とその化学転換

浅井淳子、道家真一、中村宣夫、橋本敬、西谷耕三、棚橋光彦

岐阜大学大学院応用生物科学研究科

Result of the steam distillation and the chemical changes of thujic acid under high-pressure.

Junko Asai, Shinichi Doke, Nobuo Nakamura, Takashi Hashimoto, Kouzou Yoshitani, Mitsuhiko Tanahashi

Graduate School of Applied Biological Sciences, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

Abstract: Thujic acid, known as antibacterial substance, is a component of the essential oil extracted from Western Red Cedar (*Thuja plicata*). Since the structure of thujic acid is unstable, it is expected to undergo chemical transformation easily. Therefore, the chemical transformations of thujic acid under high-pressure steam condition and under UV radiation were observed. By high-pressure steam treatment, thujic acid was transformed into cumic acid and m-cumic acid under acidic condition, while novel compound was produced under basic condition. Furthermore, thujic acid transformed into novel compounds by UV radiation.

2008-215

樹皮の酵素糖化における新規前処理技術の開発

松下泰幸<sup>\*1</sup>、山内一慶<sup>\*1</sup>、小林哲夫<sup>\*1</sup>、加藤雅士<sup>\*1</sup>、古城敦<sup>\*2</sup>、浅田隆之<sup>\*2</sup>、福島和彦<sup>\*1</sup>

<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>王子製紙株式会社

Development of novel pretreatment for enzymatic saccharification of bark.

Yasuyuki Matsushita<sup>\*1</sup>, Kazuchika Yamauchi<sup>\*1</sup>, Tetsuo Kobayashi<sup>\*1</sup>, Masashi Kato<sup>\*1</sup>, Atsushi Furuzyo<sup>\*2</sup>, Takayuki Asada<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya, 464-8601, Japan

<sup>\*2</sup>Oji Paper Co., Ltd., 1-10-6 Shinonome, Koto-ku, Tokyo, 135-8558, Japan

Abstract: In this study, saccharification of bark by enzyme hydrolysis was investigated. To enhance the enzyme accessibility to the polysaccharides in the cell wall, such as cellulose and hemicellulose, hydrothermal pretreatment with carbon dioxide was conducted. The results of the enzyme hydrolysis showed that the monosaccharide yield using pretreated bark reached 36%, whereas that using non-pretreatment sample was about 10%. More than 95% of the generated monosaccharide was glucose. This results suggested that the secondary wall which main component is cellulose hydrolyzed effectively by enzyme. The yield of glucose on the basis of  $\alpha$ -cellulose reaches about 80%.

2008-216

ユーカリ樹皮のリグニン分布と酵素糖化性

高部圭司<sup>\*1</sup>、吉永 新<sup>\*1</sup>、栗野達也<sup>\*1</sup>、福島和彦<sup>\*2</sup>、松下泰幸<sup>\*2</sup>、山内一慶<sup>\*2</sup>、小林哲夫<sup>\*2</sup>、加藤雅士<sup>\*2</sup>、古城 敦<sup>\*3</sup>、浅田隆之<sup>\*3</sup>

<sup>\*1</sup>京都大学大学院農学研究科、<sup>\*2</sup>名古屋大学大学院生命農学研究科、<sup>\*3</sup>王子製紙株式会社

Lignin distribution influences enzyme succharification of bark in *Eucalyptus*.

Keiji Takabe<sup>\*1</sup>, Arata Yoshinaga<sup>\*1</sup>, Tatsuya Awano<sup>\*1</sup>, Kazuhiko Fuknshima<sup>\*2</sup>, Yasuyuki Matsushita<sup>\*2</sup>, Kazuchika Yamauchi<sup>\*2\*3</sup>, Tetsuo Kobayashi<sup>\*2</sup>, Masashi Kato<sup>\*2</sup>, Atsushi Furujo<sup>\*4</sup>, Takayuki Asada<sup>\*5</sup>

<sup>\*1</sup>Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, <sup>\*2</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8501. <sup>\*3</sup>Graduate School of Energy Science, Kyoto University, Kyoto 606-8501. <sup>\*4</sup>Oji Paper Co., Ltd., Research & Development Division, Tokyo 135-8558. <sup>\*5</sup>Oji Paper Co., Ltd., Albany Forestry Research Centre, Albany, WA6331, Australia

Abstract: Inner bark of *Eucalyptus* is composed of sieve tube member, companion cell, phloem parenchyma cell, phloem ray parenchyma cell and phloem fiber. Phloem fiber has a thick secondary wall in which syringyl lignin is accumulated. After the inner bark is exposed to the acidified hot water with CO<sub>2</sub> at 200 degree Celsius, Primary wall of parenchyma cell shows highly swollen structure and secondary wall of phloem fiber has many clefts with a several nanometer width. These cell walls are completely degraded by the treatment with enzymes contained cellulase, xylanase, pectinase and amylase.

2008-217

*Gmelina arborea* と *Swietenia macrophylla* の樹皮から新規フェニルプロパノイド関連成分の単離同定とそれらの抗酸化活性

Syamsul Falah、鈴木利貞、片山健至

香川大学農学部

Chemical constituents from *Gmelina arborea* and *Swietenia macrophylla* bark and their antioxidant activity.

Syamsul Falah, Toshisada Suzuki, Takeshi Katayama

Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795, Japan

Abstract: A new phenylethanoid glycoside, (-)-p-hydroxyphenylethyl[5'''-O-(3,4-dimethoxy-cinnamoyl)-β-D-apiofuranosyl(1''''→6'')]-β-D-glucopyranoside, was isolated from *Gmelina arborea* bark together with tyrosol, (+)-balanophonin, gmelinol, 2,6-dimethoxy-p-benzoquinone, and 3,4,5-trimethoxyphenol. The 3,4,5-trimethoxyphenol exhibited a moderate antioxidant activity. From *Swietenia macrophylla* bark, a new phenylpropanoid-substituted catechin, namely, swietemacrophyllanin [(2R\*,3S\*,7''R\*)-catechin-8,7''-7,2''-epoxy-(methyl 4'',5''-dihydroxyphenyl-propanoate)] was isolated together with catechin and epicatechin. The swietemacrophyllanin had strong antioxidant activity.

2008-P01

担子菌のラッカーゼ遺伝子を導入した組換え植物における雄性不稔の解析

Zannatul Nasrin<sup>\*1</sup>, 吉川海郷<sup>\*1</sup>、園木和典<sup>\*2</sup>、飯村洋介<sup>\*3</sup>、佐藤かんな<sup>\*1</sup>、片山義博<sup>\*1</sup>、梶田真也<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>弘前大学農業生物科学部、<sup>\*3</sup>産業技術総合研究所

Analysis of male sterility in transgenic plants with the chimeric gene for fungal laccase.

Zannatul Nasrin<sup>\*1</sup>, Misato Yoshikawa<sup>\*1</sup>, Tomonori Sonoki<sup>\*2</sup>, Yosuke Iimura<sup>\*3</sup>, Kanna Sato<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Shinya Kajita<sup>\*1</sup>

<sup>\*1</sup>BASE, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan, <sup>\*2</sup>Faculty of Agriculture and Life Science, Hirosaki University. Hirosaki, Aomori 036-8561, Japan, <sup>\*3</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8569, Japan

Abstract: Transgenic tobacco plants with the chimeric gene for fungal laccase exhibited male sterility without any influence of pollen viability. Frequencies of the male sterility in the plants depended on the laccase activities in their anther tissues. Since lignification in endothecium of the

anther tissue is essential for normal dehiscence of the organ to distribute pollen grains, we analyzed lignin characteristics in the tissue. Results from histochemical and wet chemical analyses indicate that lignin contents in the transgenic tissues are unchanged. By contrast, abnormal deposition of flavonoid in epidermis layer of the transgenic anther was revealed by vanillin staining of the anthers. These results suggest that laccase expression does not affect the lignin biosynthesis but does flavonoid deposition in the transgenic anthers.

2008-P02

カバノアナタケ菌 IO-U1 株に感染した 2 種類のシラカンバ幼植物体クローンにおけるフェノール性化合物の沈着とペルオキシダーゼ活性

高島有哉<sup>\*1</sup>、Md. Mababubur Rahman<sup>\*1\*2</sup>、鈴木美帆<sup>\*3</sup>、石栗太<sup>\*3</sup>、飯塚和也<sup>\*3</sup>、吉澤伸夫<sup>\*3</sup>、横田信三<sup>\*3</sup>

<sup>\*1</sup> 東京農工大学大学院農学研究院、<sup>\*2</sup> 京都大学生存圏研究所、<sup>\*3</sup> 宇都宮大学農学部、  
Phenolics deposition and peroxidase activity in two types of Japanese birch plantlet clones infected with *Inonotus obliquus* IO-U1 strain.

Yuya Takashima<sup>\*1</sup>, Md. Mahabubur Rahman<sup>\*1\*2</sup>, Miho Suzuki<sup>\*3</sup>, Futoshi Ishiguri<sup>\*3</sup>, Kazuya Iizuka<sup>\*3</sup>, Nobuo Yoshizawa<sup>\*3</sup>, Shinzo Yokota<sup>\*3</sup>

<sup>\*1</sup>United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology, Fuchu, 183-8509, Japan, <sup>\*2</sup>Current affiliation: Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto 611-0011, Japan, <sup>\*3</sup>Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Japan

Abstract: Two types of Japanese birch clone (Tohoku and No.8) plantlets were used in order to investigate the time-course changes of phenolics deposition and peroxidase activity in Japanese birch (*Betula platyphylla* var. *japonica*) plantlets infected with *Inonotus obliquus* which causes a canker-rot disease of birch tree. In intact and wounded plantlets after 12 hrs of treatments, phenolics deposition was not detected in the both clones. On the other hand, in infected both clones, phenolics deposition was observed in the vessels, wood fibers, and parenchyma cells. In the case of Tohoku clone, peroxidase activity was detected near the infection site after 2 hrs of inoculation, in the vessel cells after 4 hrs, and in the sclerenchyma cells after 30 days.

2008-P03

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株における新規リグニンペルオキシダーゼ高発現株の特性

杉浦立樹<sup>\*1</sup>、山岸賢治<sup>\*2</sup>、平井浩文<sup>\*3</sup>

<sup>\*1</sup> 静岡大学創造科学技術大学院、<sup>\*2</sup> 東北農業研究センター、<sup>\*3</sup> 静岡大学農学部

Properties of novel lignin peroxidase-high expression transformants from *Phanerochaete sordida* YK-624.

Tatsuki Sugiura<sup>\*1</sup>, Kenji Yamagishi<sup>\*2</sup>, Hirofumi Hirai<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*2</sup>National Agricultural Research Center for the Tohoku Region, National Agriculture and Food Research Organization, Fukushima 960-2156, Japan, <sup>\*3</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan

Abstract: In our previous reports, we have cloned YK-LiP1 and YK-LiP2 encoding genes (*ylpB* and *ylpA*, respectively) from *Phanerochaete sordida* YK-624, and constructed homologous expression transformants introducing these genomic DNAs which were regulated by GPD promoter. In the present study, we investigated ligninolytic properties of these transformants, A-11 (*ylpA* transformant) and B-3 (*ylpB* transformant). These transformants A-11 and B-3 showed higher

ligninolytic activity than wild type *P. sordida* YK-624. Moreover, high glucose conversion was observed in the enzymatic saccharification of wood meal which was inoculated with A-11 or B-3, compared with wild type *P. sordida* YK-624. These results suggest that high expression of YK-Lip genes improve ligninolytic activity and selectivity of *P. sordida* YK-624.

2008-P04

白色腐朽菌の菌体外ペルオキシダーゼ反応の局在化について

高野麻理子、中村雅哉、山口宗義

森林総合研究所

Localized extracellular peroxidase reaction of a white-rot fungus *Phanerochaete crassa* WD1694.

Mariko Takano, Masaya Nakamura, Muneyoshi Yamaguchi

Forestry and Forest Products Research Institute, Matsunosato 1, Tsukuba, Ibaraki 305-8687, Japan

Abstract: Distribution of extracellular peroxidase reaction of a white-rot fungus *Phanerochaete crassa* WD1694 was visualized by peroxidase activity staining. The results showed that the extracellular peroxidase reaction of *P. crassa* WD1694 occurred only on the fungal bodies and not in the culture fluids. Further studies about the extracellular peroxidase reaction on the fungal bodies of *P. crassa* WD1694 revealed the occurrence of intense peroxidase reaction at the hyphal tips that lacked fungal slime. Manganese peroxidase and glyoxal oxidase were determined as major enzymes that worked in the peroxidase reaction at the hyphal tips. The significance of the extracellular peroxidase reaction at the hyphal tips on the ligninolytic mechanism of white-rot fungi was discussed.

2008-P05

The pretreatment of corn stover by wood-rotting fungi for the production of bio-ethanol.

Ziqing Gao, Ryuichiro Rondo

Faculty of Agriculture, Kyushu University, Fukuoka, 812-8581, Japan

Abstract: 40 strains of wood-rotting fungi (33 strains of white-rot fungi and 7 strains of brown-rot fungi) were screened for the pretreatment of bio-ethanol production made of corn stover. Cellulase was used for cellulose saccharification from corn stover pretreated by wood-rotting fungi to test the efficiency of pretreatment. As a result, B-2 a strain of brown-rot fungus was selected for corn stover pretreatment. We determine the composition in corn stover pretreated by B-2 fungus. Although the lignin content increased to 28.3% (control: 25.7%), the glucose yield in cellulose saccharification in corn stover pretreated by B-2 was increased by 150%.

2008-P06

糖質結合モジュール(CBM-CFP)融合タンパクを用いた木材酵素糖化前処理物の解析

川久保武<sup>\*1</sup>、親泊政二三<sup>\*1</sup>、渡連崇人<sup>\*1</sup>、本田与一<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>、苅田修一<sup>\*2</sup>

<sup>\*1</sup> 京大生存圏研究所、<sup>\*2</sup> 三重大学大学院生物資源学研究所

Surface analysis of wood biomass pretreated for enzymatic saccharification by carbohydrate binding module (CBM)-cyan fluorescent protein (CFP) complexes.

Takeshi Kawakubo<sup>\*1</sup>, IMasafumi Oyadomari<sup>\*1</sup>, Takahito Watanabe<sup>\*1</sup>, Yoichi Honda<sup>\*1</sup>, Syuichi Karita<sup>\*2</sup>, Takashi Watanabe<sup>\*1</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan, <sup>\*2</sup>Graduate School of Bioresource, Mie University, 1577 Kurima-Machiyacho, Tsu, 514-8507, Japan

Abstract: Carbohydrate binding modules (CBMs) are noncatalytic substrate binding domains of cellulolytic enzymes. Here we used fluorescent labeled recombinant CBMs specific for crystalline

cellulose (CBM3) and non-crystalline cellulose (CBM28) to analyze the complex surfaces of wood tissues pretreated by chemical, thermal and physical methods. Linear correlation between enzymatic saccharification yield and the adsorption of the two CBM-CFP complexes was obtained for the chemically delignified wood. Adsorption of the two CBM-CFP complexes to the physically disrupted wood was much lower than that of the chemically delignified wood. Fluorescent microscopy revealed that CBM-CFP complexes adsorbed preferentially on fibrillated wood tissues but direct adsorption of CBM-CFP complexes on the surface of delignified wood fibers were observed. Thus the quantitative fluorometric method clarified the linear dependency of saccharification yield on exposure of cellulose surfaces in delignified wood.

2008-P07

難揮発性化合物の高圧水蒸気蒸留

中村宣夫、浅井淳子、橋本敬、金原弥生、西谷耕三、棚橋光彦

岐阜大学大学院連合農学研究科

High-pressure steam distillation of nonvolatile compounds.

Nobuo Nakamura, Junko Asai, Takashi Hashimoto, Yayoi Kimpara, Kouzou Yoshitani, Mitsuhiko Tanahashi

Graduate School of Agriculture, Gifu University, 1-1 Yanagido, 501-1193 Gifu, Japan

Abstract: It has been reported that High-pressure steam distillation method allowed distillation of high boiling compounds and nonvolatile compounds which are considered difficult to be distilled. With using this method, thujic acid and hinokitiol were successfully distilled from *Thuja plicata* at the condition of 1.6MPa, 200°C. The aim of this study is to estimate the availability of high-pressure steam distillation method by observing the distillation behavior of model compounds for further application of this method. In this study, curcumin, known as nonvolatile compound, was chosen as model compound. Curcumin was distilled nearly 1000% within 20mins at the condition of 1.6MPa, 200°C.

2008-P08

オルガノソルブリグニンアルキルエステル／ポリ(ε-カプロラクトン)ブレンドの均一混合スケールの評価

寺本好邦<sup>\*1</sup>、李承桓<sup>\*2</sup>、遠藤貴土<sup>\*2</sup>、西尾嘉之<sup>\*1</sup>

<sup>\*1</sup>京都大学大学院農学研究科、<sup>\*2</sup>産業技術総合研究所

Evaluation of size of heterogeneity in blends of poly(ε-caprolactone) with organosolv lignin alkyl esters.

Yoshikuni Teramoto<sup>\*1</sup>, Seung-Hwan Lee<sup>\*2</sup>, Takashi Endo<sup>\*2</sup>, Yoshiyuki Nishio<sup>\*1</sup>

<sup>\*1</sup>Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

<sup>\*2</sup>National Institute of Advanced Industrial Science and Technology (AIST), Biomass Technology Research Center (BTRC), 2-2-2, Hirosuehiro, Kure, Hiroshima 737-0197, Japan

Abstract: Organosolv lignin (OSL) alkyl esters (carbon number  $n$ , 2-5) were synthesized by a homogeneous reaction with different acyl anhydrides/4-dimethylamino pyridine in pyridine solution. The miscibility of the esterified OSLs with poly(ε-caprolactone) (PCL) has been investigated previously, mainly through the evaluation of the glass transition temperature ( $T_g$ ) using differential scanning calorimetry (DSC). DSC analysis has revealed that the blends of OSL esters with  $n = 3-5$  with PCL showed a composition-dependent shift in  $T_g$ . Therefore, the blend systems can be regarded as miscible ones in a scale of  $T_g$ -detection, usually assumed to be less than a couple of tens of manometers. To ascertain the state of miscibility of the blends precisely, they were

investigated by using dynamic mechanical analysis (DMA) and solid-state  $^{13}\text{C}$  CP/MAS NMR. A detailed estimation of the  $T_g$  by DMA revealed that the blends with  $n = 3-5$  shows a single  $T_g$ , which varies with composition. Taking into account the  $T_{1\rho}^H$  estimated by solid-state NMR, it was suggested that the miscible combinations mix on a scale between ca. 5 and 15 nm.

2008-P09

リグニンの表面特性に関する研究

糟谷絵理、福島和彦、今井貴規、松下泰幸

名古屋大学大学院生命農学研究科

Study on surface properties of lignins.

Eri Kasuya, Kazuhiko Fukushima, Takanori Imai, Yasuyuki Matsushita

Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan

Abstract: Lignin chemical structures are known to differ between species, tissues, and regions. The structural heterogeneity of lignin seems to affect its characteristics, and the investigation of such relationship is significant for better utilization of lignin. In present study, the surface properties of lignins were evaluated by inverse gas chromatography (IGC). To compare interspecific difference, we used  $\alpha$ -cellulose coated with milled wood lignin (MWL) prepared from *Pinus densiflora* (Red pine) and *Fagus crenata* (Beech) as sample. By these methods, we determined Lifshitz-van der Waals component of the surface free energy ( $\gamma^w$ ) of each lignin samples.

2008-P10

イオン液体 1-*n*-ブチル-3-メチルイミダゾリウムクロライドを用いて処理されたトドマツ (*Abies sachalinensis*) 木粉の化学的特徴 ~リグニンと糖の関係に関する考察~

岸野正典\*<sup>1</sup>、岸本崇生\*<sup>2</sup>、久保智史\*<sup>3</sup>、山田竜彦\*<sup>3</sup>、折橋健\*<sup>1</sup>、槍山亮\*<sup>1</sup>

\*<sup>1</sup>北海道林産試験場、\*<sup>2</sup>富山県立大学、\*<sup>3</sup>森林総合研究所

Chemical characteristics of *Abies sachalinensis* sawdust treated with an ionic liquid, 1-*n*-butyl-3-methyl-imidazolium chloride. Discussion on relationship between lignin and carbohydrate.

Masanori Kishino\*<sup>1</sup>, Takao Kishimoto\*<sup>2</sup>, Satoshi Kubo\*<sup>3</sup>, Tatsuhiko Yamada\*<sup>3</sup>, Ken Orihashi\*<sup>1</sup>, Ryo Hiyama\*<sup>1</sup>

\*<sup>1</sup>Hokkaido Forest Products Research Institute, Asahikawa, Hokkaido, Japan, \*<sup>2</sup>Faculty of Engineering, Toyama Prefectural University, Imizu, Toyama, Japan, \*<sup>3</sup>Forestry and Forest Products Research Institute, Tsukuba, Ibaraki, Japan

Abstract: We investigated chemical characteristics of the insoluble fraction obtained by treatment of *Abies sachalinensis* sawdust with 1-*n*-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}]\text{Cl}$ ) as one of the ionic liquids (ILs) at 100 and 120°C for periods ranging from 2 to 24h. Galactose contents in the insoluble fraction increase with as lignin contents increase, whereas other monosaccharide contents except for xylose tend to decrease. These results suggest the existence of lignin bonded closely to galactose in hemicellulose as a structure of lignin-carbohydrate complex (LCC) in *Abies sachalinensis* sawdust.

2008-P11

アカシアファイバーのイオン液体 1-*n*-ブチル-3-メチルイミダゾリウムクロライドへの溶解挙動  
谷口僚\*<sup>1</sup>、中川明子\*<sup>1</sup>、大井洋\*<sup>1</sup>、岸野正典\*<sup>2</sup>

\*<sup>1</sup>筑波大学大学院生命環境科学研究科、\*<sup>2</sup>北海道立林産試験場

Dissolution behavior of acacia fiber in 1-*n*-butyl-3-methylimidazolium chloride as an ionic liquid.

Ryo Taniguchi\*<sup>1</sup>, Akiko Nakagawa-izumi\*<sup>1</sup>, Masanori Kishino\*<sup>2</sup>, Hiroshi Ohi\*<sup>1</sup>

\*<sup>1</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8572 Japan, \*<sup>2</sup>Hokkaido Forest Products Research Institute, Hokkaido, 071-0198 Japan

Abstract: To make the selectively dissolving condition of cellulose in wood components during the dissolution in 1-*n*-butyl-3-methylimidazolium chloride ([bmim]Cl) clear, *Acacia mangium* fiber, milled fiber and wood meal were heated in [bmim]Cl. After the treatment for 24 hours at 100°C, the yield of residue from milled fiber, fiber and wood meal were 71, 84 and 88%, respectively. The residue from milled fiber treated with [bmim]Cl decreased with increasing temperature and time. In addition, glucose, which is hydrolyzed by the carbohydrate analysis from, wood materials treated with [bmim]Cl decreased rapidly, although their acid insoluble parts increased. The result indicates that the dissolution rate of carbohydrates such as cellulose in wood components is faster than that of lignin.

2008-P12

リグニン分析法のエーテル結合開裂能の評価 —  $\beta$ -O-4 型人工リグニンポリマーの分解性—  
金澤香枝\*<sup>1</sup>、幸田圭一\*<sup>1</sup>、浦木康光\*<sup>1</sup>、岸本崇生\*<sup>2</sup>

\*<sup>1</sup>北海道大学大学院農学研究科、\*<sup>2</sup>富山県立大学

Quantifiability of ether bond cleavage of lignin analysis method. —Degradability of  $\beta$ -O-4 type artificial lignin polymer—

Yoshie Kanazawa\*<sup>1</sup>, Keiichi Koda\*<sup>2</sup>, Yasumitsu Urak\*<sup>2</sup>, Takao Kishimoto\*<sup>3</sup>

\*<sup>1</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-85 89, Japan, \*<sup>2</sup>Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan, \*<sup>3</sup>Faculty of Engineering, Toyama Prefectural University, Toyama 939-0398, Japan

Abstract: Thioacidolysis and nitrobenzene oxidation are methods for analyzing lignin structure by cleavage of aryl ether linkages in lignin. However, the reaction efficiencies of the cleavage to polymeric materials are not clear yet. In this study, we evaluated thioacidolysis and nitrobenzene oxidation reactivity to cleavage of aryl ether linkages,  $\beta$ -O-4 linkage in particular, by using the artificial lignin polymer, which was comprised of only  $\beta$ -O-4 linkage. The yields of monomeric product by thioacidolysis and nitrobenzene oxidation under the conventional conditions were about 70% and 50%, respectively. These results reveal that these methods incompletely decompose  $\beta$ -O-4 macromolecule.

2008-P13

$\beta$ -O-4 結合の新規な選択的開裂法 —  $\beta$ -phenoxy sulfone elimination method ( $\beta$ -PSE 法)—  
安藤大将、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

New selective stepwise cleavage method for the  $\beta$ -O-4 linkages. — $\beta$ -phenoxy sulfone elimination method—

Daisuke Ando, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: We develop the new selective stepwise cleavage method for the  $\beta$ -O-4 linkages with a quantitative yield carried out under the mild reaction conditions without any side reactions. This degradation method involves basically three reaction steps: 1) Nucleophilic substitution of the  $\gamma$ -primary or  $\alpha$ -secondary hydroxyl group in the  $\beta$ -O-4 structure with inodorous alkylthiol such as C<sub>12</sub>H<sub>25</sub>SH, 2) Oxidation of the thioether to sulfone, and finally 3)  $\beta$ -Elimination of  $\beta$ -phenoxy sulfone under the mild alkaline conditions, *i.e.*, 0.1N-NaOH to produce  $\alpha$ ,  $\beta$ -unsaturated sulfone with spontaneous  $\beta$ -O-4 bond cleavage. This method may be useful especially for the elucidation of

LCC-structures.

2008-P14

*t*-BuOK/*t*-BuOH 系におけるリグニン  $\beta$ -O-4 結合の挙動

竹野甲子夫、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Behavior of lignin  $\beta$ -O-4 bond in *t*-BuOK/*t*-BuOH system.

Kineo Takeno, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: We have focused on *t*-BuOK as a base and investigated the efficiency of the *t*-BuOK/*t*-BuOH system to cleave  $\beta$ -O-4 bond in lignin under mild conditions (0.5 mol/l *t*-BuOK/*t*-BuOH, 30°C) using lignin model compounds, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (VG) and 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (V'G). The results showed that the  $\beta$ -O-4 bonds of VG and V'G are certainly cleaved and 2-methoxyphenol is quantitatively detected from both compounds. This is surprising because much severer conditions (*ca.* 2 mol/l NaOH, >150°C) are commonly required to cleave these bonds in aqueous media. The degradation of both compounds was approximated to pseudo-first-order rate equations, and the rate constants of VG and V'G were 0.0022 and 0.0015 min<sup>-1</sup>, respectively, which shows the faster degradation of VG than V'G and suggests the contribution of the *g*-position of VG to this cleavage reaction. However, wood meal was not delignified well and relatively large amounts of carbohydrates were removed when it was treated in the *t*-BuOK/*t*-BuOH system at the elevated temperature. This result suggests that delignification is not controlled only by potential ability to cleave chemical bonds between lignin subunits but by various topochemical factors.

2008-P15

非木質組織のリグニン定量

戸田守一、中村裕貴、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科木材化学研究室

Determination of lignin content in non-wood tissues and plants.

Morikazu Toda, Yuki Nakamura, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: It has been presumed that Klason method overestimates the lignin content of non-wood tissues or plants, but a method to determine the "true" lignin content of these samples has not been established yet. Our previous studies showed that wood and non-wood are reasonably distinguished by the yields of specific lignin degradation products obtained by nitrobenzene oxidation and ozonation analysis but not by their Klason lignin contents. The yields of these degradation products from non-woods were always lower than a certain level although their Klason lignin content is sometimes extremely high. On the other hand, woods always gave higher values than this certain level. These results suggested that Klason residue obtained from non-woods contain large amount of non-lignin substances. However, one possibility was still remaining; that is the lignin structure of non-wood plants or tissues is rich in condensed type so that these specific degradation products can be given only in small yields. If we can "count" the number of aromatics contained in the Klason residue, we can verify this possibility. For this purpose, we developed a method based on IR absorption and applied to Klason residues of both wood and non-wood samples. It was successfully shown that the number of aromatics in the Klason residue from non-wood was very low compared

with that of woods, and it was corresponding well to the low yield of lignin degradation products from non-wood samples. Further research is conducted to elucidate what are included as non-lignin substances in the Klason residue of non-wood samples.

2008-P16

カシノナガキクイムシによる病傷害を受けたコナラ辺材のリグニン構造

山ぎし崇之、横山朝哉、山田利博、松本雄二

東京大学大学院農学生命科学研究科

Structure of lignin in the sapwood of *Quercus serrata* Thunb. infected by *Platypus Quercivora*.

Takayuki Yamagishi, Tomoya Yokoyama, Toshihiro Yamada, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, Tokyo, Japan

Abstract: When the sapwood of *Quercus serrata* is wounded by an insect of *Platypus Quercivora*, the area surrounding the wounded part is infected by a symbiotic fungi of this insect, *Raffaerea quercivora*, which results in a discoloration of this area. As a defense response of the tree, polymeric substances are secreted at the boundary of this discolored area and normal area. Because these substances are positive to phloroglucinol-HCl colorization reaction, these are often called "lignin-like compounds". In order to analyze the any change caused in lignin structure of discolored area, we prepared samples along several lines that extended to different directions from the center of discolored area, and the change of structure and amount of lignin along these lines were examined. If we can find a clear tendency from the center to outer part beyond the difference of direction, it is reasonably assumed that the change corresponds to the discoloration. According to this strategy, about 20 samples were prepared from different parts in one discolored area, and, Klason lignin determination, nitrobenzene oxidation and ozonation analysis were performed. Even though the difference was not large, a clear tendency was found in the change of Klason lignin content, SN ratio or the total yield of aromatic aldehydes obtained by nitrobenzene oxidation along the lines beyond the difference of direction. We are now looking into in more detail how these difference were created based on the hypothesis that these were initiated by fungal infection.

2008-P17

アカマツ木粉の熱分解生成物の分析～回収留分の定量的検討と熱分解残漆の分析～

錦織香、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Quantitative analysis of pyrolysis products derived from red pine wood meal "liquid products and pyrolysis residue".

Kaoru Nishikior, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural & Life Sciences, the University of Tokyo, 1-1-1, Yayoi, Bunkyo-ku, Tokyo, 113-8657 Japan

Abstract: Red Pine wood meals were pyrolysed by tube type kiln under various conditions and quantitative analysis by GC was performed on the main 18 compounds in the fraction recovered as a liquid pyrolyzate. These determined compounds accounted for only about 10% of all liquid pyrolyzate. Determination of water in this fraction by <sup>1</sup>H-NMR suggested that 60% of the fraction was water.

2008-P18

泥炭を通過した水中に存在するリグニンの研究

勝亦京子\*1、松本雄二\*1、金貞福\*2、飯山賢治\*3

\*<sup>1</sup> 東京大学大学院農学生命科学研究科、\*<sup>2</sup> 浙江林業大学、\*<sup>3</sup> 国際農林水産業研究センター3

Lignin in dissolved organic matter obtained from peat swamp water.

Kyoko S. Katsumata\*<sup>1</sup>, Yuji Matsumoto\*<sup>1</sup>, Zhenfu Jin\*<sup>2</sup>, Kenji Iiyama\*<sup>3</sup>

\*<sup>1</sup> Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi.

Bunkyo-ku, 113-8657 Tokyo, Japan, \*<sup>2</sup> Zhejiang Forestry University, China, \*<sup>3</sup> Japan International Research Center for Agricultural Sciences

**Abstract:** It is well known that lignin is highly resistant against biological attack. Some part of biologically modified lignin in peat would be expected to dissolve in water. In this study, dissolved organic matters (DOM) isolated from water soaked out of Ishikari (Japan) and To Daeng (Thailand) peat swamps were investigated. Well-defined lignin structural features, *e.g.*, products of alkaline nitrobenzene oxidation, methoxyl group, and resonance signals for  $\beta$ -O-4 linkage around 6 ppm in <sup>1</sup>H-NMR spectrum, were hardly detected in DOM. Successive treatment consisting of diazomethane methylation and saponincation suggested that DOM has 0.09–0.14 mol/C mol of acidic hydroxyl groups, among which 0.05–0.08 mol/C mol were unstable to alkali when methylated. Average molecular weight of DOM was at MW 1,600. It was considered that lower part of molecular weight of peat in which much of hydrophilic functional group was introduced by biological modification, was dissolved into water. In <sup>1</sup>H-NMR spectrum of DOM obtained from Ishikari showed weak but clear peak attributable to aromatic proton.

2008-P19

Spectral study on reaction mechanism of etherification of rice straw.

Yu Huang, Linshan Wang, Ying Xing

Department of Chemistry, Northeastern University, China

**Abstract:** Etherification of rice straw with epoxy chloropropane was carried out at 120°C for 1–8h in toluene with NaOH as a base. The extent of etherification was estimated by the use of weight percent gain (WPG) as an indication. FT-IR spectroscopy were used to investigate the changes in composition and structure of rice straw that had been subjected to pretreatment and epoxy chloropropane modification. WPG of epoxy chloropropane modified rice straw increased with reaction time. The increase was first significant with the progress of reaction time, and the increment became slight after 5h. FT-IR analyses of epoxy chloropropane modified rice straws agreed with the well established reaction mechanism of epoxy chloropropane. Namely, two –OH groups of rice straw were replaced by two ether links in the former three steps, and one –OH group generated in propane chain derived from epoxy chloropropane in the fourth step.

## 第 54 回 (2009.10.29–30) 静岡県男女共同参画センター

2009-101

改変型植物酸性 Peroxidase の酵母での発現と精製(3)

吉中喬慈、川合伸也

東京農工大学大学院農学府

Heterogeneous expression and purification of modified plant peroxidase (3)

Kyoji Yoshinaka, Shinya Kawai

Tokyo University of Agriculture and Technology

**Abstract:** Lignin peroxidase of *Phanerochaete chrysosporium* can oxidize the many environmental pollutants and lignin by assuming Trp-171 near the surface of the enzyme of the catalytic site. CWPO-C that is one of popular POXs can oxidize sinapyl alcohol polymers, and is

presumed that Tyr-177 and Tyr-74 exposed to the surface of the enzyme are the catalytic sites. Moreover, the surrounding amino-acid residues of the catalytic sites influenced the specificity of substrates. We introduced the mutations into *prxA3a*, a POX gene of *Populus kitakamiensis*, to change the corresponding amino acid residues at the positions to Trp residue of Lignin Peroxidase and Tyr residues of CWPO-C and to change the surrounding amino acid residues of the catalytic sites, and examined the changes in the substrate specificities.

2009-102

タバコ・ポプラにおける細胞分裂マーカー-*cycB pro::GUS* を利用した維管束形成層の細胞分裂評価

藤井武郎<sup>\*1</sup>、古市孝行<sup>\*1</sup>、松井紀子<sup>\*1</sup>、佐藤かなな<sup>\*1</sup>、梶田真也<sup>\*1</sup>、片山義博<sup>\*1</sup>、西窪伸之<sup>\*2</sup>

<sup>\*1</sup> 東京農工大学大学院生物システム応用科学府、<sup>\*2</sup> 理化学研究所植物科学センター

Analyze of cell division on vascular cambium with the marker *cycBpro::GUS* in tobacco and poplar. Takeo Fujii<sup>\*1</sup>, Takayuki Furuichi<sup>\*1</sup>, Noriko Matsui<sup>\*1</sup>, Kanna Sato<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Nobuyuki Nishikubo<sup>\*2</sup>

<sup>\*1</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 naka-cho, Koganei-city, Tokyo, 184-8588, Japan, <sup>\*2</sup> RIKEN Plant Science Center, 1-7-22 Suehiro-cho, Tsurumi-ku, Yokohama City, Kanagawa, 230-0045, Japan

Abstract: The researches about components of cell wall have been investigated with model plants, for example *Arabidopsis thaliana* or *Oryza sativa*. To keep plant biomass sustainably in 21st century, we indicate that the research should be approached with woody plant. Woody plant has vascular cambium, and show thickening growth and a lot of biomass accumulation. We indicated the regulation of cell division on vascular cambium effects beneficial change about plant biomass production. Therefore, we approached analysis about cell number, cell differentiation, and cell wall formation in vascular cambium. In this work, we have made transgenic tobacco and poplar. First, it is overexpressed cell cycle G1/S phase regulated factor, *cycD2*, E2F, DP, and E2F/DP, and the cambium was enlarged In Only *cycD2* transgenic plant. Second, we approached with cell division marker *cycB1:3pro::GUS* to check cell cycle regulation. As a result, the activity was not secondary meristem we targeted, but primary meristem.

2009-103

イネをモデルとした植物細胞壁形成過程に関する研究 (4) -Glycosyl-phosphatidylinositol-anchored protein はイネの細胞壁高次構造形成にどのように関わるのか? -

伊藤幸子<sup>\*1</sup>、片山義博<sup>\*1</sup>、佐藤かなな<sup>\*1</sup>、鈴木 瑠<sup>\*1</sup>、半 智史<sup>\*2</sup>、船田 良<sup>\*2</sup>、梶田真也<sup>\*1</sup>、北野英己<sup>\*3</sup>

<sup>\*1</sup> 東京農工大学大学院生物システム応用科学府、<sup>\*2</sup> 東京農工大学大学院農学府、<sup>\*3</sup> 名古屋大学生物機能開発利用研究センター

Study of plant cell wall formation in *Oryza sativa* L. (4) -How does glycosylphosphatidylinositol-anchored protein relate to cell wall conformation in rice plant (*Oryza sativa* L.)? -

Sachiko Ito<sup>\*1</sup>, Yoshihiro Katayama<sup>\*1</sup>, Kanna Sato<sup>\*1</sup>, Ryu Suzuki<sup>\*1</sup>, Satoshi Nakaba<sup>\*2</sup>, Ryo Funada<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>, Hidemi Kitano<sup>\*3</sup>

<sup>\*1</sup> Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan, <sup>\*2</sup> Graduate school of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo, 183-8509, Japan, <sup>\*3</sup> Bioscience and Biotechnology Center, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan

Abstract: Previously, we succeeded in isolating a novel mutant *cwa1*, *bc1* allele of *japonica* species of rice, which was likely to be loss-of-function mutations of AtCOBL4 ortholog encoding a putative glycosylphosphatidylinositol (GPI)-anchored COBRA family protein and unable to

synthesize normal secondary walls. The novel rice mutant *cwa1* has lost a regulation of deposition and assembly of cell wall materials to form the architecture of the even pattern of thickening secondary cell wall in the sclerenchymatous cells of rice internodes. So far, the primary function of AtCOBRA is hypothesized to be orienting cellulose microfibrils, presumably through some sort of interaction with the AtCesA complex and microtubules. One hypothesized way of achieving this is through the putative carbohydrate binding module (CBM) present on the AtCOB protein. In rice genome, the BC1 gene encodes a plant-specific GPI-anchored COBRA family protein with a putative CBM. In this study, by 3-amino acid substitution in the putative CBM, we examine the function of putative CBM in cell wall formation process through binding to cell wall matrix carbohydrate.

2009-104

イネ CAD 遺伝子変異体 *gh2* の稲わらの糖化効率

村上真也<sup>\*1</sup>、服部武文<sup>\*1</sup>、向井まい<sup>\*1</sup>、宮尾安藝雄<sup>\*2</sup>、池 正和<sup>\*3</sup>、鈴木史朗<sup>\*4</sup>、徳安 健<sup>\*3</sup>、廣近洋彦<sup>\*2</sup>、坂本正弘<sup>\*5</sup>、梅澤俊明<sup>\*1\*4</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> 農業生物資源研究所、<sup>\*3</sup> 食品総合研究所、<sup>\*4</sup> 京都大学生存基盤科学研究ユニット、<sup>\*5</sup> 京都大学大学院農学研究科地域環境科学専攻

Saccharification degree of lingo-cellulose in rice straw of a cinnamyl alcohol dehydrogenase mutant, *gh2*.

Shinya Murakami<sup>\*1</sup>, Takefumi Hattori<sup>\*1</sup>, Mai Mukai<sup>\*1</sup>, Akio Miyao<sup>\*2</sup>, Masakazu Ike<sup>\*3</sup>, Shiro Suzuki<sup>\*4</sup>, Ken Tokuyasu<sup>\*3</sup>, Hirohiko Hirochika<sup>\*2</sup>, Masahiro Sakamoto<sup>\*5</sup>, Toshiaki Umezawa<sup>\*1\*4</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University. Uji, Kyoto 611-0011,

<sup>\*2</sup>National Institute of Agrobiological Science. 2-1-2 Kannondai, Tsukuba, Ibaraki 305-8602

<sup>\*3</sup>National Food Research Institute. 2-1-12 Kannondai, Tsukuba, Ibaraki 305-8642, <sup>\*4</sup>Institute of Sustainability Science, Kyoto University. Uji, Kyoto 611-0011, <sup>\*5</sup>Graduate School of Agriculture, Kyoto University. Sakyo-ku, Kyoto 606-8502

Abstract: We are attempting the alteration of the cinnamate/monolignol pathway to improve bioethanol production from rice straw. In this study, we focused on cinnamyl alcohol dehydrogenase (CAD). CADs are the enzymes that reduce the *p*-hydroxycinnamaldehydes to the corresponding alcohols. The *brown midrib 1* mutant of maize is known to have low activity of CAD and used as forage crop because of its high digestivity. We found a rice mutant having retrotransposon insertion in a CAD gene. It had lower lignin content in all tissues compared to those of control plants. We investigated the enzymatic saccharification of the plants and found higher degree in the mutant.

2009-105

ゴマの抗酸化リグナンであるセサミノールの生合成経路

藤原利彦<sup>\*1</sup>、小山晴菜<sup>\*1</sup>、小幡昌代<sup>\*1</sup>、塩手直樹<sup>\*1</sup>、川原夏美<sup>\*1</sup>、鈴木利貞<sup>\*1</sup>、片山健至<sup>\*1</sup>、並木満夫<sup>\*2</sup>、田代 亨<sup>\*3</sup>

<sup>\*1</sup> 香川大学農学部、<sup>\*2</sup> 名古屋大学農学部 (名大名誉教授)、<sup>\*3</sup> 千葉大学園芸学部

Biosynthesis of sesaminol, an antioxidant lignan in *Sesamum indicum* seeds.

Toshihiko Fujiwara<sup>\*1</sup>, Haruna Koyama<sup>\*1</sup>, Masayo Obata<sup>\*1</sup>, Naoki Shiote<sup>\*1</sup>, Natsumi Kawahara<sup>\*1</sup>, Toshisada Suzuki<sup>\*1</sup>, Takeshi Katayama<sup>\*1</sup>, Mitsuo Namiki<sup>\*2</sup>, Toru Tashiro<sup>\*3</sup>.

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795, <sup>\*2</sup>Faculty of Agriculture, Nagoya University, Furou-cho, Chikusa, Nagoya, Aichi 464-8601, <sup>\*3</sup>Faculty of Horticulture, Chiba University, 648 Matsudo, Chiba 271-8510

Abstract: Sesame seeds contain sesaminol, a phenolic and antioxidant lignan, with sesamin and sesamolin. However, biosynthetic pathway to sesaminol peculiar to the sesame seeds was unknown.

To clarify the biosynthetic pathway to sesaminol and the related sesame lignans, isolation and identification of sesaminol, minor sesame lignans, and lignan glycosides from the sesame seeds, and enzymatic formation of sesaminol were carried out. Pinoresinol, piperitol, sesamololol, 7-episesaminol, and sesamololol diglucoside were isolated and identified together with sesaminol and sesaminol triglucoside. It was suggested that incubation of sesamin with a microsome fraction from the sesame seeds gave sesaminol.

2009-106

*Phanerochaete chrysosporium* のリグニン分解酵素発現におけるカルモデュリン阻害剤の影響  
阪本鷹行・北浦博法・南 正彦・上田暁生・鈴木一実・入江俊一  
滋賀県立大学大学院 環境科学研究科

Effect of calmodulin inhibitors on the production of ligninolytic enzymes in *Phanerochaete chrysosporium*.

Takaiku Sakamoto, Hironori Kitaura, Masahiko Minami, Akio Ueda, Kazumi Suzuki and Toshikazu Irie  
Department of Environmental Science, The University of Shiga Prefecture

Abstract: Our previous study revealed that the calmodulin (CaM) gene was upregulated during initiation of lignin peroxidases (LiPs) and manganese peroxidases (MnPs) production in *Phanerochaete chrysosporium*. In this study, we investigated effects of CaM inhibitors, trifluoperazine (TFP), W-7 and W-5 on the enzymes production in *P. chrysosporium* to confirm the role and involvement of CaM in the enzyme expression. When the chemicals were added into reaction mixtures including the crude enzymes, W-7 and W-5 didn't influence the enzyme activities, but, unexpectedly, TFP specifically inhibited LiP reaction. When 100  $\mu$ M of W-7 was added into the fungal culture within 72 h of the culture start, the enzyme expression was inhibited. Using a contrast medicine, W-5 instead of W-7, about 50% of the enzyme activities were still observed, which indicates that the inhibition mechanism of W-7 was interaction with CaM. Real time RT-PCR analysis revealed that 12 genes of LiPs and MnPs were transcribed parallel with the enzyme activities under the culture condition and the all genes were inhibited by W-7 at transcription level.

2009-107

土壤から単離した菌類によるクリセンの分解  
アセップ ヒダヤット、伊藤和貴、橘 燦郎  
愛媛大学農学部

Degradation of chrysene by a fungus isolated from soil.

Asep Hidayat, Kazutaka Itoh, Sanro Tachibana

Department of Applied Bioscience, Faculty of Agriculture, Ehime University, 3-5-7 Tarumi,  
Matsuyama, Ehime 790-8566, Japan

Abstract: Chrysene, a polycyclic aromatic hydrocarbon (PAH), is an important class of environmental pollutants because it has been found to have a variety of toxic, mutagenic, and resist biodegradation. The degradation of chrysene in a liquid medium by a fungus isolated from soil is studied. A single strain fungus was found for the best ability to degrade chrysene in an agar medium. This fungus, *Fusarium* sp. F092, was tested to degrade chrysene in both saline and non-saline conditions. Effects of surfactant concentration and agitated culture were also conducted to improve the fungus ability for degradation of chrysene. Salinity level of sea water (35‰) had no significant effect on the degradation of chrysene in both on solid and liquid media. The degradation of chrysene in a liquid medium had improved 1.5 folds when the culture agitated at 120 rpm. Several non-ligninolytic enzymes secreted by a fungus were detected in a liquid medium. The highest activity of 1,2-dioxygenase reached 203.5 U $l^{-1}$  on 30 days and 29.7 U $l^{-1}$  for 2,3-dioxygenase on 40 days.

These results show that *Fusarium* sp. F092 is a potential fungus for bioremediation.

2009-108

白色腐朽菌 *Phlebia* 属菌による有機塩素系農薬の処理

肖 鹏飞<sup>\*1</sup>、森 智夫<sup>\*2</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学府、<sup>\*2</sup>九州大学大学院農学研究院

Biodegradation of organochlorine pesticides by white rot fungi, *Phlebia* genus.

Pengfei Xiao, Toshio Mori, Ryuichiro Kondo

Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: The organochlorine pesticides, dieldrin and heptachlor were used as substrate for degradation experiment by 20 white rot fungi belonging to *Phlebia* genus. *Phlebia acanthosystis*, *Phlebia brevispora* and *Phlebia aurea* were selected based on the degradation ability of dieldrin. Dieldrin was biotransformed to hydroxyl dieldrin and several unidentified metabolites by *Phlebia acanthosystis*, *Phlebia brevispora* and *Phlebia aurea*. Heptachlor was degraded rapidly by almost all of white rot fungi belonging to *Phlebia* genus. The degradation rate of heptachlor was higher than that of dieldrin. Heptachlor epoxide, 1-hydroxychlorodene and 1-hydroxy-2,3-epoxychlorodene were detected as metabolites from the cultures treated by most of *Phlebia* fungi.

2009-109

DDT degradation potential of mushroom waste medium

Adi Setyo Purnomo, Ichiro Kamei, Toshio Mori and Ryuichiro Kondo

Faculty of Agriculture, Kyushu University, Fukuoka, 812-8581, Japan

Abstract: *Pleurotus ostreatus* (Hiratake) had high ability to degrade and mineralize DDT (1,1,1-trichloro 2,2 bis (4-chlorophenyl) ethane) in potato dextrose broth (PDB) medium. *P. ostreatus* also degraded DDT in solid medium higher than *Gloeophyllum trabeum* and *Phanerochaete chrysosporium*. *P. ostreatus* medium before and after mushroom production (waste medium) were used and compared. DDT was degraded 23% and 31% during 4 weeks incubation by *P. ostreatus* medium before and after mushroom production, respectively. Mineralization of <sup>14</sup>C-DDT was also investigated. <sup>14</sup>C-DDT was mineralized 3.2% and 3.4% during 4 weeks incubation by *P. ostreatus* medium before and after mushroom production, respectively. It indicated that waste medium was more effective to degrade DDT. For application purposes, degradation potential in artificial DDT-contaminated soil was also investigated. The waste medium of *P. ostreatus* degraded DDT 40% and 60% during 4 weeks incubation in sterile and un-sterile soils, respectively. DDD (1,1-dichloro-2,2 bis (4-chlorophenyl) ethane) was detected in un-sterile soil, indicated involvement of soil microorganisms. <sup>14</sup>C-DDT was mineralized 3.0% and 4.1% in sterile and un-sterile soil, respectively. These results indicated that mushroom waste medium of *P. ostreatus* is the potential nature source which can be used for bioremediation of DDT.

2009-110

イオン液体 1-*n*-ブチル-3-メチルイミダゾリウムクロライドに対する木材構成成分の反応性

谷口 僚<sup>\*1</sup>、蓮見 愛<sup>\*1</sup>、中川明子<sup>\*1</sup>、大井 洋<sup>\*1</sup>、岸野正典<sup>\*2</sup>

筑波大学大学院生命環境科学研究科、北海道立林産試験場

Reactivity of wood components against an ionic liquid 1-*n*-butyl-3-methylimidazolium chloride.

Ryo Taniguchi<sup>\*1</sup>, Ai Hasumi<sup>\*1</sup>, Akiko Nakagawa-izumi<sup>\*1</sup>, Hiroshi Ohi<sup>\*1</sup>, Masanori Kishino<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, <sup>\*2</sup>Hokkaido forest Products Research Institute)

Abstract: Japanese red pine (*Pinus densiflora*) and Japanese beech (*Fagus crenata*) woods

were treated with one of ionic liquids: 1-*n*-butyl-3-methylimidazolium chloride. *P. densiflora* dissolved more rapidly compared to *F. crenata*, but its tendency was reversed at the end of treatment for 24 hours. After the treatment at 120°C for 72 hours, approximately 70% of glucan in *Acacia mangium* fibers was denatured. Although cellulose was dissolved by the treatment at 120°C for 24 hours, the residue of *A. mangium* fibers kept containing a lignin-carbohydrate complex (LCC). The structure of LCC was estimated a complex of  $\beta$ -O-4 type structural element and xylan. We synthesized an LCC model compound with veratrylglycerol- $\beta$ -syringyl ether and methyl- $\beta$ -D-xylopyranoside to clarify the stability of LCC during the ionic liquid treatment.

2009-111

イオン液体/DMSO 混合溶媒系に於けるリグニンモデル化合物の分解挙動

久保智史、山田竜彦、橋田 光、菱山正二郎、細谷修二

独立行政法人森林総合研究所

Decomposition of a  $\beta$ -O-4 type lignin model compound in the mixed solvent system of ionic liquid and DMSO.

Satoshi Kubo, Tatsuhiko Yamada, Koh Hashida, Shojiro Hishiyama, Shuji Hosoya  
Forestry and Forest Products Research Institute

Abstract: Structural stabilities of phenolic  $\beta$ -O-4 lignin model compounds in the mixed solvent system of ionic liquid and DMSO (IL/DMSO) were examined. Decomposition rate of the model compound, threo-guaiacylglycerol-beta-guaiacyl ether (T-GG), in IL was not significantly affected by the incorporating of 90% of DMSO. However, decomposition of T-GG became gradually slow, if more than 95% of DMSO was incorporated to IL. Enol-ether, one of the primary decomposition products of GG, was also detected in the T-GG decomposition in the IL/DMSO, even in the mixed solvent having very low content of IL (IL/DMSO=0.25/99.75 w/w), although EE was not formed in the pure DMSO. This result suggested that decomposition mechanism of T-GG in pure DMSO was different from that in IL/DMSO.

2009-112

アルカリ処理オゾン酸化クラフトリグニンとアルミニウムとの錯体形成

相見 光<sup>\*1</sup>、栗本康司<sup>\*1</sup>、山内 繁<sup>\*1</sup>、田原 恒<sup>\*2</sup>

<sup>\*1</sup>秋田県立大学木材高度加工研究所、<sup>\*2</sup>独立行政法人森林総合研究所

Formation of a complex with aluminum by ozone-treated kraft lignins and their low molecular weight fragments.

Hikaru Aimi<sup>\*1</sup>, Ko Tahara<sup>\*2</sup>, Yasuji Kurimoto<sup>\*1</sup>, Shigeru Yamauchi<sup>\*1</sup>

<sup>\*1</sup>Institute of Wood Technology, Akita Prefectural University, 11-1 Kaieisaka, Noshiro, Akita 016-0876, Japan, <sup>\*2</sup>Department of Molecular and Cell Biology, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan

Abstract: The formation of a complex with aluminum by low molecular weight compounds and saponified ozone-treated kraft lignins was evaluated based on the decrease in pH of their solutions on the addition of 0.1 M AlCl<sub>3</sub>. Decreases in pH were observed with the solutions containing compounds having adjacent carboxyl groups (oxalic acid), carboxyl/alcoholic hydroxyl groups (glycolic acid), carboxyl/formyl groups (glyoxylic acid), and phenolic hydroxyl groups (protocatechuic acid) on the addition of 0.1 M AlCl<sub>3</sub>. The malonic and phthalic acids, having two carboxyl groups, were also effective. These results show that the compounds were effective in forming complexes with aluminum. This finding corresponds to the fact that aluminum toxicity is reduced by formation of a complex with aluminum, except in phthalic acid. The chemical structures stated above in ozone-treated kraft lignins contribute, at least partly, to the complex with aluminum. The pH of

solutions containing saponified ozone-treated kraft lignins and alkaline-treated kraft lignin decreased more than that without modified kraft lignins on the addition of 0.1 M AlCl<sub>3</sub>, showing that they were effective in forming a complex with aluminum.

2009-特別講演

木材腐朽菌の新たな機能を求めて — 環境浄化と健康増進 —

近藤隆一郎

九州大学大学院農学研究院

Invited Lecture: New functions of wood-rotting fungi –Bioremediation and functional food–  
Ryuichiro Rondo

Faculty of Agriculture, Kyushu University, Fukuoka, Japan

Abstract: Environmental pollutants are a serious concern worldwide because of the hazards they pose to the health of humans and animals. One method that has become increasingly popular for decontamination of the environment has been bioremediation. One of the early reports indicated that lignin-degrading white-rot fungi, as exemplified by *Phanerochaete chrysosporium*, can degrade an extremely diverse group of environmental pollutants. For thousands of years, mushrooms have been known as a source of medicine. In East Asia, the fruiting body of the fungus *Ganoderma lucidum* has been used for centuries. In this presentation, new functions of wood-rotting fungi, bioremediation and functional food, will be discussed.

2009-201

非木質組織のリグニン定量

戸田守一、中村裕貴、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

On the determination of lignin content in non-wood tissues and plants.

Morikazu Toda, Hirotaka Nakamura, Tomoya Yokoyama, Yuji Matsumoto

Wood Chemistry Laboratory, Graduate School of Agricultural and Life Sciences, the University of Tokyo, Japan

Abstract: In previous studies it was clarified that as Klason residue of non-woody tissues contain definite amounts non-lignin substances, Klason method overestimates the lignin content of non-wood tissues or plants. To see the effect of various kind of extraction to lignin measurement, 9 kinds of extractions were carried to ginkgo leaf and zelkova leaf. After pre-extraction, amounts of lignin measured by Klason method and acetyl bromide method were lower than those of non-extracted samples in most case. But it is not sure whether we can use these extractions to other species.

2009-202

アシドリシスにおいて酸の種類が及ぼすリグニン β-O-4 結合開裂機構への影響について

今井貴章、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Effect of kind of acid on the mechanism of the β-O-4 bond cleavage during acidolysis.

Takaaki Imai, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: In the acidolyses of veratrylglycerol-β-guaiacyl ether (VG) using HBr, guaiacol (G) was quantitatively produced on the disappearance of VG, but the formation of a Hibbert's ketone, 1-hydroxy-3-(3,4-dimethoxyphenyl)propan-2-one (HK), started after certain lag time and was not

quantitative. In the HCl system, both G and HK were quantitatively produced. In the H<sub>2</sub>SO<sub>4</sub> system, another Hibbert's ketone, 3,4-dimethoxyphenylacetaldehyde (HK'), was fairly produced with the quantitative formation of G, but only trace amount of HK was detected. By the addition of KBr to the HBr system, the disappearance rate of VG was not affected, but the formation of HK as well as G became quantitative. The addition of KCl to the HBr system did not affect the disappearance rate of VG, but the difference in the formation rates between G and HK become smaller than that in the HBr system without KCl. The addition KBr to the HCl system enhances the disappearance rate of VG and formation rate of G. Consequently, the formation rate of HK was slower than G in this case. In all these cases, the formation of G was almost quantitative, but the reaction rate and probably the reaction mechanisms themselves are greatly affected by the kind and amount of counter anion of the acid.

2009-203

レーザー脱離イオン化法によるリグニンの質量分析

吉岡康一<sup>\*1</sup>、安東大介<sup>\*1</sup>、西村裕志<sup>\*1</sup>、岸本崇生<sup>\*2</sup>、渡邊崇人<sup>\*1</sup>、本田与一<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> 富山県立大学工学部

Mass spectrometry of lignin by laser desorption/ionization.

Koichi Yoshioka<sup>\*1</sup>, Daisuke Ando<sup>\*1</sup>, Hiroshi Nishimura<sup>\*1</sup>, Takao Kishimoto<sup>\*2</sup>, Takahito Watanabe<sup>\*1</sup>, Yoichi Honda<sup>\*1</sup>, Takashi Watanabe<sup>\*1</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, <sup>\*2</sup>Faculty of Engineering, Toyama Prefectural University

Abstract: Synthetic and natural lignins were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and a matrix free-LDI-MS method, named nano-assisted laser desorption/ionization time-of-flight mass spectrometry (NALDI-TOF MS). In the analysis of MALDI with 2,5-dihydroxybenzoic acid as a matrix, peaks originating from various lignin samples, such as, dehydrataion polymer (DHP),  $\beta$ -O-4 type artificial lignin and MWL (milled wood lignin) were detected with high reproducibility. MALDI mass spectra of  $\beta$ -O-4 type artificial lignin were obtained in a high molecular weight area (over m/z 5,000). Close similarity was found between NALDI-MS and MALDI-MS of the lignins. The soft LDI method is useful for the structural analysis of lignin.

2009-204

*p*-ハイドロキシフェニル核をビフェニル骨格に有する新規ジベンゾジオキソシン構造

秋山拓也<sup>\*1</sup>、Hoon Kim<sup>\*2</sup>、Richard A. Dixon<sup>\*3</sup>、John Ralph<sup>\*2</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> ウィスコンシン大学生化学部、<sup>\*3</sup> サミュエルロバーツノーブル財団植物生物学部門

Novel dibenzodioxocin structures involving *p*-hydroxyphenyl units on their biphenyl units.

Takuya Akiyama<sup>\*1</sup>, Hoon Kim<sup>\*2</sup>, Richard A. Dixon<sup>\*3</sup>, John Ralph<sup>\*2</sup>

<sup>\*1</sup>The University of Tokyo, Graduate School of Agricultural and Life Sciences, 1-1-1Yayoi, Bunkyo, Tokyo 113-8657, John Ralph<sup>\*2</sup>University of Wisconsin-Madison, Department of Biochemistry, Enzyme Institute, 1710 University Ave., Madison, WI 53726, USA, John Ralph, <sup>\*3</sup>Plant Biology Division, Samuel Roberts Noble Foundation, Ardmore, OK73401, USA

Abstract: Cross-coupling of monolignols with biphenyl compounds consisting of *p*-hydroxyphenyl (H) and/or guaiacyl (G) moieties, using Ag<sub>2</sub>O, formed dibenzodioxocins. HH-, GH-, and GG-biphenyl types of dibenzodioxocins were found HSQC spectra of H-enriched lignins isolated from C3H deficient alfalfa. Of the three types, the GH-biphenyl type was a major structure. When a GH-biphenyl unit is etherified by 4-O-coupling with another monomer only a single regioisomer is

observed – that in which the G-unit is etherified. The other regioisomer  $\beta$ -O-4-linked on the H unit was not found either in the lignin or in the cross-coupling products.

2009-205

マイクロ波増感触媒反応を利用したバイオリファイナリーシステムの開発

大橋康典、内藤喜之、渡邊崇人、本田与一、渡辺隆司

京都大学生存圏研究所

Development of biorefinery system using microwave-sensitized catalytic reaction system.

Yasunori Ohashi, Yoshiyuki Naito, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 6110011, Japan

Abstract: Recently, increase in oil price caused by fossil fuel depletion and global warming by use of the fuel become serious problem. Therefore bioethanol production from wood, which is the most abundant biomass and distributed worldwide will be developed as an alternative energy resource. Usually sugars obtained from biomass were utilized effectively as resource of many chemicals and polymers. On the other hand, lignin, the second abundant natural polymer has often been burned or discarded without use for chemical resources. Therefore we stated to develop environmentally-benign lignobiorefinery system using microwave-sensitized catalytic reactions.

2009-206

半流通型加圧熱水処理におけるブナリグニンの挙動

山内一慶、Natthanon Phaiboonsilpa、河本晴雄、坂志朗

京都大学大学院エネルギー科学研究科

The behavior of lignin in Japanese beech as treated by semi-flow hot-compressed water.

Kazuchika Yamauchi, Natthanon Phaiboonsilpa, Haruo Kawamoto, Shiro Saka

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi. Sakyo-ku, Kyoto 606-8501, Japan

Abstract: Japanese beech (*Fagus crenata*) wood was treated by two-step semi-flow hot-compressed water (the first step: 230°C/10MPa/15min and the second step: 270°C/10MPa/15min). To study a behavior of lignin during the treatment, water-soluble portion and residue were fractionated and Klason lignin, acid-soluble lignin and alkaline nitrobenzene oxidation products were determined. As a result, about 17wt% on wood basis (64wt% on lignin basis) was found as lignin in water-soluble portion at the first step, while about 4wt% (13wt% on lignin basis) at the second step. In the residue, at the end of the second stage, only 3% of lignin (11wt% on lignin basis) was found. Interestingly, the lignin structures in these fractions were different.

2009-207

スギの半流通型2段階加圧熱水処理におけるスギリグニンの分解

ナッタノン パイブーンズウィルパ、山内一慶、河本晴雄、坂志朗

京都大学大学院エネルギー科学研究科

Decomposition of lignin in two-step semi-flow hot-compressed water treatment of Japanese cedar.

Natthanon Phaiboonsilpa, Kazuchika Yamauchi, Haruo Kawamoto, Shiro Saka

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi. Sakyo-ku, Kyoto 606-8501, Japan

Abstract: Japanese cedar (*Cryptomeria japonica*) was treated by two-step semi-flow hot-compressed water (230°C/10MPa/15min and 280°C/10MPa/30min), and fractionated into water-soluble portion, precipitates and hot-compressed water-insoluble residue. The water-soluble

portion was then extracted by ethyl acetate to obtain ethyl acetate-soluble portion. For the obtained ethyl acetate-soluble portion and precipitates, consisting mainly of lignin-derived products, gel permeation chromatography (GPC) and gas chromatographic-mass spectrometric (GC-MS) analyses were conducted. As a result, GPC analysis revealed that the ethyl acetate-soluble portion contained lignin-derived monomeric, oligomeric and polymeric products, while the products with relatively higher molecular weight were found in the precipitates. GC-MS analysis of the ethyl acetate-soluble portion, on the other hand, elucidated that  $\beta$ -O-4 ether linkage of lignin as well as  $C_{\beta}/C_{\gamma}$  and  $C_{\alpha}/C_{\beta}$  linkages in the propyl sidechain of the C6-C3 units could be cleaved under the condition of hot-compressed water treatment. In addition, the alkaline nitrobenzene oxidation analysis showed a decrease in oxidation products of the hot-compressed water-insoluble residue. This observation clearly confirmed that the cleavage of the ether linkage of lignin was preferably taken place in the present hot-compressed water treatment.

2009-208

木材熱分解における針葉樹、広葉樹リグンの挙動

モハメド・アスマディ, 河本晴雄, 坂 志朗

京都大学大学院エネルギー科学研究科

Pyrolysis behaviors of softwood and hardwood lignins in wood pyrolysis.

Mohd Asmadi, Haruo Kawamoto, Shiro Saka

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Abstract: Pyrolysis behaviors of Japanese cedar (*Cryptomeria japonica*, a softwood) and Japanese beech (*Fagus crenata*, a hardwood) milled wood lignins were studied with thermogravimetry (TG) and pyrolysis in an ampoule reactor ( $N_2/600^\circ C/40-600s$ ). Guaiacol and syringol were also used to understand the behaviors of the guaiacyl- and syringyl-types of aromatic rings in lignin, respectively. As a result, the following results were obtained; 1) DTG peak temperature: lower in beech, corresponding to the low-temperature shoulders of cedar and beech wood samples, 2) devolatilization efficiency: beech > cedar, 3) coke formation: beech > cedar, 4) tar composition: similar after long heating time. Some of these features are explained with the different pyrolysis behaviors of guaiacol and syringol.

2009-209

Relationships between hemicellulose composition and lignin structure in hardwoods.

Yu Huang<sup>\*1\*1</sup>, Linshan Wang<sup>\*2</sup>, Yuesheng Chao<sup>\*2</sup>, Deded Sarip Nawawi<sup>\*3</sup>, Takuya Akiyama<sup>\*1</sup>, Tomoya Yokoyama<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>

<sup>\*1</sup>Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>School of Sciences, Northeastern University, China, <sup>\*3</sup>Bogor Agricultural University, Indonesia

Abstract: The composition and the absolute amount of neutral sugars were determined for 48 hardwood species (including 17 hardwoods of genus *Acacia*, 14 hardwoods of genus *Eucalyptus* and 17 hardwoods of different other genus) by aldito1-acetate method, and their relationships to the syringyl ratio ( $S/(S+V)$ ) of lignin, which was determined by nitrobenzene oxidation, was investigated. It was suggested that it is hemicellulose but not cellulose that changes with certain tendency in the conjugation with the change of lignin structure. The relationships between syringyl ratio and characteristic peak area ratios of aromatic ring in IR spectrum were also studied.

2009-210

炭水化物 C-2 位に対する活性酸素種の反応性の評価

中川明彦、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科生物材料科学専攻木材化学研究室

Evaluation of the reactivity of active oxygen species toward the C-2 position of carbohydrate.

Akihiko Nakagawa, Tomoya Yokoyama, and Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: The reactivity of active oxygen species (AOS) toward carbon-hydrogen bonds at the C-2 positions of carbohydrate was examined using methyl  $\beta$ -D-glucopyranoside (MGP), methyl  $\beta$ -D-mannopyranoside (MMP  $\beta$ ), and methyl  $\beta$ -D-(2-<sup>2</sup>H)glucopyranoside (MGP  $\beta$ -2D). In this study, AOS were *in situ* generated by subjecting phenolic compounds, 2,4,6-trimethylphenol (TMPH) and 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, VA), to the oxygen oxidation. MMP  $\beta$  was degraded greater than MGP  $\beta$  when they were treated together in the presence of each phenolic compound, which suggests that the stereo configurational difference in their C-2 positions has a certain effect on their reactions with AOS. The degradations of the carbohydrate model compounds seemed to be slightly but clearly dependent on kind of AOS origin. In the absence of the phenolic compounds, MMP  $\beta$  was degraded slightly in the oxygen alkaline treatment although MGP  $\beta$  was stable in the same system, suggesting that the stereo configuration at the C-2 position has an influence on the lability to oxygen oxidation.

2009-211

Dissolution of ethylenediamine pretreated high kappa pulp in LiCl/DMSO.

Zhiguo Wang, Tomoya Yokoyama, Yuji Matsumoto

Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo

Abstract: Various hardwood and softwood chemical pulps, including those with relatively high lignin content (up to ca.10.5%), were completely dissolved without milling in LiCl/DMSO after a pretreatment with ethylenediamine (EDA). Because the milling of the sample is not required, degradation of cell wall components caused by milling does not take place. After the EDA pretreatment, the crystallinity of pulps were found to be kept as high as the corresponding original pulps although the crystal structure was changed. It is the first time that transparent solutions of underivatized pulps with high lignin content were obtained in a simple organic solvent system. Formation of pulp-EDA complex with proper EDA ratio seems to be critical for the dissolution in LiCl/DMSO. The NMR spectrum of EDA treated pulp solution provided good resolution even though the DP of cellulose in the pulp is very high.

2009-212

ポリサルファイド蒸解と修正蒸解の最適な組み合わせに関する検討

渡部啓吾<sup>\*1</sup>、清水正裕<sup>\*1</sup>、黒須一博<sup>\*1</sup>、南里泰徳<sup>\*1\*2</sup>、大井 洋<sup>\*3</sup>

<sup>\*1</sup> 日本製紙株式会社技術研究所、<sup>\*2</sup> 株式会社日本紙パルプ研究所、<sup>\*3</sup> 筑波大学大学院生命環境科学研究科

Application of new cooking system using highly concentrated polysulfide to modified cooking with multi charges of cooking liquor.

Keigo Watanabe<sup>\*1</sup>, Masahiro Shimizu<sup>\*1</sup>, Kazuhiro Kurosu<sup>\*1</sup>, Yasunori Nanri<sup>\*1\*2</sup>, Hiroshi Ohi<sup>\*3</sup>

<sup>\*1</sup>Nippon Paper Industries Co., LTD, 5-21-1 Oji, Kita-ku, Tokyo, Japan, <sup>\*2</sup>Japan Pulp and Paper Research Institute, Inc., <sup>\*3</sup>Graduate School of Life and Environmental Science, University of Tsukuba, 1-1-1, Tennoudai, Tsukuba, Ibaraki, Japan

Abstract: Polysulfide cooking is one of the most efficient technologies to increase pulp yields. The polysulfide has to be produced from white liquor (WL) to keep the  $\text{Na}^+$  and  $\text{S}^{2-}$  balance in the WL recovery cycle. When we try applying the polysulfide to iso-thermal cooking (ITC), not only NaOH but also  $\text{Na}_2\text{S}$  at a start of the cooking are diluted by sequential charges of cooking liquor. Therefore, a new electrolysis method of WL has been developed to produce the polysulfide efficiently. In this study, the combinatorial use of ITC and polysulfide cooking were evaluated, expecting a process in which the mill scale pilot electrolyzers were installed.

2009-213

硫酸リグニンを原料としたポリエステル合成

松下泰幸<sup>\*1</sup>、猪又豊生<sup>\*1</sup>、高木康雄<sup>\*2</sup>、長谷川達也<sup>\*3</sup>、福島和彦

<sup>\*1</sup>名古屋大学大学院生命農学研究科、<sup>\*2</sup>名古屋市工業研究所、<sup>\*3</sup>名古屋大学エコトピア科学研究所

Synthesis of polyester using sulfuric acid lignin.

Yasuyuki Matsushita<sup>\*1</sup>, Toyoki Inomata<sup>\*1</sup>, Yasuo Takagi<sup>\*2</sup>, Tatsuya Hasegawa<sup>\*3</sup>, Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, <sup>\*2</sup>Nagoya municipal Industrial Research Institute, 3-4-41 Rokuban, Atsuta-ku, Nagoya 456-0058, <sup>\*3</sup>EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601

Abstract: In this study, polyesters were synthesized using sulfuric acid lignin. First, sulfuric acid lignin was converted into water-soluble polymer (HSAL) by hydrothermal reaction under alkali condition. H-SAL was introduced carboxyl group during the hydrothermal reaction and the acid-type HSAL (-COOH) could be dissolved into  $\epsilon$ -caprolactone. The polyesters were synthesized using the acid-type H-SAL and  $\epsilon$ -caprolactone with varying ratio of them. The prepared polyesters with high H-SAL content exhibited the swellability in organic solvent. The thermal properties of the prepared polyesters were measured by DSC. From the results, an endothermal peak, which corresponds to the crystalline fusion of the polycaprolactone (PLA) segment was shifted at lower temperature and the area was smaller with increase the H-SAL content in the polymer.

2009-214

リグノスルホン酸/ピロリドン環含有ポリマー複合体の調製と吸着機能材料としての応用

仲西雄亮、寺本好邦、西尾嘉之

京都大学大学院農学研究科

Abstract: Preparation of lignosulfonic acid/polymer containing pyrrolidone rings and application to absorbents

Yusuke Nakanishi, Yoshikuni Teramoto, and Yoshiyuki Nishio

Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

abstract: In order to utilize lignosulfonic acid (LSA) as absorbents of bio-related substances, LSA-containing composites were prepared by (a) immersion of polyvinylpyrrolidone or cellulose acetate (CA)/poly(N-vinyl pyrrolidone) (PVP) complex in a LSA solution and (b) re-precipitation from a solution of CA/PVP/LSA mixture. Chemical compositions of the products were successfully determined by FT-IR measurements. LSA was effectively incorporated into the composites via hydrogen bonding with vinylpyrrolidone unit. An adsorption property of the composites to catch nicotine was evaluated with Freundlich and Langmuir models, revealed the occurrence of a strong interaction between LSA and nicotine especially in the composites prepared by (a).

2009-215

リグニンスルホン酸塩及び芳香族エポキシ化合物を原料とするエポキシ樹脂の合成と熱的性質  
廣瀬重雄<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup>産業技術総合研究所・環境化学、<sup>\*2</sup>リグノセルリサーチ、<sup>\*3</sup>福井工業大学工学部

Synthesis and thermal properties of epoxy resins derived from sodium ligninsulfonate and aromatic epoxy compound.

Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>, Hyoue Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Research Institute for Innovation in Sustainable Chemistry' AIST, Central 5, 1-1-4 Higashi, Tsukuba, Ibaraki 305-8565, Japan, <sup>\*2</sup>Lignocel Research Ltd., Fukui-City, Fukui, 910-3558 Japan, <sup>\*3</sup>Fukui University of Technology, 3-6-1 Gakuen, Fukui-City, Fukui 901-8505, Japan

Abstract: Sodium ligninsulfonate (LS) was dissolved in ethylene glycol (EG) and the obtained mixture was allowed to react with succinic anhydride in order to obtain a mixture of ester-carboxylic acid derivatives (LSEG polyacid, LSEGPA). EGPA was also synthesized from EG. LSEGPA was allowed to react with phthalic acid diglycidyl ester (PhADGE) in the presence of a catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[ACID] ratios, mol/mol) was maintained at 1.0. The contents of LSEGPA in the mixture of LSEGPA and EGPA (LSEGPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures ( $T_g$ 's) of epoxy resins increased with increasing LSEGPA contents, suggesting that lignin acts as a hard segment in epoxy resin polymer networks. Thermal decomposition temperatures ( $T_d$ 's) of epoxy resins were almost constant regardless of LSEGPA contents.

2009-216

リグニン由来エポキシ樹脂の合成とその応用

香川博之<sup>\*1</sup>、岡部義昭<sup>\*1</sup>、中村嘉利<sup>\*2</sup>、佐々木千鶴<sup>\*2</sup>、高橋昭雄<sup>\*3</sup>

<sup>\*1</sup>日立製作所材料研究所、<sup>\*2</sup>徳島大院ソシオテクノサイエンス研究部、<sup>\*3</sup>横浜国立大大学院工学研究  
院

Synthesis of lignin-derived epoxy resin and its application

Hiroyuki Kagawa<sup>\*1</sup>, Yoshiaki Okabe<sup>\*1</sup>, Yoshitoshi Nakamura<sup>\*2</sup>, Chizuru Sasaki<sup>\*2</sup>, Akio Takahashi<sup>\*3</sup>

<sup>\*1</sup>Material Research Laboratory, Hitachi, Ltd., <sup>\*2</sup>Department of Biological Science and Technology Institute of Technology and Science, The University of Tokushima Graduate School, <sup>\*3</sup>Department of Advanced Materials Chemistry, Yokohama National University

Abstract: We have tried to apply epoxy resin derived from woody lignin to copper-clad laminates and printed-circuit boards. Lignin (L) and lignophenol (LP), which was lignin derivatives extracted by phenol from wood, were successfully converted to organic-solvent-soluble epoxidized-lignin (EL) and epoxidized-lignophenol (ELP) by using tetramethyl ammonium hydroxide. EL and ELP as epoxy resins, L and LP as hardeners were applied to copper-clad laminates. Glass transition temperatures of lignin-derived epoxy resin hardeners were over 200 degrees C, and higher than those of commercially available epoxy resin hardeners that were derived from oil. The properties of copper-clad laminates using lignin-derived epoxy resin hardeners were almost the same as those of commercially available laminates.

2009-P01

豪雪地帯に生育する樹木の根元曲がり材の主成分について

小林慧、唐田信吾、芦谷竜矢、高橋孝悦

山形大学農学部

Chemical composition of basal bending wood in heavy snowfall region.

Kei Kobayashi, Shingo Karata, Tatsuya Ashitani, Kouetsu Takahashi

Faculty of Agriculture, Yamagata University,

Abstract: Basal bending of trees was formed by snow pressure in the snowfall region. We analyzed chemical composition of normal and basal bending Sugi (*Cryptomeria japonica* D. Don) wood. As a result, lignin contents of basal bending wood were higher than normal wood, holocellulose contents of normal wood were higher than basal bending wood. In eccentric thickening growth part of basal bending wood, range of lignin and holocellulose contents were similar to normal wood. It was suggested that the basal bending part, except compression wood, was normal type growth.

2009-P02

ハンゲショウにおける 9,9'-デオキシ型ネオリグナンおよびリグナンの立体化学と生合成

牧野啓輔、片山健至、鈴木利貞

香川大学農学部

Stereochemistry and biosynthesis of 9,9'-deoxy-neolignans/lignans by *Saururus chainensis*.

Keisuke Makino, Takeshi Katayama, Toshisada Suzuki

Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795, Japan

Abstract: 9,9'-Deoxy-lignans/neolignans have been isolated and identified in mainly Myristicaceae or Lauraceae plants. However, their biosynthesis is unknown. The present report describes stereochemistry and biosynthesis of  $\Delta 8'$ -4,7-dihydroxy-3,3'-dimethoxy-8-O-4'-neolignan, whose *erythro* and *threo* isomers are named as Machilins C and D, respectively, in *Saururus chainensis*, that is, (1) dehydrogenative polymerization of isoeugenol with horseradish peroxidase and H<sub>2</sub>O<sub>2</sub> (*erythro* : *threo* = 16 : 84), (2) isolation of the 9,9'-deoxy-8-O-4' neolignans from the root of *S. chainensis* (4 : 96), (3) dehydrogenative polymerization of isoeugenol with a cell-free extract from *S. chainensis* and H<sub>2</sub>O<sub>2</sub> (14 : 86). The diastereomeric ratios of the 9,9'-deoxy-8-O-4'-neolignan are shown in parentheses. A peroxidase activity in *S. chainensis* gave Machilin C and Machilin D, but the ratio of the latter to the former is the same as the case in horseradish peroxidase (1). However, the ratio in the neolignan from the plant (3) is larger than the above ratios in (1) and (2). Therefore, the presence of a specific Machilin D synthase was suggested.

2009-P03

シラカンバ No. 8 幼植物体におけるカバノアナタケ菌 IO-U1 株感染部位縦断面でのフェノール性化合物の堆積及びペルオキシダーゼ活性の経時変化

鈴木美帆<sup>\*1</sup>、高島有哉<sup>\*2</sup>、石栗 太<sup>\*1</sup>、飯塚和也<sup>\*1</sup>、吉澤伸夫<sup>\*1</sup>、横田信三<sup>\*1</sup>

<sup>\*1</sup>宇都宮大学農学部、<sup>\*2</sup>東京農工大学大学院農学研究院

Time-course changes in accumulation of phenolic compounds and peroxidase activity in the longitudinal sections from *Betula platyphylla* var. *japonica* No. 8 plantlets infected with *Inonotus obliquus* IO-U1 strain.

Miho Suzuki<sup>\*1</sup>, Yuya Takashim<sup>\*2</sup>a, Futoshi Ishiguri<sup>\*1</sup>, Kazuya Iizuka<sup>\*1</sup>, Nobuo Yoshizawa<sup>\*1</sup>, Shinzo Yokota<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Tochigi, Japan, <sup>\*2</sup>United Graduate School of Agricultural Science, Tokuyomi University of Agriculture and Technology, Fuchu 183-8509, Japan

Abstract: It is well known that *Inonotus obliquus* is a fungus causing canker disease of birch trees. Purpose of this study is to clarify the defense mechanisms of *Betula platyphylla* plantlets against infection with *I. obliquus*. Time-course changes in accumulation of phenolic compounds and peroxidase activity were observed in the longitudinal sections from birch plantlets. The accumulation

of phenolic compounds and peroxidase activity were found in both wounded and infected plantlets, especially they were prominent in the infected plantlets. In the infected plantlets, the accumulation of phenolic compounds and peroxidase activity were observed in the vessels located above and below the infected portion. These results suggest that phenolic compounds might be polymerized by the peroxidases, forming barrier to protect the vessels from invasion of the fungal hyphae.

2009-P04

木材腐朽担子菌におけるシトクロム P450 分子種の多様性

井手正迪<sup>\*1</sup>、一瀬博文<sup>\*2</sup>、割石博之<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学府森林資源科学部門生物資源化学分野、<sup>\*2</sup>九州大学大学院農学研究院森林資源科学部門生物資源化学分野

The diversity of cytochrome P450 of wood-rotting basidiomycetes.

Masamichi Ide<sup>\*1</sup>, Hirofumi Ichinose<sup>\*2</sup>, Hiroyuki Wariishi<sup>\*2</sup>

<sup>\*1</sup>Graduate School of Bioresource and Bioenvironmental Sciences, Department of Forest and Forest Products Sciences, Kyushu University; <sup>\*2</sup>Faculty of Agriculture, Department of Forest and Forest Products Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: We explored the molecular diversity of cytochrome P450 (P450) in the brown-rot fungus *Postia placenta* using bioinformatic and experimental approaches. Based upon bioinformatic survey, 325 putative coding sequences of cytochrome P450s were discovered from the genome database. To facilitate molecular and functional diversities of *P. placenta* P450s (PpCYPs), we attempted to isolate and characterize cDNAs using RT-PCR. To date, we confirmed the gene expression of 157 PpCYPs and cloned 123 PpCYPs as full-length cDNAs encoding a mature open reading frame. In addition, phylogenetic analysis was done suggesting that white-rot and brown-rot basidiomycetes have been developed through vigorous evolution of P450s to meet their unique metabolic diversities.

2009-P05

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株リグニン分解関連酵素遺伝子のクローニング及び発現解析

三隅健太<sup>\*1</sup>、杉浦立樹<sup>\*2</sup>、山口真也<sup>\*1</sup>、平井浩文<sup>\*1</sup>

<sup>\*1</sup>静岡大学農学部、<sup>\*2</sup>静岡大学創造科学技術大学院

Cloning and transcriptional analysis of genes which are involved in the lignin degradation by *Phanerochaete sordida* YK-624.

Kenta Misumi<sup>\*1</sup>, Tatsuki Sugiura<sup>\*2</sup>, Shinya Yamaguchi<sup>\*1</sup>, Hirofumi Hirai<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan. <sup>\*2</sup>Graduate School of Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan

Abstract: Genes of 5-aminolevulinic acid synthase (ALAS) and 1,4-benzoquinone reductase (BQR) were cloned from hyper lignin-degrading fungus *Phanerochaete sordida* YK-624. ALAS gene from *P. sordida* YK-624 (*PsALAS*) showed highest identity (93.0%) with ALAS from *Phanerochaete chrysosporium* ME-446. BQR gene from *P. sordida* YK-624 (*PsBQR*) showed highest identity (93.1%) with the predicted BQR coding gene in genomic sequence of *P. chrysosporium* RP78 which has been named as e\_gwh2.5.446.1. The expression of *PsALAS* showed significant correlation with the production of ligninolytic peroxidases such as manganese peroxidase and lignin peroxidase. The expression of *PsBQR* was strongly induced by the addition of vanillin.

2009-P06

The enhancement of cellulose saccharification in corn stover by pretreatment with brown-rot fungi.

Ziqing Gao, Ryuichiro Kondo

Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University,  
6-10-1 Hakozaki, 812-8581, Japan

Abstract: *Gloeophyllum trabeum* KU-41 was chosen for corn stover pretreatment for bio-ethanol production. Alditol acetate method was used to determine the changes of sugar content in corn stover pretreated by *G. trabeum* KU-41. The content of xylan has been decreased by 25% in comparison to the control. For cellulose crystallinity determination by X-ray diffraction, the crystallinity in corn stover pretreated didn't change significantly compared to the control. The activity of xylanase secreted by *G. trabeum* KU-41 was much higher than that of other *G. trabeum* strains. Xylan was degraded and hemicellulose might be disentangled during the pretreatment

2009-P07

パラコッカス属細菌による黒液リグニンの分解と分解産物の定性

平田真寛<sup>\*1</sup>、高木博子<sup>\*1</sup>、本田宗央<sup>\*1</sup>、松下泰幸<sup>\*2</sup>、福島和彦<sup>\*2</sup>

<sup>\*1</sup>イビデン株式会社、<sup>\*2</sup>名古屋大学大学院生命農学研究科

Biodegradation of black liquor lignin and identification of degradation products by *Paracoccus*.sp..

Masahiro Hirata<sup>\*1</sup>, Hiroko Takagi<sup>\*1</sup>, Munetaka Honda<sup>\*1</sup>, Yasuyuki Matusita<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*2</sup>

<sup>\*1</sup>IBIDEN Co.,Ltd, <sup>\*2</sup>Graduate School of Bioagricultural Science, Nagoya University, Nagoya 464-8601, Japan

Abstract: In this study, we isolated a lignin degradation bacterium from IBIDEN activated sludge. The bacterium was identified as *Paracoccus* species by the 16s rDNA genetic analysis. *Paracoccus* sp. was degraded black liquor lignin to some products with a liquid shaking culture for 7 days at 30°C. Low molecular aromatic compounds such as salicylic acid, 2,3-dihydroxybenzoic and 3,4-dihydroxybenzoic acid were detected in a bacterium treated sample with GC/MS. In our results, there is a possibility of efficiency biotechnology refinery of black liquor lignin by bacteria.

2009-P08

白色腐朽菌由来の粗酵素を用いたアゾ染料の分解

大森元樹、伊藤和貴、橘 燦郎

愛媛大学農学部

Degradation of azo dyes with a crude enzyme from white rot fungi.

Motoki Omori, Kazutaka Itoh, Sanro Tachibana

Department of Applied Bioscience, Faculty of Agriculture, Ehime University

3-5-7 Tarumi, Matsuyama, Ehime 790-8566, Japan

Abstract: To purify effluents from textile industries and so forth, degradation of three azo dyes, Reactive Red 4 (RR4), Reactive Black 5 (RB5) and Reactive Green 19 (RG19) by a crude enzyme from a white-rot fungus, PL1 was conducted. Degradation rate of the dyes by the enzyme was about 10 to 20%. To enhance the degradation rate, effects of pH, hydrogen peroxide and manganese sulfate concentrations, and mediators on degradation of the dyes were investigated. Using the optimum reaction conditions found, degradation of the dyes by the enzyme was further conducted. It was found that 90 to 95% of each dye could be degraded for within 24 hours by the enzyme.

2009-P09

白色腐朽菌由来の酵素による1-ニトロピレンの分解

木村 萌、河合真吾、西田友昭

静岡大学農学部

Degradation of 1-nitropyrene by enzymes from white rot fungi.

Megumi Kimura, Shingo Kawai, Tomoaki Nishida

Department of Environment and Forest Resources Science, Faculty of Agriculture, Shizuoka University

**Abstract:** Nitropolycyclic aromatic hydrocarbons (NPAHs) are a widely distributed class of environmental contaminants which can be formed in the atmosphere by reaction of nitrogen oxides with polycyclic aromatic hydrocarbons. In the present study, 1-nitropyrene, one of NPAHs was treated with each two ligninolytic enzymes, laccase (Lac) and manganese peroxidase (MnP) prepared from the culture of white rot fungi. The Lac-HBT (1-hydroxybenzotriazole) system in the presence of Tween 80 decreased 1-nitropyrene by 30% after 24 h of treatment, however, Lac-HBT system in the presence of Tween 20 did it only by 10%. On the other hand, MnP in the presence of Tween 80 (MnP-Tween 80) decreased 1-nitropyrene by 50% after 24 h of treatment. These results indicate that, among the three enzymatic treatments, MnP-Tween 80 is most effective in removing 1-nitropyrene.

2009-P10

Separation of wood cell components by the use of two dissolving procedures, "ball-milling and dsdsolution in LiCl/DMSO" and "EDA-treatment and dissolution in LiCl/DMSO".

Zhiguo Wang, Tomoya Yokoyama, Yuji Matsumoto

Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo

**Abstract:** The different fractions of wood cell components were separated by the dissolution of wood meal in lithium chloride/dimethyl sulfoxide (LiCl/DMSO). By putting milling pretreated wood meal in to DMSO containing different amount of LiCl, series of soluble fractions and residual fractions can be obtained. The lignin in the residual fractions has always higher syringyl ratio ( $S/(S+V)$ ) and higher yield of nitrobenzene oxidation products ( $S+V$ ) than that of corresponding soluble fractions. However, lignin in the soluble fractions, which was separated from ethylenediamine (EDA) pretreated wood meals had more non-condensed type than residual fractions. Both the yield of  $S+V$  and the ratio of  $S/(S+V)$  of soluble fraction from EDA pretreated wood were higher than those of residual fraction. Characteristic carbohydrates found in the most difficult parts to be dissolved in milling pretreated wood meals were hemicelluloses rather than cellulose. Contrary, the weight ration of xylose was relatively higher in soluble fraction than residual part separated from EDA pretreated wood meals.

2009-P11

フリーラジカルによるリグニンモデル化合物の反応部位に関する研究(2)

大橋康典、渡邊崇人、本田与一、渡辺隆司

京都大学生存圏研究所

Study on reactive position of lignin model compounds with free radicals (2).

Yasunori Ohashi, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

**Abstract:** A white rot fungus, *Ceriporiopsis subvermispota* degrades lignin by radical reactions of low molecular mass metabolites at a site far from enzymes. As a possible ligninolytic system by the fungus, in situ radical reactions have been proposed. Our previous experiments clearly indicate that carbon-centered (CR) and alkoxy (AR) radicals degrade non-phenolic lignin model compounds (LMCs) through hydrogen abstraction at benzyl position of LMC, but peroxy radical (PR) does not. Furthermore, direct detection of free radicals using ESR support this reactivity of AR with LMCs. In

the present study reactivity and LMC degradation mechanism of CR produced from azo-compounds was analyzed by UV-ESR method.

2009-P12

*tert*-ブトキシドを塩基とする反応系における  $\beta$ -O-4 結合開裂機構の検討

竹野甲子夫、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Investigation into the mechanism of the  $\beta$ -O-4 bond cleavage in a reaction system using *tert*-butoxide as a base.

Kineo Takeno, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: The  $\beta$ -O-4 bond cleavage of dimeric non-phenolic lignin model compounds, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (2), 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (3), and 1-methoxy-2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethane (4) was examined in a potassium *tert*-butoxide/*tert*-butanol (KO<sup>t</sup>Bu/<sup>t</sup>BuOH) system. The  $\beta$ -O-4 bonds of (2) and (3) cleaved in 0.5 mol/l KO<sup>t</sup>Bu at 30°C, which were much milder than those in general alkaline based pulping processes. The disappearance of (3) was much faster than (2), which was similar to the results in aqueous NaOH system reported by Gierer. An oxidized product, 3,4-dimethoxybenzoic acid (6), was detected, which is a characteristic in this reaction system. The  $\beta$ -O-4 bond of (4) did not cleave in the same system, indicating that the initial reaction of (2) is the dissociation of the  $\alpha$ -hydroxy group induced by <sup>-</sup>O<sup>t</sup>Bu.

2009-P13

ヨウ化アルミニウム(III)試薬によるリグニン高分子モデル化合物の低分子化

幸田圭一<sup>\*1</sup>、岸本崇生<sup>\*2</sup>、塩澤洋介<sup>\*3</sup>、浦木康光<sup>\*3</sup>

<sup>\*1</sup>北海道大学大学院農学研究院、<sup>\*2</sup>富山県立大工学部、<sup>\*3</sup>北海道大学大学院農学院

Depolymerization of a lignin polymer model compound with aluminium iodide (III).

Keiichi Koda<sup>\*1</sup>, Takao Kishimoto<sup>\*2</sup>, Yosuke Shiozawa<sup>\*3</sup>, Yasumitsu Uraki<sup>\*3</sup>

<sup>\*1</sup>Research Faculty of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, Hokkaido 060-8589, Japan, <sup>\*2</sup>Faculty of Engineering, Toyama Prefectural University, 5180 Kurokawa, Imizu, Toyama 939-0398, Japan, <sup>\*3</sup>Graduate School of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, Hokkaido 060-8589, Japan

Abstract: Aluminium iodide (III), an effective reagent for cleavage of low-molecular-weight alkyl-aryl ethers, was used to observe if it was able to cleave and depolymerize a lignin polymer model compound consisting of guaiacyl units exclusively with  $\beta$ -O-4 linkages. The AlI<sub>3</sub> reagent degraded the lignin polymer model compound to give some low-molecular-weight compounds, one of which was increasing in peak intensity (in total ion chromatogram) with increasing AlI<sub>3</sub> Charge ratio and reaction time. The reagent, however, did not cleave all the  $\beta$ -O-4 linkages of the lignin polymer model compound as it did those of a lignin dimer model compound.

2009-P14

スギ針葉中のリグニン -DFRC 法による分析の試み-

松井直之、大平辰朗

森林総合研究所 樹木抽出成分研究室

Detection of lignin in sugi leaves. -An attempt of DFRC analysis-

Naoyuki Matsui, Tatsuro Ohira

Forestry and Forest Products Research Institute, Wood Extractives Lab., Matsunosato 1, Tsukuba, 305-8687 Japan

Abstract: Many questions are left in lignins of tree leaves and needles, beginning with in their occurrence, structure and functions. The Klason method often gives excessive results because of insoluble contaminants. In this study, DFRC (Derivatization Followed by Reductive Cleavage) method, that can degradate the arylether structure in lignin selectively, was employed to sugi (*Cryptomeria japonica*) leaves. This method gave the lignin-specific C6-C3 degradation products from sugi leaves, that show the existence of lignin in leaves.

2009-P15

$\beta$ -O-4 結合の新規な選択的開裂法: $\beta$ -PSE 法の検討(1) -開裂条件の最適化-

安藤大将、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Studies on new selective cleavage method for  $\beta$ -O-4 linkages of lignin ( $\beta$ -PSE method) (1).  
-Optimization of mild alkali cleavage reaction condition-

Daisuke Ando, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: New selective  $\beta$ -O-4 cleavage method (named  $\beta$ -PSE method) which consisted of four reactions has been proposed. In this study, the final reaction (dilute alkali cleavage) of G-type lignin dimer was investigated to determine its optimum conditions. The yield of degradation product reached a peak after 1~3 h and decreased, and it was significantly affected by reaction temperature. As a result, the yield was maximum in the conditions (NaOH concentration:0.03N, temperature:25°C, reaction time:1.5h). The cleavage reaction of S-type and P-type lignin dimers in the same conditions also gave the degradation product in high yield.

2009-P16

MWL 抽出残渣の分画と分析 - Hemicellulose-Lignin fraction (HCL) のキャラクターゼーション-

宮川泰幸、竹本央記、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Fractionation and analysis of wood meal after extraction of MWL. -Characterization of Hemicellulose-Lignin fraction (HCL) -.

Yasuyuki Miyagawa, Ooki Takemoto, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Forest and Biomaterials Science, Graduate school of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: Wood meal after extraction of MWL and the following extraction with LiCl/DMAc was extracted with 3M NaOH solution to get Hemicellulose-Lignin fraction (HCL). HCL was composed of much hemicellulose and lignin in it. But the presence of Lignin-Carbohydrate Complex (LCC) bonds was unclear by the combination method of enzymatic treatment and GPC analysis. Then, HCL was further acetylated and extracted with chloroform to afford Xylan-Lignin fraction (XL). XL had much xylan and lignin, and lignin-xylan bonds strongly suggested by the above combination method. Accordingly, XL may be a useful fraction for the LCC bonds analysis.

2009-P17

リグニンモデル化合物の間接電解酸化反応(2) -mediator の検討-

白石 匠、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Indirect electrooxidation of lignin model compounds (2). —mediated by 1-hydroxybenzotriazole, violuric acid and 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate)—.

Takumi Shiraishi, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: Indirect electrooxidation of lignin model compound, 1-(4'-ethoxy-3'-methoxy-phenyl)ethanol (1G) using laccase mediators, such as 1-hydroxybenzotriazole (HOBT), violuric acid (VLA), 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), was investigated to introduce carbonyl group at  $\alpha$ -position. The yields of the corresponding carbonyl compound 2G were about 50% (HOBT or VLA mediated) and 20% (ABTS mediated). They are useful mediators for the indirect electrooxidation of natural lignin, although yields of 2G by these mediators were lower than that by N-hydroxyphthalimide (NHPI).

2009-P18

木材の酵素糖化におけるイオン液体前処理の効果

宮田賢二、宮藤久士、坂 志朗

京都大学大学院エネルギー科学研究科

Pretreatment with ionic liquids for enzymatic saccharification of wood.

Kenji Miyata, Hisashi Miyafuji, Shiro Saka

Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Abstract: Pretreatment with ionic liquids, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) or 1-butyl-3-methylimidazolium acetate ([C4mim][Ac]) was studied for producing glucose from Japanese beech by enzymatic hydrolysis. Beech wood was easily liquefied by [C4mim][Ac] treatment than [C2mim][Cl] treatment. Decrystallization of cellulose in wood was significant by [C4mim][Ac] treatment. Wood components liquefied in ionic liquids were recovered by adding water to the ionic liquids. By enzymatic saccharification with cellulase for these recovered wood components, it was found that ionic liquids pretreatment was effective to enhance glucose productivity. It was also clarified that much glucose yields can be attained by the pretreatment with [C4mim][Ac], compared to that with [C2mim][Cl].

2009-P19

イオン液体中での非フェノール性  $\beta$ -O-4 型リグニンモデル化合物の反応挙動

橋田 光、久保智史、山田竜彦、菱山正二郎、細谷修二

森林総合研究所

Reaction behaviors of non-phenolic  $\beta$ -O-4 type lignin model compounds in ionic liquids.

Koh Hashida, Satoshi Kubo, Tatsuhiko Yamada, Shojiro Hishiyama, Shuji Hosoya

Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan

Abstract: Reaction behaviors of non-phenolic  $\beta$ -O-4 type lignin model compounds in ionic liquids have been examined. In ionic liquids at 150°C, guaiacyl type model compounds, erythro (E) and threo (T) form veratrylglycerol- $\beta$ -guaiacyl ethers (VG), were decomposed slower than corresponding phenolic model compounds, guaiacylglycerol- $\beta$ -guaiacyl ethers (GG). In the ionic liquid of 1-Butyl-3-methylimidazolium chloride, E-VG was decomposed faster than T-VG. By contrast, significant differences in the decomposition rates were not observed in 1-Ethyl-3-methylimidazolium acetate. Syringyl type non-phenolic model compound of T-veratrylglycerol-beta-syringyl ether was decomposed slower than VGs. This result would be related with the difference in the decomposition rate appeared between softwood and hardwood in an ionic liquid.

2009-P20

### 両親媒性リグニンの調製及びセメント分散剤としての評価

本間春海<sup>\*1</sup>、久保智史<sup>\*2</sup>、山田竜彦<sup>\*2</sup>、幸田圭一<sup>\*3</sup>、松下泰幸<sup>\*4</sup>、福島和彦<sup>\*4</sup>、浦木康光<sup>\*3</sup>

<sup>\*1</sup>北海道大学大学院農学院、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>北海道大学大学院農学研究院、<sup>\*4</sup>名古屋大学大学院生命農学研究科

Preparation of amphiphilic lignin derivatives and evaluation of their viability as cement dispersant.

Harumi Homma<sup>\*1</sup>, Satoshi Kubo<sup>\*2</sup>, Tatsuhiko Yamada<sup>\*2</sup>, Keiichi Koda<sup>\*3</sup>, Yasuyuki Matsushita<sup>\*4</sup>, Kazuhiko Fukushima<sup>\*4</sup>, Yasumitsu Uraki<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, Japan, <sup>\*2</sup>Department of Biomass Chemistry, Forestry and Forest Products Research Institute, Tsukuba, 305-8687, Japan

<sup>\*3</sup>Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan, <sup>\*4</sup>Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan

Abstract: Several polyethylene glycols were introduced to isolated lignins to prepare amphiphilic lignin derivatives. Among them, a lignin derivative with dodecyloxy-polyethylene glycol glycidyl ether (DAEO) showed as high surface activity as a commercially available surfactant. To use those derivatives as cement dispersants, the dispersibility was evaluated. Although LS is actually used as a dispersant of cement, most lignin derivatives showed much better dispersibilities than LS. In addition, the dispersibility of LS was dramatically improved by the reaction with a small amount of DAEO. Thus, this study demonstrated that the amphiphilic lignin derivatives in this study were useful for cement dispersants.

2009-P21

### リグニン/PEO ポリマーブレンドの熱流動特性

久保智史<sup>\*1</sup>、木口実<sup>\*1</sup>、山田竜彦<sup>\*1</sup>、堀沢栄<sup>\*2</sup>、辻知宏<sup>\*2</sup>、本間春海<sup>\*3</sup>、浦木康光<sup>\*3</sup>、John Kadla<sup>\*4</sup>

<sup>\*1</sup>森林総合研究所、<sup>\*2</sup>高知工科大学、<sup>\*3</sup>北海道大学大学院農学研究院、<sup>\*4</sup>University of British Columbia

Thermal fluidity of the polymer blend of lignin and PEO.

Satoshi Kubo<sup>\*1</sup>, Makoto Kiguchi<sup>\*1</sup>, Tatsuhiko Yamada<sup>\*1</sup>, Sakae Horisawa<sup>\*2</sup>, Tomohiro Tsuji<sup>\*2</sup>, Harumi Homma<sup>\*3</sup>, Yasumitsu Uraki<sup>\*3</sup>, John Kadla<sup>\*4</sup>

<sup>\*1</sup>Department of Biomass Chemistry, Forestry and Forest Products Research Institute. 1 Matsunosato Tsukuba, Ibaraki, <sup>\*2</sup>Kochi University of Engineering, <sup>\*3</sup>Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan, <sup>\*4</sup>University of British Columbia

Abstract: Thermal viscous behavior of the blends of alcohol lignin (AL) and PEO were examined using thermo-mechanical analysis (TMA) and capillary viscometer. Both of the initiation temperature of the thermal flow and thermal viscosity of AL was decreased by the blending with PEO. However, by contraries, that temperature and thermal viscosity was increased by the incorporation of excess amount of PEO. Those thermal behaviors are good agreement with the changes in the thermal formability of AL/PEO blend, such as thermal spinning temperature.

2009-P22

### バイオディーゼル燃料生産副産物グリセリンと工業リグニン由来原料からのポリウレタン誘導体の調製と物性

辻本泰人<sup>\*1</sup>、鹿瀬重雄<sup>\*2</sup>、畠山立子<sup>\*3</sup>、島田幹夫<sup>\*1</sup>、畠山兵衛<sup>\*1</sup>

<sup>\*1</sup>福井工業大学工学部、<sup>\*2</sup>産業技術総合研究所、<sup>\*3</sup>リグノセルリサーチ

Preparation and properties of polyurethane foams derived from industrial lignins and crude glycerin from BDF industry.

Yasuto Tsujimoto<sup>\*1</sup>, Shigeo Hirose<sup>\*2</sup>, Tatsuko Hatakeyama<sup>\*3</sup>, Mikio Shimada<sup>\*1</sup>, Hyoe Hatakeyama<sup>\*1</sup>  
<sup>\*1</sup>Fukui University of Technology, 3-6-1, Gakuen, Fukui 910-8505, <sup>\*2</sup>AIST, 1-1-4 Higashi, Tsukuba, 305-8565, <sup>\*3</sup>Lignocell Research, 73-8, Yatsumata, Fukui 910-3558

Abstract: Polyurethane (PU) foams were prepared using crude glycerin (CG) obtained as a by-product of the biodiesel fuel (BDF) industry and lignosulfonate (LS) obtained as a by-product of the pulping industry. LS and CG were dissolved in polyethyleneglycol (PEG), and two kinds of polyols LSP and CGP were prepared. CG content was varied 0, 5, 10, 15, 20 % in polyols. The above polyols were reacted with poly(phenylene methylene) polyisocyanate (MDI). Water was used as a foaming reagent. Apparent density of PU foams was in a range from 0.09 to 0.07 g cm<sup>-3</sup>. Compression strength ( $\sigma_{10}$ ) was in a range from 0.31 to 0.51 MPa. Scanning electron micrographs of the prepared PU foams were examined.

2009-P23

木質系バイオマス糖化残漆を主成分とする低炭素型プラスチック充填材の製造に関する研究  
松永興哲<sup>\*1</sup>、坂西欣也<sup>\*1</sup>、西本徹郎<sup>\*2</sup>、平田雅章<sup>\*2</sup>

<sup>\*1</sup>産業技術総合研究所、<sup>\*2</sup>株式会社ジュオン

Research on the production of plastic filler by utilization of fermentation residue obtained from the wood-derived bio-ethanol production process.

Kotetsu Matsunaga<sup>\*1</sup>, Kinya Sakanishi<sup>\*1</sup>, Tetsuro Nishimoto<sup>\*2</sup>, Masayuki Hirata<sup>\*2</sup>

<sup>\*1</sup>National Institute of Advanced Industrial Science and Technology (AIST), AIST Chugoku, Suehiro 2-2-2, Hiro, Kure, Hiroshima 737-0197, Japan, <sup>\*2</sup>JUON CO. Ltd., 1-28-7, Gion, Asaminami-ku, Hiroshima, 731-0138, Japan

Abstract: In the production procedure of ethanol from woody biomass, about 60-80 wt% of fermentation residue is produced on the base of wood feedstock. We produced the neat biomass-derived synthesized resin complex from the mixed feedstock of the fermentation residue obtained from the wood-derived bio-ethanol production process with glycerol and poly-lactic acid. In the evaluation of the biomass-derived synthesized resin complex as plastic filler, its blending with poly-propylene resin exhibited the better dispersion compatibility and processing performance compared to those produced from the crude saccharification residue. In addition, the melting viscosity of the complex resin was not affected so much by its addition, keeping the stable processing performance, while the addition of the crude residue considerably increased the viscosity.

2009-P24

リグニンからの紫外線吸収剤の開発

内藤喜之<sup>\*1</sup>、大橋康典<sup>\*1</sup>、吉岡康一<sup>\*1</sup>、渡辺崇人<sup>\*1</sup>、本田与一<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>、菅原智<sup>\*2</sup>、小池謙造<sup>\*2</sup>  
京大生存圏研究所、花王株式会社

Development of ultraviolet absorbers from lignin.

Yoshiyuki Naito<sup>\*1</sup>, Yasunori Ohashi<sup>\*1</sup>, Koichi Yoshioka<sup>\*1</sup>, Takahito Watanabe<sup>\*1</sup>, Yoichi Honda<sup>\*1</sup>, Takashi Watanabe<sup>\*1</sup>, Satoshi Sugawara<sup>\*2</sup>, Kenzo Koike<sup>\*2</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan, <sup>\*2</sup>Kao Corporation, 2-1-3 Bunka, Sumidaku, Tokyo 131-8501, Japan

Abstract: Currently, ultraviolet absorbers are becoming popular due to cosmetic and medical purposes. Exposure of skins to ultraviolet rays from the sun causes damage of the skins. Excessive exposure induces skin cancer and aging. Although the demand for UV absorbers with high safety and minimum environmental impact is becoming increasing, most of the organic UV absorbers currently available are synthetic compounds from petroleum. Therefore, we started the research to develop

UV absorbers from natural aromatic polymer, lignin. By extensive screening of degradation products from lignin, we found the products having high absorbance in UV A and UV B regions.

## 第 55 回 (2010.10.20-21) 京都大学 百周年時計台記念館

2010-101

イネ節間の細胞壁成分合成が異常になる *d50* 変異体の解析と *D50* 遺伝子の同定  
佐藤かな<sup>\*1</sup>、中野仁美<sup>\*1</sup>、西窪伸之<sup>\*2</sup>、田村克徳<sup>\*3</sup>、半 智史<sup>\*4</sup>、船田良<sup>\*4</sup>、梶田真也<sup>\*1</sup>、  
芦荻基行<sup>\*5</sup>、北野英己<sup>\*5</sup>、片山義博<sup>\*6</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>王子製紙株式会社、<sup>\*3</sup>九州沖縄農研究センター、<sup>\*4</sup>東京農工大学  
大学院農学研究院、<sup>\*5</sup>名古屋大学大学院 BBC、<sup>\*6</sup>日本大学生物資源学部

Histochemical analysis of rice *d50* mutant internodes exhibiting abnormal synthesis of cell wall materials and isolation of *D50* gene.

Kanna Sato<sup>\*1</sup>, Yoshimi Nakano<sup>\*1</sup>, Nobuyuki Nishikubo<sup>\*2</sup>, Katsunori Tamura<sup>\*3</sup>, Satoshi Nakaba<sup>\*4</sup>, Ryo Funada<sup>\*4</sup>, Shinya Kajita<sup>\*1</sup>, Motoyuki Ashikari<sup>\*5</sup>, Hidemi Kitano<sup>\*5</sup>, Yoshihiro Katayama<sup>\*6</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan, <sup>\*2</sup>Forestry Research Institute, Oji Paper Company Limited, 24-9 Nobono-cho, Kameyama, Mie 519-0212, Japan, <sup>\*3</sup>National Agricultural Research Center for Kyushu Okinawa Region, 496 Izumi, Chikugo, Fukuoka, 833-0041, Japan, <sup>\*4</sup>Graduate School of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8538, Japan, <sup>\*5</sup>Bioscience and Biotechnology Center, Nagoya University, Furo-cho, Nagoya, Aichi 464-8601, Japan. <sup>\*6</sup>College of Bioresource Sciences, Nihon University, 1866 Kameino, Fujisawa, Kanagawa 252-0880, Japan

Abstract: Previously, we reported that parenchyma cells in the elongated internodes of Fukei 71 (*d50* mutant) ectopically deposit grass-specific cell wall material, polysaccharide-linked hydroxycinnamoyl esters. Through map-based cloning, we revealed that the *D50* encodes putative inositol polyphosphate 5-phosphatase, which may be involved in phosphoinositide signaling pathways required for many essential cellular functions including cytoskeleton organization, endocytosis and vesicular trafficking in eukaryotes. Further analyses of *d50* phenotype revealed that the *d50* mutation induced abnormally oriented cell division, ectopic deposition of cell wall pectins and thick actin bundles in the parenchyma cells of the intercalary meristem.

2010-102

*Sphingobium* sp. SYK-6 株由来の *ligD* 遺伝子を発現する遺伝子組換え植物の作出と解析  
石川靖之<sup>\*1</sup>、大浦良<sup>\*1</sup>、辻幸子<sup>\*1</sup>、上杉幹子<sup>\*1</sup>、佐藤かな<sup>\*1</sup>、片山義博<sup>\*2</sup>、原啓文<sup>\*3</sup>、菱山正二郎<sup>\*4</sup>、  
政井英司<sup>\*5</sup>、梶田真也<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院 BASE、<sup>\*2</sup>日本大学生物資源学部、<sup>\*3</sup>岡山理科大学工学部、<sup>\*4</sup>森林総合研究所、<sup>\*5</sup>長岡技術科学大学工学部

Generation and analysis of transgenic plants with *ligD* gene isolated from *Sphingobium* sp. SYK-6.

Yasuyuki Ishikawa<sup>\*1</sup>, Ryo Oura<sup>\*1</sup>, Yukiko Tsuji<sup>\*1</sup>, Mikiko Uesugi<sup>\*1</sup>, Kanna Sato<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Hirofumi Hara<sup>\*3</sup>, Shojiro Hishiyama<sup>\*4</sup>, Eiji Masai<sup>\*5</sup>, Shinya Kajita<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan, <sup>\*2</sup>College of Bioresource Sciences, Nihon University, Kanagawa, 252-0880, Japan, <sup>\*3</sup>Department of Biomedical Engineering, Okayama University of Science, Okayama 700-0005, Japan, <sup>\*4</sup>Forestry and Forest Products Research Institute, Ibaraki 305-8687, Japan, <sup>\*5</sup>Department of Bioengineering, Nagaoka University of Technology, Niigata 940-2188, Japan

Abstract: *Sphingobium* sp. SYK-6 can catabolite various types of phenolic compounds including monolignols, their precursors and lignin dimers. Several genes involved in the catabolism of these compounds have been isolated from this strain in our previous studies. For modification of lignin biosynthesis in plant cell, we focus on *ligD* gene, which encodes C $\alpha$  dehydrogenase for first step of cleavage of ether bond in compounds with  $\beta$ -O-4 bond. After optimization of codon usage of the gene for efficient expression, we introduced a modified *ligD* gene into tobacco BY-2 cells and *Arabidopsis* plants. Characterization of the transgenic cells and plants will be discussed.

2010-103

高機能性微生物による木質バイオリファイナリー ～*Phanerochaete sordida* YK-624 株におけるリグニン分解性ペルオキシダーゼと 5-アミノレブリン酸シンターゼの関係～

三隅健太<sup>\*1</sup>、渡辺裕也<sup>\*1</sup>、平井浩文<sup>\*1</sup>、河岸洋和<sup>\*1\*2</sup>、亀井一郎<sup>\*3</sup>、森智夫<sup>\*4</sup>、近藤隆一郎<sup>\*4</sup>

<sup>\*1</sup> 静岡大学農学部、<sup>\*2</sup> 静岡大学創造科学技術大学院、<sup>\*3</sup> 宮崎大学農学部、<sup>\*4</sup> 九州大学大学院農学研究院

Woody biorefinery with functional microorganisms. — Relationship between ligninolytic peroxidases and 5-aminolevulinic acid synthase in *Phanerochaete sordida* YK-624 —.

Kenta Misumi<sup>\*1</sup>, Yuya Watanabe<sup>\*1</sup>, Hirofumi Hirai<sup>\*1</sup>, Hirokazu Kawagishi<sup>\*1\*2</sup>, Ichiro Kamei<sup>\*3</sup>, Toshio Mori<sup>\*4</sup>, Ryuichiro Kondo<sup>\*4</sup>

<sup>\*1</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*2</sup>Graduate School of Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*3</sup>Faculty of Agriculture, University of Miyazaki, Miyazaki 889-2192, Japan, <sup>\*4</sup>Faculty of Agriculture, Kyushu University, University, Fukuoka 812-8581, Japan

Abstract: To overproduce ligninolytic peroxidases (manganese peroxidase (MnP) and novel lignin peroxidase) in *Phanerochaete sordida* YK-624, the gene of 5-aminolevulinic acid synthase (ALAS), *aas*, is involved in the production of 5-aminolevulinic acid which is the rate-limiting step in the biosynthesis of heme, was cloned. The deduced amino acid sequence of *aas* showed highest identity (93.0%) with ALAS from *P. chrysosporium* ME-446. The promoter of glyceraldehyde-3-phosphate dehydrogenase (GPD) gene cloned from *P. sordida* YK-624 was used to drive the expression of *aas*. The expression vector was transformed into a *P. sordida* YK-624 uracil auxotrophic mutant, UV-64. Three transformants showed high MnP activities compared with control transformants into which only *ura5* was introduced.

2010-104

高機能性微生物による木質バイオリファイナリー ～新規リグニン分解特異的プロモーターを用いた超高活性リグニン分解菌の分子育種～

杉浦立樹<sup>\*1</sup>、三隅健太<sup>\*2</sup>、渡辺裕也<sup>\*2</sup>、平井浩文<sup>\*2</sup>、河岸洋和<sup>\*1\*2</sup>、亀井一郎<sup>\*3</sup>、森智夫<sup>\*4</sup>、近藤隆一郎<sup>\*4</sup>

<sup>\*1</sup> 静岡大学創造科学技術大学院、<sup>\*2</sup> 静岡大学農学部、<sup>\*3</sup> 宮崎大学農学部、<sup>\*4</sup> 九州大学大学院農学研究院

Woody biorefinery with functional microorganism. Molecular breeding of superior lignin-degrading fungi using novel ligninolytic condition-specific promoter.

Tatsuki Sugiura<sup>\*1</sup>, Kenta Misumi<sup>\*2</sup>, Yuya Watanabe<sup>\*2</sup>, Hirofumi Hirai<sup>\*2</sup>, Hirokazu Kawagishi<sup>\*1\*2</sup>, Ichiro Kamei<sup>\*3</sup>, Toshio Mori<sup>\*4</sup>, Ryuichiro Kondo<sup>\*4</sup>

<sup>\*1</sup>Graduate School of Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*2</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*3</sup>Faculty of Agriculture, University of Miyazaki, Miyazaki 889-2192, Japan, <sup>\*4</sup>Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

Abstract: BUNA2 is one of high produced proteins from hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under wood-rotting condition. In the transcriptional analysis, the gene of BUNA2 (*bee2*) was stably and strongly transcribed during 20 days cultivation in beach wood meals. A promoter region of *bee2* (*bee2* promoter) was cloned using TAIL PCR and inverse PCR method. The obtained promoter was used to drive the expression of Lip gene (*ylpA*) or MnP gene (*mnp4*), and these plasmids (pBUNA2pro-*ylpA* and pBUNA2pro-*mnp4*) were constructed. Protoplasts of UV-64 were mixed with DNA solution containing pBUNA2pro-*ylpA*, pBUNA2pro-*mnp4* and p*PsURA5*, and co-transformed by PEG method. With the same method, DNA solution containing pBUNA2pro-*ylpA* and p*PsURA5*, and pBUNA2pro-*mnp4* and p*PsURA5* were co-transformed respectively. We obtained 17 of *ylpA* & *mnp4*-introducing clones, 9 of *ylpA*-introducing clones, and 14 of *mnp4*-introducing clones.

2010-105

高機能性微生物による木質バイオリファイナリー ～新規糖化酵素産生微生物の探索～  
亀井一郎<sup>\*1</sup>、森智夫<sup>\*2</sup>、平井浩文<sup>\*3</sup>、目黒貞利<sup>\*1</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup> 宮崎大学農学部、<sup>\*2</sup> 九州大学大学院農学研究院、<sup>\*3</sup> 静岡大学農学部

Woody biorefinery with functional microorganisms. –Screening of functional saccharification enzyme-producing microorganisms–.

Ichiro Kamei<sup>\*1</sup>, Toshio Mori<sup>\*2</sup>, Hirofumi Hirai<sup>\*3</sup>, Sadatoshi Meguro<sup>\*1</sup>, Ryuichiro Kondo<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, University of Miyazaki, <sup>\*2</sup>Faculty of Agriculture, Graduate School of Kyushu University, <sup>\*3</sup>Faculty of Agriculture, Shizuoka University,

Abstract: To isolate functional saccharification enzyme-producing bacteria, a decayed wood-pulp perfusion system was developed and applied. An enrichment culture in decayed wood-pulp perfusion system contained at least ten bacteria after two month perfusion and then two strains (E814-1 and E814-2) were isolated as cellulase-producing microorganisms. Among them, strain E814-2 was identified as *Paenibacillus* sp. using 16S rDNA sequencing and this strain closely related to *Paenibacillus curdlanolyticus* which was reported recently as multienzyme complex (cellulosome)-producing bacteria. This result indicates that pulp perfusion system is a useful method for isolate saccharification enzyme-producing bacteria. Additionally, to identify potential enzymes from nonculturable microbes, metagenomic libraries were constructed from several lignocellulose-rich environments. Around 7.5 kbp eDNAs were successfully cloned and applied to plate assay for screening.

2010-106

リグニン分解酵素による医薬品類の除去  
新館秀章、畑貴之、河合真吾、西田友昭  
静岡大学農学部

Elimination of pharmaceutically active compounds by ligninolytic enzymes.

Hideaki Shintate, Takayuki Hata, Shingo Kawai, Tomoaki Nishida

Department of Environment and Forest Resources Science, Faculty of Agriculture, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan

Abstract: Carbamazepine (CBZP) is used as an antiepileptic drug and is highly persistent. In this study, CBZP was treated with manganese peroxidase (MnP), laccase and the laccase-mediator system with 1-hydroxybenzotriazole (HBT). The laccase-HBT system is most effective in eliminating CBZP among the three enzymatic treatments. A single treatment with laccase and HBT eliminated CBZP by about 22% after 24 h, and repeated treatments with laccase and HBT, which were added to the reaction mixture every 8 h, helped eliminate about 60% of CBZP after 48 h. This

suggests that repeated treatment is effective in eliminating CBZP. Mass spectrometric analyses demonstrated that two degradation products of CBZP, 10,11-dihydro-10,11-epoxycarbamazepine and 9(10H)-acridone, were formed via repeated treatment with laccase and HBT. Furthermore, the anti-inflammatory drug indomethacin (IMC) was also treated with MnP, laccase and the laccase-HBT system. MnP and the laccase-HBT system almost completely eliminated IMC after 4 h of treatment, suggesting that these two enzymatic treatments are effective in eliminating IMC.

2010-107

Bioremediation of DDT by *Pleurotus ostreatus* spent mushroom waste: involvement of ligninolytic enzymes and application in historically contaminated soil.

Adi Setyo Purnomo<sup>\*1\*2</sup>, Toshio Mori<sup>\*1</sup>, Eri Takata<sup>\*1</sup>, Kazuhiro Takagi<sup>\*3</sup>, Yuji Tsutsumi<sup>\*1</sup>, Ryuichiro Kondo<sup>\*1</sup>

<sup>\*1</sup>Department of Agro-environmental Sciences, Faculty of Agriculture, Kyushu University,

<sup>\*2</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, Institut Teknologi Sepuluh Nopember, Indonesia. <sup>\*3</sup>National Institute for Agro-environmental Sciences.

Abstract: In our previous work, spent mushroom waste (SMW) of *Pleurotus ostreatus* (Hiratake) was shown to have high ability to degrade and mineralize DDT (1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane) in artificially contaminated soil. In present study, SMW of Hiratake was applied to the historically contaminated soil which collected from pesticide manufacturing site in Japan. DDT concentration in the historically contaminated soil is 0.4 mmol/g dry weight of soil. After 28 days incubation, approximately 70% of DDT was degraded compared with autoclave-killed control. Degradation mechanisms especially involvement of ligninolytic enzymes were investigated. SMW of Hiratake has 0.26, 1.90, and 0.13 mmol/min/ml of laccase, MnP, and LiP activities, respectively. High MnP activity suggested MnP seems a key enzyme for degradation of DDT. DDT was treated with purified MnP, and DDD (1,1-dichloro-2,2-bis-(4-chlorophenyl) ethane) and DBP (4,4-dichlorobenzophenone) were detected as metabolic products.

2010-108

白色腐朽菌 *Phlebia* 属菌によるクロルデンの処理

肖 鹏飞<sup>\*1\*2</sup>、森 智夫<sup>\*3</sup>、近藤隆一郎<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院生物資源環境科学府、<sup>\*2</sup>東北林業大学、<sup>\*3</sup>九州大学大学院農学研究院

Biodegradation of chlordane by white rot fungi, *Phlebia* genus.

Pengfei Xiao<sup>\*1\*2</sup>, Toshio Mori<sup>\*3</sup>, Ryuichiro Kondo<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, 6-10-1

Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan, <sup>\*2</sup>College of Forestry, Northeast Forestry

University, Harbin 150040, China, <sup>\*3</sup>Graduate School of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan,

Abstract: The organochlorine pesticide, chlordane was used as the substrate for degradation experiment with the white rot fungi *Phlebia lindtneri*, *Phlebia brevispora* and *Phlebia aurea*, which are capable of degrading dieldrin, heptachlor and heptachlor epoxide. Pure culture of fungi with chlordane (0.25mmol/flask) showed that over 50% of chlordane disappeared in Kirk (LN) medium and PDB medium after 42-day incubation period. Chlordane was biotransformed to heptachlor, heptachlor epoxide, dichlorochlordene, oxychlordane and several hydroxylated metabolites, which have not been reported as bacterial metabolite. 1-aminobenzotriazole and piperonyl butoxide strongly inhibited the degradation of chlordane and concomitant accumulation of metabolites, indicating cytochrome P450 mediated metabolism.

2010-109

C heavy oil degradation in sea water liquid medium by *Fusarium* sp. F092.

Asep Hidayat, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Oil contamination have become serious problem in environmental generated via several accident on production. Experiments were carried out to evaluate the ability of *Fusarium* sp. F092 to degrade C heavy oil on sea water liquid medium. The strain F092 grew 0.41 cm/day on potato glucose (PG) agar medium containing C heavy oil. C heavy oil used in our experiment contained 44% of aliphatic, 31% of aromatic, 8% of nitrogen, sulfur and oxygen (NSO) and 17% of asphaltene. At 60 days incubation, degradation of C heavy oil by strain F092 fungus was obtained at the level 77% on those aliphatic and aromatic fractions, and 56 % of total petroleum hydrocarbon (TPH) degradation. The effect of manganese (Mn) addition, could increase 20% of TPH degradation, those are 75% of (NSO) and 31% of asphaltene. The highest activity of manganese peroxidase and laccase reached at 69  $UI^{-1}$  and 49  $UI^{-1}$  on 20 days, while 1,2- and 2,3-dioxygenase showed the highest level after 20 days.

2010-110

Degradation of 2,4,8-Trichlorodibenzofuran by fungi selected from nature.

Ajeng Arum Sari, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: Dioxin can be serious problem for environmental because of its strong toxicity and mutagenicity. White rot fungi are well known for their outstanding ability to produce extracellular oxidative enzymes, which are involved in the degradation of either lignin than a wide range of pollutants include dioxins. Fungus U97 screened from nature had ability to degrade 2,4,8-TCDF by 43%, on 15 days and 61%, on 30 days, respectively. The maximum enzyme activity of strain U97 during 2,4,8-TCDF degradation was 1,2-dioxygenase (262.8  $UI^{-1}$ ) and Lip (93.6  $UI^{-1}$ ). Carbon source, surfactant and agitation have no negative effect on the growth of U97 during biodegradation of 2,4,8-TCDF on 15 and 30 days. The finding suggest that U97 can metabolize 2,4,8-TCDF to 3,5-dichlorosalicylic acid.

2010-111

白色腐朽菌由来の酵素および酵素製剤を用いたアゾ染料の分解

大森元樹、伊藤和貴、橘 燦郎

愛媛大学農学部

Degradation of azo dyes with a crude enzyme and immobilized enzyme from white rot fungi.

Motoki Omori, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University

Abstract: To purify effluents from textile industry, food industry and so forth, degradation of three kinds of azo dyes, Reactive Red (RR4), Reactive Black 5 (RB5) and Reactive Green 19 (RG19) was conducted by using a crude enzyme and immobilized enzyme from a white rot fungus, PL1. Degradation rate of the dyes by the crude enzyme in liquid medium was about 20 to 87 %. However, the degradation rate was increased to about 90 to 95% by addition of Tween 80. On the contrary, degradation rate of the dyes by the immobilized enzyme (double capsule) in the medium was about 80 to 93%. To conduct the degradation of the dyes using bioreactor packed with the double capsule, effects of flow rate on degradation of the dyes were investigated. It was found that the degradation rate was increased when the flow rate became faster, or the treatment time got longer. The maximum degradation rate of RG19 was 95% when the treatment was conducted for 48 hours at

7.0/min.

2010-112

シロイヌナズナ T87 培養細胞のリグニン分析

山村正臣<sup>\*1</sup>、和田将平<sup>\*1</sup>、榑原和紀<sup>\*1\*2</sup>、中坪朋文<sup>\*1</sup>、鈴木史朗<sup>\*1\*3</sup>、服部武文<sup>\*1</sup>、竹田みぎわ<sup>\*4</sup>、桜井望<sup>\*4</sup>、鈴木秀幸<sup>\*4</sup>、柴田大輔<sup>\*4</sup>、梅澤俊明<sup>\*1\*3</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> 徳島文理大学、<sup>\*3</sup> 京大生存基盤科学研究ユニット、<sup>\*4</sup> かずさ DNA 研究所

Lignin analyses of *Arabidopsis thaliana* T87 cells.

Masaomi Yamamura<sup>\*1</sup>, Shohei Wada<sup>\*1</sup>, Kazunori Sakakibara<sup>\*1\*2</sup>, Tomoyuki Nakatsubo<sup>\*1</sup>, Shiro Suzuki<sup>\*1\*4</sup>, Takefumi Hattori<sup>\*1</sup>, Migiwa Takeda<sup>\*4</sup>, Nozomu Sakurai<sup>\*4</sup>, Hideyuki Suzuki<sup>\*4</sup>, Daisuke Shibata<sup>\*4</sup>, Toshiaki Umezawa<sup>\*1\*3</sup>

<sup>\*1</sup> Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto 611-0011,

<sup>\*2</sup> Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, Sanuki, Kagawa 769-2193, <sup>\*3</sup> Institute of Sustainability Science, Kyoto University, Uji, Kyoto 611-0011,

<sup>\*4</sup> Kazusa DNA Research Institute, Kisarazu, Chiba 292-0818

Abstract: *Arabidopsis thaliana* is the most widely used model plant in the area of plant bioscience sector. T87 is one of the typical lines of *A. thaliana* cultured cells. This cell line has various advantages in the research of plant metabolism, as well as intact *A. thaliana* plants. However, nothing is known about the lignins of T87 cells. In this study, we characterized lignins of T87 cells using six lignin analytical methods, phloroglucino1-hydrochloric acid staining, thioacidolysis, nitrobenzene oxidation, alkaline hydrolysis, and Klason and acetyl bromide methods. These analyses clearly showed that lignins of T87 cells are composed of guaiacyl and *p*-hydroxyphenyl units, and are quite different from lignin found in the *A. thaliana* inflorescence stem, which are composed of guaiacyl and syringyl units.

2010-113

The finding and characterization of hindered LCC by the fractionation of wood cell wall components using LiCl/DMSO system.

Zhiguo Wang, Takuya Akiyama, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, Japan

Abstract: The fractionation of wood cell wall components was achieved by the application of the LiCl/DMSO solvent system developed in our previous study. Various soluble and insoluble fractions were prepared from beech milled wood by extractions with DMSO containing different amounts of lithium chloride (LiCl) for the study of lignin-carbohydrate complex (LCC). Nitrobenzene oxidation (NO) analyses demonstrated that the lignin in the soluble fractions always has lower yields of NO products consisting of syringaldehyde + syringic acid (S) and vanillin + vanillic acid (V). The syringyl ratios, S/(S+V), were also lower than in insoluble fractions. Accordingly, lignins with lower syringyl ratios are better soluble than those with higher ones. The former is typical in primary wall and the latter in secondary wall. Solubilization of glucan is significantly dependent on the LiCl concentration in DMSO. In the absence of LiCl, only about 6% of glucan was found in the soluble fraction, but about 40% of lignin and xylan were solubilized. The additional 40% of lignin and xylan became soluble together with glucan solubilization by the addition of LiCl up to 3% concentration. However, a fraction amounting to 13% (based on the whole wood) is still remained as a residue under these conditions. Glucan solubilization could not be the reason for this observation as ball-milled cellulose is soluble in 3% LiCl/DMSO. Probably, strong interactions between lignin and carbohydrates prevent

solubilization of this fraction, which is denominated here as “hindered LCC”, that has never been isolated and analyzed in previous studies. The “hindered LCC” contains non-condensed-type lignin and featured by strong interactions between lignin, hemicelluloses, and cellulose. On the other hand, Björkman LCC, which is obtained when LiCl concentration is 0%, is rich in condensed-type lignin and characterized by interactions between lignin and hemicelluloses.

2010-114

Relationships between hemicellulose composition and lignin structure of LCC fractions.

Yu Huang<sup>\*1\*2</sup>, Zhiguo Wang<sup>\*1</sup>, Linshan Wang<sup>\*2</sup>, Yuesheng Chao<sup>\*2</sup>, Takuya Akiyam<sup>\*1</sup>, Tomoya Yokoyama<sup>\*1</sup>, Yuji Matsumoto<sup>\*1</sup>

<sup>\*1</sup>Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>School of Sciences, Northeastern University, China

Abstract: New fractionation method of wood cell wall components was applied to selected wood species (beech and red pine). Finely ground wood meal was first extracted by aq dioxane and DMSO to obtain conventional Björkman lignin and LCC. The residue was then subjected to successive extraction by DMSO with increasing content of LiCl (0.5 to 3.0%). Relationships between lignin structure and carbohydrates in obtained fractions were examined. Syringyl ratio of soluble fractions was always lower than that obtained for corresponding insoluble fractions. It was confirmed that MWL represents very specific part of whole lignin. With the increase of LiCl concentration of the extraction solvent, the lignin content and weight ratio of hemicellulose in sugars decreased, and weight ratio of cellulose in sugars increased.

2010-115

高 CO<sub>2</sub> 下で生育した樹木の細胞壁構成成分の評価

白河 学<sup>\*1</sup>、斎藤香織<sup>\*1</sup>、渡辺陽子<sup>\*2</sup>、渡辺 誠<sup>\*3</sup>、船田 良<sup>\*3</sup>、小池孝良<sup>\*2</sup>、福島和彦<sup>\*1</sup>

名古屋大学大学院生命農学研究科、北海道大学大学院農学研究科、東京農工大学大学院共生科学技術研究院

Evaluation of wood cell wall component growing under elevated CO<sub>2</sub>.

Manabu Shirakawa<sup>\*1</sup>, Kaori Saito<sup>\*1</sup>, Yoko Watanabe<sup>\*2</sup>, Makoto Watanabe<sup>\*2</sup>, Ryo Funada<sup>\*3</sup>, Takayoshi Koike<sup>\*2</sup>, Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of bioagricultural Science, Nagoya University, Nagoya, 464-8601, <sup>\*2</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, <sup>\*3</sup>Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Fuchu, 183-8509

Abstract: Chemical characterization of the wood which was grown under free air CO<sub>2</sub> enrichment (FACE) was investigated. We focused on lignin to detect the effect of increasing atmospheric concentration of CO<sub>2</sub> to wood material. We characterized lignin using the acetylbromide method for lignin content and the thioacidolysis to examine the syringyl/guaiacyl (S/G) monomer ratios. The results show no significant difference between FACE and control samples, which indicates elevated CO<sub>2</sub> environment would not induce the change of lignin content, S/G monomer ratios.

2010-116

木質バイオマスリファイナリーのための高分解能質量分析法の開発

吉岡康一<sup>\*1</sup>、岸本崇生<sup>\*2</sup>、渡連崇人<sup>\*1</sup>、本田与一<sup>\*1</sup>、渡辺隆司<sup>\*1</sup>

<sup>\*1</sup>京都大学生存圏研究所、<sup>\*2</sup>富山県立大学工学部

Development of high-resolution mass spectrometry for woody biomass refinery.

Koichi Yoshioka<sup>\*1</sup>, Takao Kishimoto<sup>\*2</sup>, Takahito Watanabe<sup>\*1</sup>, Yoichi Honda<sup>\*1</sup>, Takashi Watanabe<sup>\*1</sup>

\*<sup>1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan, Faculty of Engineering, \*<sup>2</sup> Toyama Prefectural University, Imizu 939-0398, Japan

Abstract: Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) gives direct structural information in a wide range of molecular mass regions. However, reports on the structural analysis of lignin by MALDI-TOF MS are still limited. In this study, milled wood lignin (MWL) from Japanese cedar, *Fagus crenata* and *Eucalyptus globulus* wood were analyzed MALDI-TOF MS. The mass spectrometry provided peaks of the lignin including those characteristic to  $\beta$ -O-4 linkage, a major linkage among monomeric units in lignin. The mass spectrometry is useful for woody biomass refinery, especially for structure-based utilization of lignin.

2010-117

HSQC NMR analysis of bamboo lignin and bamboo cell walls.

Qu Chen, Takao Kishimoto, Shinjiro Ogita, Masahiro Hamada, Noriyuki Nakajima

Bioorganic Chemistry Lab, Department of Biotechnology, Toyama Prefectural University, 5180 Kurokawa, Imizu, Toyama, Japan

Abstract: In situ acetylated mature and immature hachiku bamboo (*Phyllostachys nigra* Munro var. *Henonis*) cell walls were characterized by <sup>1</sup>H-<sup>13</sup>C correlation heteronuclear single quantum coherence (HSQC) NMR spectroscopy. The lignins from mature and immature bamboo were also isolated in order to assign the lignin fraction. The HSQC spectrum of immature bamboo lignin and plant cell walls can help studying the lignification of bamboo.

2010-特別講演

リグニン利用の現状と将来展望

西盛嘉人

日本製紙ケミカル株式会社開発研究所

The current industrial applications of the lignin and its prospect.

Yoshito Nishimori

Research and Development Laboratory, Nippon Paper Chemicals Co. Ltd., 2-8-1, Iidamachi, Iwakuni, Yamaguchi 740-0003 Japan

Abstract: Commercial lignin is produced as a co-product of the pulp industry. Lignins are products of Kraft and Sulfite pulping process. The Kraft lignin is mainly used as a fuel through a recovery boiler. On the other hand, the lignosulfonate generated from the Sulfite pulping process is used as a concrete admixture, binder and for other applications due to its dispersing, binding, complexing and emulsifying properties. This presentation will introduce the current industrial applications of the lignin. Furthermore, new possible applications such as a raw material for bio-refineries are discussed as well.

2010-201

リグニンモデル化合物の間接電解酸化反応(3) - $\beta$ -O-4モデルオリゴマーのNHPI間接電解-

白石 匠、上高原 浩、高野 俊幸、中坪 文明

京都大学大学院農学研究科

Indirect electrooxidation of lignin model compounds. (3) - NHPI-mediated indirect electrooxidation of  $\beta$ -O-4 model oligomers -.

Takumi Shiraiishi, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: Indirect electrooxidation of  $\beta$ -O-4 type oligomeric lignin model compound using N-hydroxyphthalimide (NHPI) as a mediator was studied to introduce a carbonyl group at  $\alpha$ -position. It was suggested from the NMR data of the electrolysis products that a carbonyl group was introduced to  $\alpha$ -position of the oligomer in 68–84% yield. These results suggest that NHPI-mediated indirect electrooxidation is an effective method for  $\alpha$ -carbonylation of natural lignin structures.

2010-202

イオン液体中でのリグニンモデルおよびリグニンの構造変化

久保智史、橋田光、山田竜彦、菱山正二郎、細谷修二

森林総合研究所

Structure changes of lignin model compounds and lignin preparations in ionic liquids.

Satoshi Kubo, Koh Hashida, Tatsuhiko Yamada, Shojiro Hishiyama, Shuji Hosoya

Department of biomass chemistry, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki, Japan

Abstract: To examine the structure changes of lignin in ionic liquids (IL), MWL was treated with IL under the heat conditions. After IL treatments, some portions of MWL were recovered as water soluble fractions. In FT-IR analysis, the band assigned to conjugated carbonyl groups, which was clearly detected for original MWL, were dramatically decreased by the IL treatment.  $^1\text{H-NMR}$  estimated the differences in the side-chain structures between the water insoluble fractions and original MWL. In this presentation, we will discuss the structure changes of lignin preparations in ILs by comparing them with those of lignin model compounds.

2010-203

活性酸素種との反応における非フェノール性リグニンモデル化合物のベラトリル芳香環と側鎖水酸基の位置の影響について

大村知士、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Effect of veratryl aromatic ring and location of side chain hydroxyl group on the reaction of non-phenolic lignin model compounds with active oxygen species.

Satoshi Ohmura, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Each of a non-phenolic  $\beta$ -O-4 type dimeric lignin model compound, 2-(3,5-difluorophenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (VDF), or a  $\beta$ -O-4 type model compound, 2-(3,5-difluorophenoxy)propane-1,3-diol or 3-(3,5-difluorophenoxy)propane-1,2-diol, was subjected to an oxygen alkaline treatment in the presence or absence of a generator of active oxygen species (AOS), 4-hydroxy-3-methoxybenzyl alcohol (VA). AOS are generated by the reaction of VA with oxygen. The incorporation of 3,5-difluorophenoxy group in the structure of the model compounds is to detect 3,5-difluorophenol (DFPh) when DFPh is liberated from the model compound during the treatment. It was suggested that AOS attack the side chain of VDF and non-phenolic 3,5-difluorophenoxy group in VDF is converted to DFPh, a phenolic compound. The effect of existences of veratryl aromatic ring, benzyl hydroxyl group, and secondary hydroxyl group on the reaction of the model compounds with AOS is also discussed.

2010-204

過酸化水素-アルカリ処理におけるシリングルおよびグアイアシルリグニンモデル化合物の分解の比較

石川裕剛、横山朝哉、松本雄二  
東京大学大学院農学生命科学研究科

Comparison of the degradation of syringyl and guaiacyl type lignin model compounds in alkaline hydrogen peroxide treatment.

Yugo Ishikawa, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: Non-phenolic lignin model compounds, 1-(3,4-dimethoxyphenyl)ethane-1,2-diol (G), 1-(3,4,5-trimethoxyphenyl)ethane-1,2-diol (S), 1,2-dimethoxybenzene (G'), and 1,2,3-trimethoxybenzene (S'), were reacted with hydroxyl (HO<sup>•</sup>) and oxyl anion (O<sup>•-</sup>) radicals, which were generated by the decomposition of hydrogen peroxide under alkaline conditions (pH 12.0, 70°C). The degradation of G was not very different from that of S, which suggests that the difference in the aromatic structure does not have significant influence on the reaction. The degradation of G' was clearly greater than that of S' but much smaller than those of G and S. These results suggest that the side chains of G and S are predominantly attacked by O<sup>•-</sup> (and HO<sup>•</sup>) and that high electron density of aromatic ring interferes with the reaction with O<sup>•-</sup> (and HO<sup>•</sup>).

2010-205

半流通型2段階加圧熱水処理によるブナ由来水可溶性リグニンの分析

山内一慶、河本晴雄、坂 志朗

京都大学大学院エネルギー科学専攻科

Characterization of water-soluble lignin-derived products from Japanese beech as treated by semi-flow two-step hot-compressed water.

Kazuchika Yamauchi, Haruo Kawamoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Abstract: Japanese beech was treated by two-step semi-flow hot-compressed water (1st stage: 230°C/10MPa/15min, 2nd stage: 270°C/10MPa/15min). Interestingly, 34.4% of lignin was recovered in the water-soluble portion at the 1st stage. In order to characterize lignin-derived products, the water-soluble portion at the 1st stage was extracted with ethyl acetate, and ethyl acetate layer and water layer were separated. UV absorption which is characteristic of aromatic ring was detected in both the water layer and the ethyl acetate layer. Some mono-saccharides were detected from the ethyl acetate layer after hydrolysis. These results may be suggested that some lignin-derived products at the 1st stage were related with saccharides from hemicelluloses, it is likely lignin-carbohydrate complex (LCC).

2010-206

リグニン熱分解中間体としてのカテコール、ピロガロール、クレゾール、キシレノール類の熱分解反応

モハメド・アスマディ、河本晴雄、坂 志朗

京都大学大学院エネルギー科学専攻科

Pyrolysis reactions of catechols, pyrogallols, cresols and xylenols as lignin pyrolysis intermediates  
Mohd Asmadi, Haruo Kawamoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Abstract: Secondary reactions of lignin pyrolysis intermediates were studied with a closed

ampoule reactor under N<sub>2</sub> at 600°C for 40–600 s. Two types of the intermediates were used; catechols and pyrogallols as products of O–CH<sub>3</sub> homolysis pathway; cresols and xylenols as those of OCH<sub>3</sub> rearrangement pathway. As a result, it was found that additional OH and CH<sub>3</sub> (especially OH) on phenol increase the reactivity, although phenol was fairly stable under the present conditions. Accordingly, O–CH<sub>3</sub> homolysis products especially syringyl-characteristic pyrogallols were more effectively converted into the gaseous products, mainly CO, even at short heating time as 120 s. On the other hand, the OCH<sub>3</sub> rearrangement products were comparatively stable and formed CH<sub>4</sub> and H<sub>2</sub> with coke at longer heating time as 600 s. Selective demethylation at the *o*- and *p*-position to phenolic OH was also observed in cresols, xylenols and trimethylphenol. A two step mechanism was proposed for this demethylation, which include radical coupling of H and C-centered radicals (*o*- or *p*-position) formed from the phenoxy radical intermediates and the following C–CH<sub>3</sub> homolysis. This is confirmed with the calculated BDEs (–60 kcal/mol) of the C–CH<sub>3</sub> bonds in the coupling products. Based on these results of intermediates pyrolysis, pyrolysis reactions of guaiacol and syringol are discussed.

2010–207

アルカリ処理クラフトリグニンのアルミニウムとの錯体形成能およびその毒性除去能に対するフェノール性水酸基の寄与に関する研究

相見 光<sup>\*1</sup>、栗本康司<sup>\*1</sup>、山内 繁<sup>\*1</sup>、池田 努<sup>\*2</sup>、眞柄謙吾<sup>\*2</sup>

<sup>\*1</sup> 秋田県立大学木材高度加工研究所、<sup>\*2</sup> 森林総合研究所

Studies on contribution of phenolic hydroxyl groups in kraft lignin to complexation with aluminum and reducing its toxicity.

Hikaru Aimi<sup>\*1</sup>, Yasuji Kurimoto<sup>\*1</sup>, Shigeru Yamauchi<sup>\*1</sup>, Tsutomu Ikeda<sup>\*2</sup>, Kengo Magara<sup>\*2</sup>

<sup>\*1</sup>Institute of Wood Technology, Akita Prefectural University, 11–1 Kaieisaka, Noshiro, Akita 016–0876, Japan, <sup>\*2</sup>Department of Biomass Chemistry, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305–8687, Japan

Abstract: Contribution of phenolic hydroxyl groups, including catechol type structures, in alkaline-treated kraft lignin to forming complex with aluminum and reducing its toxicity was examined in this study. The soda-cooked lignin, which was shown to be effective in reducing aluminum toxicity and forming aluminum complex, was also used. The results obtained in this study indicate that contribution of catechol structures in alkaline-treated kraft lignin and soda-cooked lignin to forming complex with aluminum was insignificant. Phenolic hydroxyl groups in alkaline-treated kraft lignin may contribute indirectly to forming complex with aluminum and reducing its toxicity by increasing its water solubility.

2010–208

Effect of residual lignin in alkali pulps on enzymatic hydrolysis of cellulose.

Yi Zhang, Shiho Takahashi, Hiroshi Ohi, Keiichi Nakamata

Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Japan, Technical & Development Division, Hokuetsu Paper Mills, Ltd., Japan

Abstract: Alkaline sulfite-anthraquinone (AS-AQ) cooking was applied to the pretreatment for enzymatic hydrolysis of cellulose of Japanese larch (*Larix leptolepis*) heartwood. We changed the ratio of Na<sub>2</sub>SO<sub>3</sub> in the cooking liquors, and found that the 40% ratio of Na<sub>2</sub>SO<sub>3</sub> at chips cooking had the capability of acquiring a high pulp yield and the lowest lignin content compared to others. During the hydrolysis of AS-AQ pulps, the content of glucose hydrolyzed in the enzymatic hydrolysate of a pulp containing a small amount of lignin was higher than that of a pulp containing a large amount of lignin at any cellulase charges (Filter paper cellulase unit: FPU). We determined the enzyme

adsorption to the pulps by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).

2010-209

セルロースの芳香族ヒドロキシ酸エステルにおける熱的特性と液晶性

石井大輔、中川瑞己、林久夫

龍谷大学理工学部

Thermal and liquid crystalline properties of cellulosic aromatic hydroxyl acid esters.

Daisuke Ishii, Mizuki Nakagawa, Hisao Hayashi

Faculty of Science and Technology, Ryukoku University, 1-5 Yokotani, Seta Oe-cho, Otsu-shi, Shiga 520-2194, Japan

Abstract: Liquid crystalline properties of esterification products of cellulose and gallic acid were investigated. Cellulose gallate formed liquid crystalline mesophase on heating between 220 and 230°C. As a gallic acid molecule possesses three hydroxyl and one carboxyl groups, polycondensed gallic acids as side chain of cellulose can form hyperbranched structure. The thermotropic liquid crystallinity of cellulose gallate is attributed to the hyperbranching nature of poly(gallate) side chains that can interrupt the interaction between cellulosic backbones.

2010-210

リグノスルホン酸／ポリビニルアルコール複合ゲルの調製とキャラクタリゼーション

仲西雄亮、寺本好邦、西尾嘉之

京都大学大学院農学研究科

Preparation and characterization of lignosulfonic acid/poly (vinyl alcohol) composite hydrogel.

Yusuke Nakanishi, Yoshikuni Teramoto, Yoshiyuki Nishio

Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

Abstract: Previously, we have prepared lignosulfonic acid (LSA)/poly(vinyl alcohol) (PVA) composite hydrogels via cross-linking with glutaraldehyde (GA) in aqueous solution. In the present study, to avoid elution of the LSA component in aqueous media and increase the LSA content, LSA/PVA composite hydrogels were prepared via blend films cast from their mixed aqueous solutions. Cross-linking moiety was introduced into the blend films by thermal treatment and/or reaction with GA. The retentivity of LSA in aqueous media was improved by formations of hydrogen bonding and sulfonate ester between LSA and PVA, both of which were corroborated by FT-IR measurement. The salt-splitting capacity and activity of the sulfo groups of LSA for the composite gel samples were found to reach ~0.7 mmol/g-gel and ~47 %, respectively.

2010-211

リグニンのエポキシ成形材料への応用検討

香川博之<sup>\*1</sup>、岡部義昭<sup>\*1</sup>、中村嘉利<sup>\*2</sup>、佐々木千鶴<sup>\*2</sup>

<sup>\*1</sup>日立製作所材料研研究所、<sup>\*2</sup>徳島大学大学院ソシオテクノサイエンス研究部

Possible application of lignin derivatives to molding compounds.

Hiroyuki Kagawa<sup>\*1</sup>, Yoshiaki Okabe<sup>\*1</sup>, Yoshitoshi Nakamura<sup>\*2</sup>, Chizuru Sasaki<sup>\*2</sup>

<sup>\*1</sup>Material Research Laboratory, Hitachi, Ltd. 7-1-1 Omika-cho, Hitachi-shi, Ibaraki-ken, 319-1292, Japan, <sup>\*2</sup> Department of Biological Science and Technology, Institute of Technology and Science, The University of Tokushima Graduate School, 2-1 Minamijosanjima-cho, Tokushima-shi, Tokushima-ken, 770-8501, Japan

Abstract: A more sustainable society by promoting global production that reduces the environmental burden of a product throughout its life cycle is required. We are currently researching

the use of woody biomass, particularly the application of woody lignin to the epoxy resin widely used in modern electric and electronic equipment. We have investigated the use of lignin derivatives as molding materials. Melt viscosities of molding compounds containing lignin derivatives as hardening agents were higher than that of a commercially-available molding compound. However, other mechanical and electrical properties of hardened compounds were comparable to those of the hardened commercially-available molding compound. We have successfully applied the molding compound containing lignin to mold a stator of a prototype of motor. Results suggest that woody lignin has great potential for application to electric devices.

2010-212

アシル化リグニンを原料とするエポキシ樹脂の合成と熱的性質

廣瀬重雄<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*3</sup>

<sup>\*1</sup>産業技術総合研究所、<sup>\*2</sup>リグノセルリサーチ、<sup>\*3</sup>福井工業大学工学部

Synthesis and thermal properties of epoxy resins derived from acetylated alcoholysis lignin.

Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*3</sup>

<sup>\*1</sup>Research Institute for Innovation in Sustainable Chemistry, AIST, Central 5, 1-1-4 Higashi, Tsukuba, Ibaraki 305-8565, Japan, <sup>\*2</sup>Lignocel Research Ltd., Fukui-City, Fukui, 910-3558 Japan, <sup>\*3</sup>Fukui University of Technology, 3-6-1 Gakuen, Fukui-City, Fukui 910-8505, Japan

Abstract: Acetylated alcoholysis lignin (AcAL) was allowed to react with bisphenol A diglycidyl ether (BPADGE) in the presence of a catalytic amount of phosphorous compound. The molar ratio of epoxy groups to acetoxyl groups ([EPOXY]/[PhOAc] ratios, mol/mol) was varied from 0.9 to 1.2. The chemical structure of the obtained epoxy resins was determined by FT-infrared spectra of epoxy resins. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures ( $T_g$ 's) of epoxy resins showed a maximum value at 1.1 of [EPOXY]/[PhOAc] ratio. The activation energy ( $E$ ) of curing reaction was determined by the integral method using values of reaction heats which were obtained by heating samples at various heating rates. The obtained value of  $E$  was ca. 90-210 kJ/mol. Thermal decomposition temperatures ( $T_d$ 's) of epoxy resins were almost constant regardless of [EPOXY]/[PhOAc] ratios, while the residue at 500 °C ( $MR_{500}$ ) of epoxy resins showed a maximum value at of 1.0 of [EPOXY]/[PhOAc] ratio.

2010-213

両親媒性リグニン誘導体の利活用

本間春海<sup>\*1\*2</sup>、及川千括<sup>\*2</sup>、幸田圭一<sup>\*2</sup>、平井卓郎<sup>\*2</sup>、浦木康光<sup>\*2</sup>、山田竜彦<sup>\*3</sup>

<sup>\*1</sup>ドーコン株式会社、<sup>\*2</sup>北海道大学大学院農学研究科、<sup>\*3</sup>森林総合研究所

Utilization of amphiphilic lignin derivatives.

Harumi Homma<sup>\*1\*2</sup>, Chihiro Oikawa<sup>\*2</sup>, Keiichi Koda<sup>\*2</sup>, Takuro Hirai<sup>\*2</sup>, Tatsuhiko Yamada<sup>\*3</sup>, Yasumitsu Uraki<sup>\*2</sup>

<sup>\*1</sup>Docon Co., Ltd., Sapporo 004-8585, Japan, <sup>\*2</sup>Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan, <sup>\*3</sup>Department of Biomass Chemistry, Forestry and Forest Products Research Institute, Tsukuba 305-8687, Japan

Abstract: Three types of polyethylene glycol (PEG) derivatives with epoxy group, PEGDE, EPEG and DAEO, were reacted with several isolated lignins to prepare amphiphilic lignin derivatives. The relationships between surface activities of the lignin derivatives and dispersibility or efficiency of cellulase activity enhancement were investigated to make use of the lignin derivatives as cement dispersants and cellulase-aid agents. DAEO-Lignin showed the highest surface activity, followed by EPEG-Lignin and PEGDE-Lignin. These lignin derivatives improved the enzymatic saccharification

yield of unbleached pulp. This effect of lignin derivatives is closely related to their surface activities. On the other hand, EPEG lignin had the highest dispersibility. This effect of cement dispersibility did not simply obey the surface activity.

2010-P01

高機能性微生物による木質バイオリファイナリー ～高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株のリグニン分解時に産生されるタンパク質のプロテオーム解析～

八木澤俊倫<sup>\*1</sup>、杉浦立樹<sup>\*2</sup>、平井浩文<sup>\*1</sup>、河岸洋和<sup>\*1\*2</sup>、亀井一郎<sup>\*3</sup>、森 智夫<sup>\*4</sup>、近藤隆一郎<sup>\*4</sup>

<sup>\*1</sup> 静岡大学農学部、<sup>\*2</sup> 静岡大学大学院創造科学院、<sup>\*3</sup> 宮崎大学農学部、<sup>\*4</sup> 九州大学大学院農学研究

Wood biorefinery with functional microorganisms. — Proteomic analysis of proteins produced by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under the ligninolytic condition—. Toshimichi Yagisawa<sup>\*1</sup>, Tatsuki Sugiura<sup>\*2</sup>, Hirofumi Hirai<sup>\*1</sup>, Hirokazu Kawagishi<sup>\*1\*2</sup>, Ichiro Kamei<sup>\*3</sup>, Toshio Mori<sup>\*4</sup>, Ryuichiro Kondo<sup>\*4</sup>

<sup>\*1</sup> Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*2</sup> Graduate School of Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*3</sup> Faculty of Agriculture, University of Miyazaki, Miyazaki 889-2192, Japan, <sup>\*4</sup> Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

Abstract: Proteomic analyses of proteins produced by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under differential ligninolytic condition were carried out. In the fungal-treated unbleached hardwood kraft pulp (under low lignin content condition), some ligninolytic enzymes were mainly detected. On the other hand, catalase, glutathione S-transferase, 1,4-benzoquinone reductase, enolase, mannose-6-phosphatase, and D-xylose reductase, including ligninolytic enzymes, were detected in the fungal-treated beech wood meals (under high lignin content condition). These results suggest that secreted proteins were different by lignin content of the culture, and that multiple metabolic pathways were activated under high lignin content condition.

2010-P02

高機能性微生物による木質バイオリファイナリー

森 智夫<sup>\*1</sup>、亀井一郎<sup>\*2</sup>、平井浩文<sup>\*3</sup>、近藤隆一郎<sup>\*1</sup>

<sup>\*1</sup> 九州大学大学院農学研究院、<sup>\*2</sup> 宮崎大学農学部、<sup>\*3</sup> 静岡大学農学部

Wood biorefinery with functional microorganisms.

Toshio Mori<sup>\*1</sup>, Ichiro Kamei<sup>\*2</sup>, Hirofumi Hirai<sup>\*3</sup>, Ryuichiro Kondo<sup>\*1</sup>

<sup>\*1</sup> Faculty of Agriculture, Graduate School of Kyushu University, <sup>\*2</sup> Faculty of Agriculture, Miyazaki University, <sup>\*3</sup> Faculty of Agriculture, Shizuoka University,

Abstract: Biorefinery process is environmental friendly and low-energy cost technology. Ethanol can be also biorefined from lignocellulosic material. There are two big problems on the biorefinery of woody materials for ethanol fermentable sugar. First is low-efficiency of biological treatment for lignin removal. Second, enzymatic saccharification process is less efficiency and its cost is quite expensive comparing with chemical process. Our final goal is the establishment of biorefinery process that can obtain fermentable sugars from woody material, especially from cedar wood. We are constructing functional organism that is capable to effective lignin-removal from wood, and screening of environmental microorganisms that produce functional glycosidases.

2010-P03

パラコツカス属細菌によるリグニンの分解

松下泰幸<sup>\*1</sup>、平田真寛<sup>\*2</sup>、高木博子<sup>\*2</sup>、本田宗央<sup>\*2</sup>、福島和彦<sup>\*1</sup>

\*<sup>1</sup> 名古屋大学大学院生命農学研究科、\*<sup>2</sup> イビデン株式会社

Biodegradation of lignin by *Paracoccus*. sp.

Yasuyuki Matsushita\*<sup>1</sup>, Masahiro Hirata\*<sup>2</sup>, Hiroko Takagi\*<sup>2</sup>, Munechika Honda\*<sup>2</sup>, Kazuhiko Fukushima\*<sup>1</sup>

\*<sup>1</sup> Graduate School of Bioagricultural Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, \*<sup>2</sup> IBIDEN Co., Ltd, Aoyanagi-cho 300, Ogaki, Gifu, 503-8503

Abstract: In this study, DHPs were subjected to the degradation by *Paracoccus*. sp. and the degradation products were investigated. After the degradation, the molecular weight of DHP was decreased and some phenolic compounds, such as salicylic acid, 2,3-dihydroxybenzoic acid, vanillin and vanillic acid were produced. When the <sup>13</sup>C-[ $\alpha$ ]-labeled DHP was degraded, <sup>13</sup>C-[ $\alpha$ ]-labeled vanillin and vanillic acid were yielded. Salicylic acid and 2,3-dihydroxybenzoic acid were also produced, however they were not labeled. These four compounds were not yielded when the culture was occurred with glycerin as a sole carbon source. Thus it can be concluded that salicylic acid and 2,3-dihydroxybenzoic acid were also produced from DHP.

2010-P04

カワラタケの産生する天然型ラッカーゼメディエータ

萩原通子、宮崎恵、鈴木綾乃、臼井明由美、林佳美、河合真吾、西田友昭

静岡大学農学部

Natural laccase mediator from the culture fluid of *Trametes versicolor*.

Michiko Hagiwara, Megumi Miyazaki, Ayano Suzuki, Ayumi Usui, Yoshimi Hayashi, Shingo Kawai, Tomoaki Nishida

Department of Environment and Forest Resources Science, Faculty of Agriculture, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan

Abstract: To elucidate the presence of natural laccase mediator, we searched for components in the culture fluid of laccase-producing medium of *Trametes versicolor*. Anthracene, which is not oxidized by laccase alone, was used for the assay of the ability of laccase mediator. An active fraction was obtained from the ethyl acetate extracts by repeated chromatography, and it was analyzed by GC-MS. It is revealed that *p*-hydroxybenzoic acid (HBA) was contained in the fraction. Then, to clarify the mediator ability of HBA, the oxidations of anthracene, reactive black 5 and nonphenolic  $\beta$ -O-4 lignin substructure model compound by laccase-HBA couple were conducted. The results demonstrated that all substrates were extensively decreased by this treatment.

2010-P05

アイソザイム分析及びNALDI-TOF-MS分析によるカバノアナタケ菌 IO-U1 株に感染したシラカンパ No. 8 幼植物体の防御応答の解明

鈴木美帆、鈴木 拓、高島有哉、石栗 太、飯塚和也、吉澤伸夫、横田信三

宇都宮大学農学部

Clarifying defence responses in Japanese birch No.8 plantlets infected with *Inonotus obliquus* IO-U1 strain by analyses of peroxidase isozyme and NALDI-TOF-MS.

Miho Suzuki, Hiromu Suzuki, Yuya Takashima, Futoshi Ishiguri, Kazuya Iizuka, Nobuo Yoshizawa, Sinzo Yokota

Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Japan

Abstract: It has been found that lignin and phenolic compounds accumulate, and peroxidase activity appears in Japanese birch plantlets immediately after the infection with *Inonotus obliquus*. In this study, invasion of the fungal hypha into tissues of the plantlets was observed by a scanning electron microscope. After 10 and 30 days of infection, invasion of the fungal hypha into vessels and wood fibers were observed in the plantlets. These results suggest that lignin and phenolic

compounds were accumulated to protect the plantlets from invasion of the fungal hypha. Analyses of peroxidase isozyme and Nano-Assisted Laser Desorption / Ionization (NALDI) –TOF–MS are currently under way.

2010–P06

ポプラ引張あて材細胞壁の木化過程

吉永 新<sup>\*1</sup>、楠元大志<sup>\*1</sup>、Françoise Raulans<sup>\*2</sup>、Gilles Pilate<sup>\*2</sup>、高部圭司<sup>\*1</sup>

<sup>\*1</sup>京都大学大学院農学研究科、<sup>\*2</sup>フランス国立農業研究所(INRA)オルレアン

Lignification process of lignified cell wall layers in poplar tension wood.

Arata Yoshinaga<sup>\*1</sup>, Hiroshi Kusumoyo<sup>\*1</sup>, Françoise Laurans<sup>\*2</sup>, Gilles Pilate<sup>\*2</sup>, Keiji Takabe<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Agriculture, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606–8502 Japan, <sup>\*2</sup>Forest Tree Improvement, Genetics and Physiology Research Unit, INRA–Orléans, 2163 Avenue de la Pomme de Pin, CS40001 Ardon, 45075, Orléans Cedex 2, France

Abstract: Lignification process of delignified cell wall layers namely, S1, S2 and compound middle lamella in poplar tension wood fibers was examined by UV microscopy and TEM. Formation process of G layer was compared to clarify that these lignified cell wall layers finish lignification before G layers are deposited or that lignification of these layers progresses during G layer formation. As a result, the UV absorption and also contrast in potassium permanganate staining in TEM in these lignified cell wall layers increased during G layer formation. This result suggests that lignification of these layers progresses during G layer formation.

2010–P07

MWL 抽出残渣の分画と分析(II) – Xylan–Lignin fraction (XL) のキャラクタリゼーション –

宮川泰幸、上高原浩、高野俊幸、中坪文明

京都大学大学院農学研究科

Fractionation and analysis of wood meal after extraction of MWL. ( II ) –Characterization of Xylan–Lignin fraction (XL)–.

Yasuyuki Miyagawa, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606–8502, Japan

Abstract: Xylan–lignin fraction (XL), which was prepared by several fractionation steps from wood meal after extraction of MWL, was characterized by conventional analytical methods. XL was found to be mainly composed by syringyl lignin with  $\beta$ –O–4 structure and xylan. Furthermore, XL was fractionated with dioxane/water (9:1) to give a soluble fraction (named DL) and a insoluble fraction (DLR). The former and the latter are mainly composed by syringyl lignin with  $\beta$ –O–4 structure and xylan, respectively. DLR is one of promising fractions for elucidation of LCC–bonds.

2010–P08

ケイ素吸収欠乏イネ突然変異体 *lsi1* におけるリグニン分析

山畑 梓<sup>\*1</sup>、鈴木利貞<sup>\*1</sup>、片山健至<sup>\*1</sup>、武田 真<sup>\*2</sup>

<sup>\*1</sup>香川大学農学部、<sup>\*2</sup>岡山大学資源植物研究所

Analysis of the lignin in a silicon uptake–deficient mutant *lsi1* of rice.

Azusa Yamahata, Toshisada Suzuki, Takeshi Katayama, Shin Taketa

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761–0795, <sup>\*2</sup>Institute of Plant Science and Resources, Okayama University, 2–20–1 Chuo, Kurashiki, Okayama 710–0046

Abstract: A rice mutant *lsi1* accumulates less silicon in the shoots than a wild type rice (cv. Oochikara). The mutant *lsi1* and the wild type were planted in seedling cases, lignin contents in leaf

and stem tissues were determined with Klason method. Lignin contents in leaves and stems of *lsi1* were higher than those of the wild type. Lignin contents in leaves and stems of *lsi1* planted in silicon addition soil (Si+) were lower than those in control soil (Si-). While cellulose contents in leaves and stems of *lsi1* were slightly higher than those of the wild type. These results suggested that silicon accumulation in rice might have a negative influence on the deposition of lignin and cellulose, and formation of the secondary cell walls, and thus it affected mechanical strength of rice.

2010-P09

DFRC 法による針葉樹の葉リグニンの検出

松井直之、大平辰朗

森林総合研究所

Detection of leaf lignin in Japanese gymnosperms by DFRC analysis.

Naoyuki Matsui, Tatsuro Ohira

Forestry and Forest Products Research Institute, Wood Extractives Lab. Matsunosato 1, Tsukuba, 305-8687 Japan

Abstract: A small amount of guaiacyl lignin was detected in sugi leaf by DFRC analysis in our previous report. In this study, the analysis was subjected to major Japanese gymnospermous leaves, hinoki, pine and ginkgo. Pine needle gave relatively much lignin degradates, in contrast, hinoki and ginkgo leaves gave only trace amount. Therefore, there is no lignin with arylether interunit linkages in hinoki and ginkgo leaves. This result shows the obvious difference in leaf-lignin distribution in gymnospermous species. The existence of well-developed cambial tissues is anticipated for the depositing site of lignin in rigid leaf, and pine and sugi leaves seem to have these characteristics.

2010-P10

ハンゲショウにおける 9,9'-デオキシネオリグナン・リグナンの生合成の検討

牧野啓輔, 博田健二, 片山健至, 鈴木利貞

香川大学農学部

Investigation of biosynthesis of 9,9'-deoxy-neolignans/lignans by *Saururus chinensis*.

Keisuke Makino, Kenji Denda, Takeshi Katayama, Toshisada Suzuki

Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795, Japan

Abstract: 9,9'-Deoxy-lignans/neolignans have been isolated from mainly Myristicaceae, Lauraceae, and Piperaceae plants. However, their biosynthesis is unknown. The present report describes stereochemistry and biosynthesis of D<sup>7</sup>-4,7-dihydroxy-3,3'-dimethoxy-8-O-4'-neolignane, whose *erythro* and *threo* isomers are named as Machilin C and D, respectively, in *Saururus chinensis* (Saururaceae). (1) The neolignans were prepared by dehydrogenative polymerization of isoeugenol with horseradish peroxidase and H<sub>2</sub>O<sub>2</sub>. The diastereomeric ratio was *erythro* : *threo* = 16 : 84. (2) The neolignans were isolated from the underground parts of *S. chinensis*. The diastereomeric ratio was 0 : 100 and the enantiomeric ratio was (+) : (-) = 2 : 98. To determine the enantiomeric ratio of the preferred diastereomer (Machilin D), its terminal double bond was saturated by catalytic reduction with palladium carbon and chiral HPLC of the resulting dihydro-Machilin D was done. (3) Dehydrogenative polymerization of isoeugenol with a cell-free extract from *S. chinensis* in the presence of H<sub>2</sub>O<sub>2</sub> gave the neolignans in the diastereomeric ratio of 14 : 86. However, this Machilin D was racemate. Furthermore, Sauchinon, a 9,9'-deoxy-lignan whose benzene ring lost its aromaticity was isolated from *S. chinensis*. A proposed biosynthetic pathway Sauchinon will be discussed.

2010-P11

### $\beta$ -1 型リグニン二量体モデル化合物の簡便な合成法

菱山正二郎<sup>\*1</sup>、大塚祐一郎<sup>\*1</sup>、中村雅哉<sup>\*1</sup>、加藤厚<sup>\*1</sup>、片山義博<sup>\*2</sup>、原啓文<sup>\*3</sup>、政井英司<sup>\*4</sup>、梶田真也<sup>\*5</sup>  
<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 日本大学生物資源学部、<sup>\*3</sup> 岡山理科大学、<sup>\*4</sup> 長岡技術大学、<sup>\*5</sup> 東京農工大学  
大学院 BASE

Efficient short step synthesis of  $\beta$ -1 lignin model compound.

Shojiro Hishiyama<sup>\*1</sup>, Yuichiro Otsuka<sup>\*1</sup>, Masaya Nakamura<sup>\*1</sup>, Atsushi Kato<sup>\*1</sup>, Yoshihiro Katayama<sup>\*2</sup>, Hirofumi Hara<sup>\*3</sup>, Eiji Masai<sup>\*4</sup>, Shinya Kajita<sup>\*5</sup>

<sup>\*1</sup>Forestry and Forest Products Research Institute, 1 Matsunosato Tsukuba, Ibaraki 305-8687, Japan, <sup>\*2</sup>College of Bioresource Science, Nihon University, Kanagawa 252-0880, Japan,

<sup>\*3</sup>Department of Biomedical Engineering, Okayama University of Science, 1-1 Ridaicho, Okayama 700-0005, Japan, <sup>\*4</sup>Department of Bioengineering, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-2188, Japan, <sup>\*5</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Abstract: Efficient short step synthesis of

1,2-Bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol [ $\beta$ -1 lignin model compound] has been achieved. The key step in the synthesis is hydroboration of

2,3-bis-(4-acetoxy-3-methoxyphenyl) acrylic acid obtained from perkin reaction of vanillin and homovanillic acid. In this strategy, only *threo* forms of desired compound is produced. The efficient conversion process of *threo* form into *erythro* form has also been discussed.

### 2010-P12

#### ジリグノールの酵素的脱水素重合

橋ヶ谷尚大、松下泰幸、今井貴規、福島和彦  
名古屋大学大学院生命農学研究科

Enzymatic dehydrogenative polymerization of dilignols.

Shota Hashigaya, Yasuyuki Matsushita, Takanori Imai, Kazuhiko Fukushima  
Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601

Abstract: To analyze the reaction kinetics of the dilignols in lignin biosynthesis, we tried enzymatic dehydrogenative polymerization of pinoresinol as a typical dilignol. LC/MS/MS analysis indicated that there were pinoresinol dimers in the reaction mixture. This results suggested that there was a possibility of the polymerization between dilignols each other in vivo. Reaction kinetics of coniferyl alcohol was compared with that of pinoresinol.

### 2010-P13

#### *tert*-ブトキシドによる $\beta$ -O-4 結合開裂反応における溶媒の影響

竹野甲子夫、横山朝哉、松本雄二  
東京大学大学院農学生命科学研究科

Effects of the solvents on the reaction of the  $\beta$ -O-4 bond cleavage using *tert*-butoxide.

Kineo Takeno, Tomoya Yokoyama, Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: The  $\beta$ -O-4 bond cleavage of a dimeric non-phenolic lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (2), was examined in systems using potassium *tert*-butoxide (KO<sup>t</sup>Bu)/THF and KO<sup>t</sup>Bu/1,4-dioxane. The  $\beta$ -O-4 bond of (2) was cleaved in both systems at 30°C and the rates were much greater than those in KO<sup>t</sup>Bu/<sup>t</sup>BuOH and KO<sup>t</sup>Bu/DMSO systems, which had been reported in our previous paper. A characteristic reaction

product 1,2-dimethoxybenzene (6), was detected in both systems. (6) was probably produced from 4-acetyl-1,2-dimethoxybenzene (4), a primary degradation product of the  $\beta$ -O-4 bond cleavage of (2).

2010-P14

Absolute configurations of erythro- and threo-syringylglycerol-8-O-4'-(sinapyl alcohol) ethers, dilignols as well as 8-O-4' neolignans.

Md. Shameul Alam, Toshisada Suzuki, Takeshi Katayama

Faculty of Agriculture, Kagawa University, Miki-cho, Kagawa 761-0795

Abstract: To clarify the stereochemical mechanism of the optically active syringylglycerol-8-O-4'-(sinapyl alcohol) ethers (SGSE) formation by the incubation of sinapyl alcohol (SA) with enzyme preparations of *Eucommia ulmoides*, absolute configuration of four stereoisomers, (+)-erythro-, (-)-erythro-, (+)-threo-, and (-)-threo isomers, of SGSEs that contain a chiral secondary benzyl alcohol were determined as (7*R*, 8*S*), (7*S*, 8*R*), (7*S*, 8*S*) and (7*R*, 8*R*), respectively, by Mosher's method [<sup>1</sup>H NMR analysis of tri-(*R*)-(+)- $\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetate (MTPA) esters of SGSEs] with our related empirical rules. Four stereoisomers of SGSEs were obtained by dehydrogenations of SA with FeCl<sub>3</sub> followed by reversed phase HPLC and chiral HPLC.

2010-P15

ヨウ化アルミニウム処理によるクラフトリグニンの構造変化

塩澤洋介<sup>\*1</sup>、幸田圭一<sup>\*2</sup>、浦木康光<sup>\*2</sup>、岸本崇生<sup>\*3</sup>

<sup>\*1</sup>北海道大学大学院農学研究院、<sup>\*2</sup>北海道大学大学院農学研究科、<sup>\*3</sup>富山県立大学工学部

Structural changes in kraft lignin by aluminium iodide (III) treatment.

Yosuke Shiozawa<sup>\*1</sup>, Keiichi Koda<sup>\*2</sup>, Yasumitsu Uraki<sup>\*2</sup>, Takao Kishimoto<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, Hokkaido 060-8589, Japan, <sup>\*2</sup>Research Faculty of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, Hokkaido 060-8589, Japan, <sup>\*3</sup>Faculty of Engineering, Toyama Prefectural University, 5180 Kurokawa, Imizu, Toyama 939-0398, Japan

Abstract: We have been trying to develop a new method to modify technical lignin chemically, aiming at fabricating a novel biomass-based polymer with functionality in terms of biorefinery. In this study, kraft lignin, an important technical lignin, was subjected to a treatment with AlI<sub>3</sub>, an effective ether-cleaving reagent under a mild reaction condition, to give lower mass compounds with higher hydroxyl content. As in the case of a lignin polymer model compound in a separate experiment, the AlI<sub>3</sub> reagent was found to degrade KL and increase hydroxyl group significantly, depending on the reaction condition.

2010-P16

フェルラ酸・グリコール酸共重合体の合成および特性解析

河村奈々絵、前田拓希、福井宙、石井大輔、林久夫

龍谷大学理工学部

Synthesis and characterization of poly(ferulic acid-*co*-glycolic acid).

Nanae Kawamura, Hiroki Maeda, Hiroshi Fukui, Daisuke Ishii, Hisao Hayashi

Faculty of Science and Technology, Ryukoku University, 1-5 Yokotani, Seta Oe-cho, Otsu, Shiga 520-2194, Japan

Abstract: Copolymerization of ferulic and glycolic acids were performed to obtain heat-resistant liquid crystal polyester. It was revealed that poly(ferulic acid-*co*-glycolic acid) obtained after a reflux in acetic anhydride/sodium acetate at 160°C for 18 h formed liquid crystalline mesophase between

162 and 213°C, in spite of its low molecular weight comprising three ferulic and two glycol units.

2010-P17

カフェ酸をモノマーとする多分岐型ポリエステル合成及び構造解析

前田拓希, 石井大輔, 林久夫

龍谷大学理工学部

Synthesis and structural analysis of poly(caffeic acid).

Hiroki Maeda, Daisuke Ishii, Hisao Hayashi

Department of Materials Chemistry, Graduate School of Science and Technology, Ryukoku University, 1-5 Yokotani, Seta Oe-cho, Otsu-shi, Shiga 520-2194, Japan

Abstract: Caffeic acid, a cinnamic acid derivative provided from lignin, can be polymerized to form multi-branched polyester, because caffeic acid has two phenolic hydroxyl groups and one carboxyl group. In this study, synthesis and characterization of poly(caffeic acid) (PCA) were performed. The polymerization was performed in a two-step process. First, caffeic acid was acetylated using acetic anhydride and sodium acetate under a reflux in 160 °C. Then a polycondensation was performed at 160 °C under a vacuum. The product was analyzed by using FT-IR, NMR, GPC, MALDI-TOF-MS, DSC and hot stage-equipped polarizing microscope. It was revealed that PCA obtained after polycondensation has a melting point at about 180 °C and forms anisotropic phase under molten state in response to external mechanical field.

2010-P18

4級アミン型リグノフェノールによる貴金属の回収

Parajuli Durga, 広田耕一, 瀬古典明

独立行政法人日本原子力研究開発機構

Recovery of precious metals using quaternary amine type lignophenol.

Durga Parajuli, Koichi Hirota, Noriaki Seko

Quantum Beam Directorate, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma, 370-1292, Japan.

Abstract: Quaternary amine type derivative of lignophenol (TMA-CLP) was prepared by electron beam irradiation followed by chemical treatment with trimethylamine. The adsorbent was tested for its adsorption behavior for a number of metal ions and found to exhibit selectivity for Au(III), Pd(II), and Pt(IV) in 0.5 to 5.0 M hydrochloric acid medium. From the adsorption isotherm study, the maximum loading capacity of TMA-CLP for Au(III), Pd(II), and Pt(IV) was evaluated as 4.3, 0.74, and 1.3 mol/kg of the dry adsorbent, respectively.

2010-P19

電子ビームによる高機能性リグノフェノール吸着剤の開発

広田耕一, Parajuli Durga, 瀬古典明

独立行政法人日本原子力研究開発機構

Development of high functional lignophenol sorbent using electron beam.

Koichi Hirota, Durga Parajuli, Noriaki Seko

Quantum Beam Directorate, Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma, 370-1292, Japan.

Abstract: Wood derived lignin has been modified with ethylenediamine after electron beam irradiation. Its performance for the recovery of precious metals has been studied and the results are compared with that of chemically modified derivative. Electron beam induced modification yielded better performing sorbent. Electron beam is a good tool for synthesis of high functional bio-sorbent.

2010-P20

糖化残渣からのリグニン抽出とその性状評価

伊藤一志<sup>\*1</sup>、星井弘道<sup>\*1</sup>、伊藤新<sup>\*1</sup>、高橋武彦<sup>\*1</sup>、小林淳一<sup>\*1</sup>、遠田幸生<sup>\*2</sup>、郷地元博<sup>\*3</sup>

<sup>\*1</sup> 秋田県立大学、<sup>\*2</sup> 秋田県産業技術総合研究センター、<sup>\*3</sup> 中央化工機商事株式会社

Extract of lignin from saccharification residue and estimation of chemical nature of the lignin.

Kazushi Ito<sup>\*1</sup>, Hiromichi Hoshii<sup>\*1</sup>, Arata Ito<sup>\*1</sup>, Takahiko Takahashi<sup>\*1</sup>, Junichi Kobayashi<sup>\*1</sup>, Yukio Enda<sup>\*2</sup>, Motohiro Gochi<sup>\*3</sup>

<sup>\*1</sup>Akita Prefectural University. 84-4 Tsuchiya-ebinokuti, Yurihonjo, Akita 015-0055, Japan, <sup>\*2</sup>Akita Research and Development Center. 4-11 Sanuki-araya, Akita 010-1623, Japan, <sup>\*3</sup>Chuo Kakohki Shoji Co., Ltd. 3-6 Kanda Nishiki Chiyoda, Tokyo 101-0054, Japan

Abstract: One of the important issues in bio-ethanol production from woody biomass is the effective usage of saccharification residue. The saccharification residue includes lignin, which is contained a variety of functional groups. It is possible to apply the lignin as raw material for chemical agents and plastics, thus there is a need for an effective extraction technique of lignin from the saccharification residue. In this study, saccharification residue was applied to the extraction technique that was reported in previous study. This report explained that the lignin was extracted from saccharification residue.

## 第 56 回 (2011.09.15-16)山形大学 農学部

2011-101

$\beta$ -1 型スピロジエノン構造に関する研究: シリングル型同モデル化合物と広葉樹リグニンの NMR 化学シフト値の比較

秋山拓也<sup>\*1</sup>、菊地淳<sup>\*2</sup>、横山朝哉<sup>\*1</sup>、松本雄二<sup>\*1</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科、<sup>\*2</sup> 理化学研究所植物科学研究センター

Study on spirodienone structures with  $\beta$ -1 linkage: NMR chemical shifts of the syringyl type model and the corresponding signals on the HSQC spectrum of hardwood lignin.

Takuya Akiyama<sup>\*1</sup>, Jun Kikuchi<sup>\*2</sup>, Tomoya Yokoyama<sup>\*1</sup> and Yuji Matsumoto<sup>\*1</sup>

<sup>\*1</sup>The University of Tokyo, Graduate School of Agricultural and Life Sciences, 1-1-1 Yayoi, Bunkyo, Tokyo 113-8657, <sup>\*2</sup>RIKEN Plant Science Center, 1-7-22, Suehiro, Tsurumi, Yokohama, Kanagawa 230-0045

Abstract: A novel lignin model compound of syringyl type spirodienone structures ( $\beta$ -1/ $\alpha$ -O- $\alpha'$ ) was obtained by oxidative coupling of sinapyl alcohol  $\gamma$ -acetate with 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanol. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of the acetylated model compound were compared with the signals on the HSQC spectrum of acetylated avicenia lignin (MWL). The <sup>1</sup>H and <sup>13</sup>C chemical shifts of signals from  $\alpha$ ,  $\beta$ , and  $\gamma$ -positions in one side chain part of the model were in well agreement with the candidate correlation signals of spirodienone structures on the HSQC spectrum of the acetylated MWL.

2011-102

Dissolution of ball-milled plant cell walls in ionic liquid systems for HSQC NMR analysis.

Chen Qu, Takao Kishimoto, Masahiro Hamada, Noriyuki Nakajima

Bioorganic Chemistry Lab, Department of Biotechnology, Toyama Prefectural University 5180, Japan

Abstract: Several ionic liquids with and without co-solvent were used to find milder conditions than those reported so far for complete dissolution of ball-milled plant cell walls in ionic liquids. Among the ionic liquids tested, 1-allyl-3-methylimidazolium chloride ([Amim]Cl) was the most

effective ionic liquid for our purposes. Some co-solvents such as N,N-dimethylacetamide (DMAc) and pyridine were found to be quite effective to increase the solubility of the cell walls. The milled fir wood prepared by ball-milling for 8 h was dissolved completely in [Amim]Cl-DMAc (2:1, w/w) and [Amim]Cl-pyridine (1:1, w/w) even at room temperature (30°C). 1H-13C correlation HSQC NMR experiments were successfully conducted with the *in situ* acetylated fir wood. The differences between the two solvent systems were discussed based on the spectra.

2011-103

木質バイオマスの定量・微細構造解析のための HSQC/HMBC NMR 法の開発

西村裕志<sup>\*1</sup>、小澤佑<sup>\*1</sup>、岡村英保<sup>\*1</sup>、佐々木碧<sup>\*2</sup>、片平正人<sup>\*1</sup>、渡辺隆司<sup>\*2</sup>

<sup>\*1</sup>京都大学 エネルギー理工学研究所 生体エネルギー研究分野 <sup>\*2</sup>京都大学 生存圏研究所 バイオマス変換分野

Developments for quantitative and microstructural analyses of woody biomass using HSQC/HMBC NMR.

Hiroshi Nishimura<sup>\*1</sup>, Yu Kozawa<sup>\*1</sup>, Hideyasu Okamura<sup>\*1</sup>, Midori Sasaki<sup>\*2</sup>, Masato Katahira<sup>\*1</sup>, Takashi Watanabe<sup>\*2</sup>

<sup>\*1</sup>Laboratory of Bioenergy, Institute of Advanced Energy (IAE), Kyoto University, Kyoto 611-0011, Japan. <sup>\*2</sup>Laboratory of Biomass Conversion, Research Institute for Sustainable Humanosphere (RISH), Kyoto University, Kyoto 611-0011, Japan

Abstract: Woody biomass is a heterogeneous material and its microstructure is not yet fully understood. Here, we developed an analytical method of intact and biodegraded wood using solution state NMR without any chemical treatment. Wood pieces were milled in mild conditions and dissolved in DMSO-*d*<sub>6</sub>. Optimization of analytical parameters gave high resolution and quantitative HSQC spectra. NMR signals of lignin microstructures were well distinguished and assigned by HMBC correlations. We applied this method to biodegraded wood by white rot fungus and demonstrate a decrease of lignin contents.

2011-104

バイオリファイナリーのためのリグニンのMALDI-FT-ICR MS

吉岡康一、渡邊崇人、本田与一、渡辺隆司

京都大学生存圏研究所

MALDI-FT-ICR MS of lignin for biorefinery.

Koichi Yoshioka, Takahito Watanabe, Yoichi Honda, Takashi Watanabe

Research Institute for Sustainable Humanosphere, Kyoto University, Kyoto 611-0011, Japan

Abstract: Mass spectrometry by MALDI ionization gives direct structural information in a wide range of molecular mass regions. However, reports on mass spectrometry of lignin by MALDI ionization are still limited. Our group has analyzed isolated and synthetic lignin using MALDI-MS. In this study, the milled wood from *Eucalyptus globulus* was analyzed with ultra-high resolution mass spectrometry with Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR MS). The mass spectrometry provided the peaks originating from the inter linkages of lignin and hexoses. The mass spectrometry is useful for wood biomass refinery, especially for structure-based utilization of lignin.

2011-105

ToF-SIMS を用いたリグニン構造の解析

井岡昂介、松下泰幸、今井貴規、齊藤香織、福島和彦

名古屋大学大学院生命農学研究科

Analysis of lignin structure using ToF-SIMS.

Kousuke Ioka, Yasuyuki Matsushita, Takanori Imai, Kaori Saito, and Kazuhiko Fukushima  
Graduate School of Bioagricultural Science, Nagoya University, Nagoya, 464-8601

Abstract: From the experiments using model compounds, when lignin is analyzed by ToF-SIMS, the common interunit linkages without 5-5' linkage are cleaved and the characteristic secondary ions of lignin are generated. In previous study, the characteristic secondary ions at  $m/z$  137 and 151 are produced from the phenylcoumaran type lignin model compound by ToF-SIMS. But it is still not clear which aromatic ring generates these ions and whether the  $\beta$ -5' linkage is cleaved by ToF-SIMS. In this study, the phenylcoumaran type lignin model compound and its deuterium-labelled compound were synthesized and analyzed by ToF-SIMS. From the result, the  $\beta$ -5' linkage seems not to be cleaved by ToF-SIMS.

2011-106

IR-SNOMによる木質組織の分析

山嵜崇之、松本雄二

東京大学大学院農学生命科学研究科生物材料科学専攻木材化学研究室

IR-SNOM analysis of wood tissue.

Takayuki Yamagishi, and Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, 113-8657, Japan

Abstract: IR-SNOM (Infrared-Scanning near-field optical microspectrometer) is potentially capable of obtaining IR spectra from a microscopic area of submicron order. After the wood fiber of *Quercus serrata* was manually isolated, it was put on the KBr tablet and subjected to IR-SNOM analysis. We succeeded in obtaining a good near-field IR spectrum by omitting the scattering light derived from surrounding tissue. The absorbance peak at around  $835\text{cm}^{-1}$  in near-field IR spectrum from wood fiber was stronger than the corresponding peak in the usual IR spectrum obtained from wood powder. Considering that the spectrum obtained from wood powder by usual FT-IR reflects the average spectrum of whole sample, peaks characteristic in near-field IR spectrum may indicate the specific feature of the observed sample.

2011-107

木材の熱分解生成物の定量的検討 ～過ヨウ素酸処理木粉の熱分解生成物とリグニン含有率の関係～

錦織香<sup>\*1</sup>、勝亦京子、秋山拓也、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科生物材料科学専攻木材化学研究室 <sup>\*1</sup>現在: Biomaterial in Tokyo

Abstract: Quantitative analysis of pyrolysis products of Wood material. -Relation with pyrolysates of periodate treated wood material and Lignin contents-

Kaoru Nishikiori<sup>\*1</sup>, Kyoko Katsumata, Takuya Akiyama, Tomoya Yokoyama, Yuji Matsumoto  
Department of Biomaterials Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo, 113-8657, Japan

<sup>\*1</sup>Present address: Biomaterial in Tokyo

Abstract: In order to understand the effect of lignin on the formation of pyrolysis products, wood meals with increased lignin content prepared by periodate pre-treatment were subjected to pyrolysis by the use of tube type kiln. Lignin content of prepared samples were 45.1% (by 4days

periodate treatment) and 67.6% (by 7 days periodate treatment) in addition to 26.2% of un-treated wood meal. The contribution of lignin to the formation of pyrolysis residue was made clear. Interestingly, the increase of lignin content by periodate treatment did not result in the increase of the total yield of aromatic type low molecular pyrolysis products. Results obtained here as well as those obtained in our former experiment by the use of chlorite pre-treatment suggested that the formation of pyrolysis products is affected not only by the amount of lignin but also by the chemical changes caused during the pretreatment.

2011-108

コニフェリルアルコール及びシナピルアルコールの熱分解反応特性とリグニン熱分解における役割  
小竹毅郎, 河本晴雄, 坂 志朗

京都大学大学院エネルギー科学研究科エネルギー社会・環境科学専攻

Pyrolytic reactivities of coniferyl alcohol and sinapyl alcohol and their roles in lignin pyrolysis.

Takeo Kotake, Haruo Kawamoto, Shiro Saka

Department of Socio-Environmental Energy Science, Graduate School of Energy Science,  
Kyoto University, Kyoto 606-8501, Japan

Abstract: Pyrolytic  $\beta$ -ether cleavage of dimers gives coniferyl alcohol and sinapyl alcohol, while their yields reported from the isolated lignins are not significant. To clarify this contradiction, pyrolytic reactivities of coniferyl alcohol and sinapyl alcohol were studied under  $N_2/200-350^\circ C/5min$ . As a result, evaporation of coniferyl alcohol was competed with some pyrolytic reactions to form condensation products and C $\gamma$ -oxidation (coniferyl aldehyde) and C $\gamma$ -reduction (isoeugenol) products at  $250-350^\circ C$ , where  $\beta$ -ether linkages in dimers are reported to be cleaved. Role of coniferyl alcohol as a pyrolysis intermediate of lignin was also discussed by the yield (coniferyl alcohol + coniferyl aldehyde + isoeugenol) from sugi (*Cryptomeria japonica*) wood and MWL. The yields were only less than 1.5 wt% under neat conditions, while the yields increased by 1.3 to 4.5 times along with the yields of dimer/trimer fractions in 1,3-diphenoxybenzene which suppressed the condensation reactivity of coniferyl alcohol.

2011-109

リグニンの  $\beta$ -O-4 結合新規選択的開裂法 ( $\gamma$ -TTSA 法) の検討(2) - DHP への適用 -

安藤大将<sup>\*1</sup>, 西村裕志<sup>\*2</sup>, 片平正人<sup>\*2</sup>, 高野俊幸<sup>\*1</sup>, 中坪文明<sup>\*3</sup>, 矢野浩之<sup>\*3</sup>

<sup>\*1</sup> 京都大学大学院農学研究科 <sup>\*2</sup> 京都大学エネルギー理工学研究所 <sup>\*3</sup> 京都大学生存圏研究所

Studies on the selective cleavage method for  $\beta$ -O-4 linkages of lignins ( $\gamma$ -TTSA method)(2)  
-Application to lignin model polymer (DHP)-

Daisuke Ando<sup>\*1</sup>, Hiroshi Nishimura<sup>\*2</sup>, Masato Katahira<sup>\*2</sup>, Toshiyuki Takano<sup>\*1</sup>, Fumiaki Nakatsubo<sup>\*3</sup>,  
Hiroyuki Yano<sup>\*3</sup>

<sup>\*1</sup> Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kyoto, 606-8502, Japan, <sup>\*2</sup> Institute of Advanced Energy, Kyoto University, Gokasho, Kyoto, 611-0011, Japan, <sup>\*3</sup> Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Kyoto, 611-0011, Japan

Abstract: Application of  $\gamma$ -TTSA method (consisted of four reactions; tosylation, thioetherification, sulfonation, alkali-treatment), which has been proposed as new selective  $\beta$ -O-4 cleavage method, to lignin model polymer (DHP) with various linkages such as  $\beta$ -5,  $\beta$ - $\beta$  and  $\beta$ -O-4 was investigated. FT-IR and  $^1H$ -NMR spectra of the four products suggested that the former three reactions proceeded in DHP as well as in  $\beta$ -O-4 model dimer. HSQC-NMR spectrum of the final product after the alkali-cleavage revealed that  $\beta$ -O-4 linkages were selectively cleaved with the reaction of other linkages such as  $\beta$ -5 and  $\beta$ - $\beta$  in the last reaction.

2011-110

活性酸素種による糖の水素引き抜き反応における速度論的同位体効果の解析

中川明彦、横山朝哉、松本雄二

東京大学大学院農学生命科学研究科

Analysis of kinetic isotope effect in hydrogen abstraction from carbohydrate by active oxygen species.

Akihiko Nakagawa, Tomoya Yokoyama, and Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo 113-8657, Japan

Abstract: In our previous studies, a clear kinetic isotope effect was observed when a pair of a carbohydrate model compound, methyl  $\beta$ -D-glucopyranoside (MGP), and its deuterated compound at the anomeric or C-2 position, methyl  $\beta$ -D-(1-2H)glucopyranoside or methyl  $\beta$ -D-(2-2H)glucopyranoside, respectively, were reacted with active oxygen species (AOS) generated by reactions of O<sub>2</sub> with a phenolic compound, 2,4,6-trimethylphenol (TMPH), under oxygen delignification conditions. This result indicates that the AOS abstract the hydrogens connected to the anomeric and C-2 positions of MGP. Contrarily, no clear kinetic isotope effect was observed when AOS were generated by reactions of O<sub>2</sub> with another phenolic compound, 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, VA), and hence, the abstraction of the hydrogens could not be confirmed in this case. In this study, a pair of MGP and its completely deuterated compound at all the positions, (2H<sub>3</sub>)methyl  $\beta$ -D-(1,2,3,4,5,6,6-<sup>2</sup>H<sub>7</sub>)glucopyranoside, was reacted with AOS generated from TMPH or VA under oxygen delignification conditions to examine whether a clear kinetic isotope effect is always observed when AOS abstract one of the hydrogens from the C-H bonds in MGP. A clear kinetic isotope effect was observed in each system of the AOS generators, which shows that AOS generated both from TMPH and VA certainly abstract the hydrogens from the C-H bonds in MGP. We further discuss on the appearance of kinetic isotope effect in the following text.

2011-111

アルカリ蒸解過程におけるリグニン  $\beta$ -O-4 結合開裂の速度論的検討(2) -芳香核構造および側鎖立体構造の影響-

清水智子、横山朝哉、秋山拓也、松本雄二

東京大学大学院農学生命科学研究科

Kinetic analysis of the  $\beta$ -O-4 bond cleavage of lignin during alkaline cooking process (2)

Effect of aromatic structure and stereo structure of side chain.

Satoko Shimizu, Tomoya Yokoyama, Takuya Akiyama, and Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 113-8657, Japan.

Abstract: In this study, it was examined how the aromatic structure and the stereo structure of side chain of non-phenolic  $\beta$ -O-4 type unit in lignin control the rate of the  $\beta$ -O-4 bond cleavage during alkaline cooking using the *erythro* and *threo* isomers of non-phenolic model compounds, 2-(methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (VG), 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (VS), and 2-(methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)propane-1,3-diol (SG). The disappearances of all the compounds used were well approximated to pseudo-first-order reactions. The rate constants (*k*) of the *erythro* isomers of all the compounds were about 4 times as large as those of the corresponding *threo* isomers. The both isomers of VS disappeared much faster than those of VG. On the other hand, SG degraded only

slightly faster than VG in any case. These results suggest that the effect of the substitution of syringyl nucleus for guaiacyl nucleus on the rate of the  $\beta$ -O-4 bond cleavage appears more strongly when syringyl nucleus exists as the cleaving phenoxy ether than when it is present as the carbon framework. Number of peaks observed in the HPLC chromatograms was larger when the mixtures obtained from the *threo* isomers of all the compounds were analyzed than when those from the corresponding *erythro* isomers were analyzed. This suggests that the mechanism of the  $\beta$ -O-4 bond cleavage of *threo* isomer is not completely the same with that of *erythro* counterpart.

2011-112

Effects of DMSO/LiCl dissolution on the structural characteristics of rice straw lignin.

Wenjuan Wu<sup>\*1\*2</sup>, Zhiguo Wang<sup>\*1\*2</sup>, Yongcan Jin<sup>\*1\*2</sup>, Yuji Matsumoto<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Agricultural and Life Sciences, The University of Tokyo, 113-8657, Japan

<sup>\*2</sup> Department of Paper Science and Technology, Nanjing Forestry University, China

Abstract: Four samples of rice straw (stem only, stem with knot, leaf including sheath, whole straw) were subjected to the dissolution in DMSO/LiCl after the planetary ball milling pretreatment. Regenerated materials from the DMSO/LiCl solution or suspension were treated by cellulolytic enzymes. The samples were almost completely dissolved in DMSO/LiCl by 1 h ball milling. The chemical nature of the regenerated materials and their residue after the enzymatic hydrolysis were analyzed and the accessibility of this rice straw to the enzymatic hydrolysis was evaluated.

2011-113

One electron oxidation of wood and carbohydrates.

Ulla Westermark<sup>\*1</sup>, Anna Pantze<sup>\*1</sup>, Olov Karlsson<sup>\*1</sup>

<sup>\*1</sup> Wood Material Science, Campus Skellefteå, Luleå University of Technology, S-931 87 Skellefteå, Sweden, <sup>\*1</sup> Present address: Hörnåkersvägen 45, SE-18365 Täby, Sweden

Abstract: One electron oxidation of lignocellulosic materials can give a material with self bonding properties on further pressing and heating. Similar oxidation gives wet strength properties to paper after short heating. One electron oxidation of lignocelluloses materials are complicated reactions and both oxidized lignin and carbohydrates can contribute to the bonding ability. This paper present results pointing to that oxidized carbohydrates of the dialdehyde type plays an important role in the bonding.

2011-114

酸性サルファイトパルプ残留リグニンがパルプの酵素糖化挙動に及ぼす影響

谷藤溪詩<sup>\*1</sup>, 張翼<sup>\*1</sup>, 高橋史帆<sup>\*2</sup>, 大井洋<sup>\*1</sup>, 中俣恵一<sup>\*3</sup>

<sup>\*1</sup> 筑波大学大学院生命環境科学研究科, <sup>\*2</sup> ニューブランズウィック州立大学, カナダ

<sup>\*3</sup> 北越紀州製紙株式会社 技術開発部

Effect of residual lignin in acid sulfite pulp on behavior of enzymatic saccharification of pulp.

Keishi Tanifuji<sup>\*1</sup>, Zhang Yi<sup>\*1</sup>, Shiho Takahashi<sup>\*2</sup>, Hiroshi Ohi<sup>\*1</sup>, Keiichi Nakamata<sup>\*3</sup>

<sup>\*1</sup> Graduate School of Life and Environmental Sciences, University of Tsukuba, 305-8572, Japan

<sup>\*2</sup> Department of Chemical Engineering, University of New Brunswick, Canada, <sup>\*3</sup> Technical and Development Division, Hokuetsu Kishu Paper Co., Ltd.

Abstract: The lignin contents of pulp with enzyme impregnated and amounts of the enzyme in pulp were analyzed by the acetyl bromide method and the K number method to establish a method for estimating amounts of enzyme adsorbed to residual lignin in the enzyme-treated pulps. The estimation is very important to develop a highly efficient enzyme-hydrolysis of ligno-cellulosics materials for bio-ethanol production. When lignin analysis was conducted by the acetyl bromide

method, the apparent lignin content of pulp with impregnation of 12.7 FPU of enzyme per one gram of pulp was about 9%, which was only 1% point higher than the lignin content of pulp (7.9%). The apparent K numbers of pulp increased with the amounts of enzyme impregnated in pulp. However, the apparent K numbers of the pulp residues decreased during the enzymatic treatment of pulps. The residual lignin of the pulps, which were less soluble in water, partly liberated from the pulps during the enzymatic treatment. In addition, a part of reducing sugars in the hydrolysate must consume the permanganate of the K number method. It is still difficult to establish it, and therefore the both methods are discussed in comparison with the pyrolysis-gas chromatography/ mass spectrometry (Py-GC/MS) method.

2011-115

Sulfurous acid treatment of wood.

Yan Shi, Tomoya Yokoyama, Yuji Matsumoto

Graduate School of Agricultural and Life Sciences, The University of Tokyo, 113-8657, Japan

Abstract: From the wood bio-refinery's point of view, now, sulfurous acid treatment is still attractive because not only lignin is effectively removed but also hemicelluloses can be hydrolyzed to monosaccharides during the treatment. So in this work, first, in order to understand the basic behavior of hemicelluloses during the dilute acid treatment, hydrolysis of Radiata Pine (RP) with dilute hydrochloric acid, sulfuric acid and sulfurous acid was conducted. Main concern was whether or not it is possible to convert as much hemicelluloses as possible into monosaccharides while depressing the further degradation of produced monosaccharides and cellulose degradation. Under the condition examined, the highest yield of each monosaccharide from hemicelluloses were as follows: mannose 87%, xylose 96%, galactose 85%, and, arabinose 98%. Second, in order to know degradation of monosaccharide in these acids, model degradation experiment was conducted. The results showed that, compared with that in HCl and in H<sub>2</sub>SO<sub>4</sub>, degradation of each monosaccharide in sulfurous acid hardly changes significantly with increase of acid concentration. In a word, sulfurous acid treatment seems to be of benefit to bio-refinery from hemicellulose.

2011-116

リグニン性状の水蒸気爆砕条件依存性

香川博之<sup>\*1</sup>、岡部義昭<sup>\*1</sup>、佐々木千鶴<sup>\*2</sup>、中村嘉利<sup>\*2</sup>

<sup>\*1</sup>(株)日立製作所日立研究所電子材料研究部、<sup>\*2</sup>徳島大学大学院ソシオテクノサイエンス研究部ライフシステム部門

Effect of the steam-explosion conditions on cedar-lignin properties.

Hiroyuki Kagawa<sup>\*1</sup>, Yoshiaki Okabe<sup>\*1</sup>, Chizuru Sasaki<sup>\*2</sup>, Yoshitoshi Nakamura<sup>\*2</sup>

<sup>\*1</sup>Hitachi Research Laboratory, Hitachi, Ltd., Hitachi, 319-1292 Japan, <sup>\*2</sup>Department of Life System, Institute of Technology and Science, The University of Tokushima, Tokushima, 770-8506, Japan

Abstract: It is required that a more sustainable society is realized by promoting global production that reduces the environmental burden of a product throughout its life cycle. We are currently researching the use of woody biomass, particularly the application of woody lignin to the epoxy resin widely used in modern electric and electronic equipment. It is preferable that the lignin has homogeneous properties when we apply it to electric and electronic devices. We have investigated the variability and dependence of lignin properties on steam-explosion conditions. The molecular weight of lignin after steam-explosion process decreased by setting the steam pressure higher and the steam time longer. However, the hydroxyl equivalent of the lignin increased under those conditions. There was less variability in the properties of the lignin obtained by steam-explosion, that is, the steam-explosion method is the manufacturing system which can produce the

lignin that have homogenous properties.

2011-117

バイオエタノール製造副産リグニンを利用したコンクリート用化学混和剤の製造

山田竜彦<sup>\*1</sup>、久保智史<sup>\*1</sup>、中嶋(浅野)勇<sup>\*2</sup>、浦木康光<sup>\*3</sup>

<sup>\*1</sup> 森林総合研究所、<sup>\*2</sup> 農業・食品産業技術総合研究機構農村工学研究所、<sup>\*3</sup> 北海道大学大学院

Production of concrete chemical admixture based on byproduct lignin of the woody bio-ethanol process.

Tatsuhiko Yamada<sup>\*1</sup>, Satoshi Kbo<sup>\*1</sup>, Isamu Nakajima-Asano<sup>\*2</sup>, Yasumitsu Uraki<sup>\*3</sup>

<sup>1</sup>Forestry and Forest Products Research Institute, Tsukuba, 305-8687, Japan, <sup>2</sup>National Institute for Rural Engineering, NARO, Tsukuba, 305-8609, Japan, <sup>3</sup>Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

Abstract: Bio-ethanol production using soft wood resources is an important national challenging issue related to the nation resource sufficiency due to the accumulating soft wood biomass in Japan. FFPRI is producing woody bio-ethanol from Japanese cedar wood in a pilot research plant on the enzyme saccharification method following the soda cooking. In the pilot process, lignin is separated into a soda solution that is so called black liquor. We are trying to find an applicable method of producing highly value added materials using by-product lignin, because producing highly value added by-products could very much accelerate the forthcoming commercial production of woody bio-ethanol. A simple method to produce amphiphilic lignins that is highly valued added functional material was studied using glycidylethers on the single reaction step in the black liquor. Concrete admixtures such as water reducing agent were produced by purifying the reacted amphiphilic lignin mixture. The performance of the produced concrete admixture as water reducing agent was 3 times higher than widely used commercial product. The admixture had enough quality on the concrete mortar strength test. The admixture showed sufficient performance of concrete air entraining agent as well.

2011-118

バイオディーゼル燃料用植物の有効成分の探索

江藤恭子<sup>\*1</sup>、松田友佳<sup>\*1</sup>、平田千恵<sup>\*1</sup>、鈴木利貞<sup>\*1</sup>、片山健至<sup>\*1</sup>、Tanachai Pankasemusk<sup>\*2</sup>

<sup>\*1</sup> 香川大学農学部、<sup>\*2</sup> チェンマイ大学農学部

Investigation of effective ingredients from a plant for biodiesel fuel production.

Kyoko Eto<sup>\*1</sup>, Yuka Matsuda<sup>\*1</sup>, Chie Hirata<sup>\*1</sup>, Toshisada Suzuki<sup>\*1</sup>, Takeshi Katayama<sup>\*1</sup>, Tanachai Pankasemusk<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, Kagawa 761-0795, Japan, <sup>\*2</sup>Faculty of Agriculture, Chiang Mai University, Chiang Mai 50200, Thailand

Abstract: *Jatropha curcas* L. is, native to tropical Latin America, an oil-bearing shrub widely harvested in tropical and sub-tropical regions throughout Africa and Asia. The plant is resistant to drought and diseases and can grow on wastelands or barrens. The seed contain about 30% oil with a fatty acid composition similar to that of palm oil. The seed oil contains toxic compounds for humans and its nutritional utilizations are impossible. For these reasons this non-edible oil from *J. curcas* is favored for biodiesel fuel production. Although irritant phorbol esters were isolated from *J. curcas*, the other chemical constituents of *J. curcas* were not fully understood. In the study, we found antioxidant activity of some extracts from the defatted seed residue of *J. curcas*. From the active extracts, one lignan and two neolignans with catechol moieties were isolated and identified. Antioxidant activity of those compounds was also found.

2011-特別講演

リグニン研究・教育五十年、「意気に感ず」

荻山紘一

山形大学名誉教授

Outlook of my study and education about woods for fifty years“ Heart to heart”.

Koichi Ogiyama

Professor Emeritus of Yamagata University

Abstract: My study of wood and forest from chemical viewpoint of components have been for ca.50-years. I am now going to outline several studies briefly and discuss with some criticisms and many renections. Main subjects are as follows, 1) Lignin structure and reaction on the nitric acid oxidation, 2) Manufacturing cellulosic pulp by non-aqueous solvent system, 3) Chemosystematic investigation of Sugi (*Cryptomerla japonica*) on the basis of heartwood or foliage extractives (diterpene, wax and phenols), 4) Chemosystematic investigation of Japanese Percimmon, Kaki (*Diospyros kaki*) on the basis of isozyme pheno-types, 5) Physiologically active compounds; plant hormones in sugi foliage, 6) Biologically active compounds of extractives of domestic wood species (*Pinus densiflora*, *Cryptomeria japonica*, *Taxodium disticum* etc.), 7) Biologically active compounds of tropical heartwood extractives (*Dalbergia latifolia*, *Artocarpus heterophylla*, *Macherium pedicellatum* etc.). From viewpoint of forest chemistry, importance of sense about the fate of tree components will be pointed out to maintain the sound forest.

2011-201

バクテリアにおけるリグニン由来ビフェニル化合物の脱メチルシステム

鈴木一也<sup>\*1</sup>、並木仁宏<sup>\*1</sup>、上村直史<sup>\*1</sup>、大塚祐一郎<sup>\*2</sup>、中村雅哉<sup>\*2</sup>、笠井大輔<sup>\*1</sup>、片山義博<sup>\*3</sup>、福田雅夫<sup>\*1</sup>、政井英司<sup>\*1</sup>

<sup>\*1</sup>長岡技術科学大学・生物、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>日本大学・生物資源科学部

Characterization of the O demethylation system essential for the catabolism of a lignin-derived biphenyl compound in *Sphingobium* sp. strain SYK-6.

Kazuya Suzuki<sup>\*1</sup>, Masahiro Namiki<sup>\*1</sup>, Naofumi Kamimura<sup>\*1</sup>, Yuichiro Otsuka<sup>\*2</sup>, Masaya Nakamura<sup>\*2</sup>, Daisuke Kasai<sup>\*1</sup>, Yoshihiro Katayama<sup>\*3</sup>, Masao Fukuda<sup>\*1</sup>, Eiji Masai<sup>\*1</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, 940-2188, <sup>\*2</sup>Forestry and Forest Products Research Institute, Tsukuba, 305-8687, <sup>\*3</sup>College of Bioresource Science, Nihon University, Fujisawa, 252-0880, Japan

Abstract: *Sphingobium* sp. strain SYK-6, a bacterial degrader of various lignin-derived biaryls and monoaryls, is able to grow on 5,5'-dehydrodivanillate (DDVA). In a previous study, *ligX*, which shows the similarity with the oxygenase component gene (*vanA*) of vanillate demethylase of *Pseudomonas putida*, was isolated as the gene involved in the O demethylation of DDVA. However, genes for electron transfer components have not yet been identified. From the genome sequence of SYK-6, we found two ferredoxin genes and two ferredoxin reductase genes as the candidate genes for electron transfer components. Disruption of each gene indicated that SS1C\_Con002\_0548 (ferredoxin) and SS1C\_Con009\_0377 (ferredoxin reductase) were essential for the growth of SYK-6 on DDVA. A mixture of crude enzymes containing the gene products of *ligX*, SS1C\_Con002\_0548, and SS1C\_Con009\_0377 produced in *Escherichia coli* catalyzed the O demethylation of DDVA in the presence of NADH. It was concluded that the DDVA O-demethylase system consists of an oxygenase component, a ferredoxin, and a ferredoxin reductase.

2011-202

Biodegradation of heptachlor and its metabolites in contaminated soil by white-rot fungi

Adi Setyo Purnomo<sup>\*1\*2</sup>, Pengfei Xiao<sup>\*1</sup>, Toshio Mori<sup>\*1</sup>, Ryuichiro Kondo<sup>\*1</sup>

<sup>\*1</sup>Department of Agro-environmental Sciences, Faculty of Agriculture, Kyushu University, 812-8581, Japan, <sup>\*2</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, Institut Teknologi Sepuluh Nopember.

**Abstract:** The ability of white-rot fungi (WRF) to degrade heptachlor and heptachlor epoxide has been investigated. During 14 days incubation, heptachlor was transformed completely to chlordene, heptachlor epoxide and 1-hydroxy-chlordene by *Pleurotus ostreatus* (hiratake) in PDB and Kirk's high nitrogen (HN) media, indicating hiratake has better ability rather than *Phlebia* fungi. For application purpose, spent mushroom waste (SMW) of hiratake and/or fungal substrates of *Phlebia* was used. After 28 days incubation, approximately 89% and 100% of heptachlor was eliminated by hiratake SMW and *P. acanthocystis* fungal substrate. Chlordene, heptachlor epoxide and 1-hydroxy-chlordene were detected as metabolites from hiratake SMW while only heptachlor epoxide was detected from *P. acanthocystis* fungal substrate. Since hiratake SMW can degrade heptachlor and heptachlor epoxide, hiratake SMW was applied to treat heptachlor in artificially contaminated soil. Approximately 89% and 92% of heptachlor was eliminated in sterilized (SL) and un-sterilized (USL) soils, respectively. Furthermore, approximately 23% of heptachlor epoxide was eliminated in SL soil. This study demonstrates that hiratake SMW was applicable for degradation of heptachlor and its resistant metabolite, heptachlor epoxide, in contaminated soil.

2011-203

Degradation of aliphatic hydrocarbons in three types of crude oil by *Fusarium* sp. F092 in sea water liquid medium.

Asep Hidayat, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University, 790-8566, Japan

**Abstract:** The capabilities of *Fusarium* sp. F092 to degrade the aliphatic fraction in comparison of three types of crude oil in sea water liquid cultures were examined. The results showed that *Fusarium* sp. F092 having the ability to degrade the aliphatic fraction in crude oil contaminating a liquid culture with artificial sea water (35‰). The aliphatic fraction was large in crude oil type-3 than crude oil type-1 or type-2 and the other fractions comprised less than 31% of the total. Crude oil type-1, type-2 and type-3 contained C13 to C31, C13 to C27 and C12 to C20, respectively. F092 showed the best performance to break down the aliphatic fraction in crude oil type-3 (98%) and type-2 (72%) and type-1 (49%) after 60 days at an initial concentration of 1000 mg L<sup>-1</sup>. Furthermore, almost all the aliphatic compounds (Up to C31) in the crude oil were degraded by F092 which preferred short and long chain hydrocarbons. Incubation of crude oil at concentration of 15000 mg L<sup>-1</sup> degraded less than 40% of the aliphatic fraction of all crude oils tested.

2011-204

高機能性微生物による木質バイオリファイナリー、～新規リグニン分解特異的プロモーターに関する研究～

大野正人<sup>\*1</sup>、杉浦立樹<sup>\*2</sup>、平井浩文<sup>\*1</sup>、河岸洋和<sup>\*1\*2</sup>、山岸賢治<sup>\*3</sup>、亀井一郎<sup>\*4</sup>、森智夫<sup>\*5</sup>、近藤隆一郎<sup>\*5</sup>

<sup>\*1</sup>静岡大学農学部、<sup>\*2</sup>静岡大学創造科学技術大学院、<sup>\*3</sup>独立行政法人農業・食品産業技術総合研究機構東北農業研究センター、<sup>\*4</sup>宮崎大学農学部、<sup>\*5</sup>九州大学大学院農学研究院

Woody biorefinery with functional microorganisms.

Masato Ohno<sup>\*1</sup>, Tatsuki Sugiura<sup>\*2</sup>, Hirofumi Hirai<sup>\*1</sup>, Hirokazu Kawagishi<sup>\*1\*2</sup>, Kenji Yamagishi<sup>\*3</sup>, Ichiro Kamei<sup>\*4</sup>, Toshio Mori<sup>\*5</sup>, Ryuichiro Kondo<sup>\*5</sup>

<sup>\*1</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*2</sup>Graduate School of

Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*3</sup>National Agricultural Research Center for the Tohoku Region, National Agriculture and Food Research Organization, Fukushima 960-2156, Japan, <sup>\*4</sup>Faculty of Agriculture, University of Miyazaki, Miyazaki 889-2192, Japan, <sup>\*5</sup>Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

Abstract: In our previous reports, we identified protein (BUNA2) as a strong and sharp spot from hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under wood-rotting condition by two-dimensional gel electrophoresis, and BUNA2 gene (*bee2*) and a promoter region of *bee2* were cloned by several PCR series. Moreover, *bee2* promoter was used to drive the expression of manganese peroxidase gene (*mnp4*) in *P. sordida* YK-624, and most of transformants showed higher ligninolytic activity and selectively than wild type. BUNA 2 was classified as oxidoreductases containing Zn-binding site. *bee2* was induced by the addition of vanillin, Mn(II), bisphenol A, and veratryl alcohol. Recently, we constructed the various EGFP-expression plasmids which were regulated by various-length *bee2* promoter in order to determine actual promoter region of *bee2* and to modify the promoter.

2011-205

高機能性微生物による木質バイオリファイナリー、～白色腐朽菌 *Phlebia* sp. MG-60 株によるセルロースの直接エタノール発酵～

亀井一郎<sup>\*1</sup>、廣田佳幸<sup>\*1</sup>、目黒貞<sup>\*1</sup>、平井浩文<sup>\*2</sup>、山岸賢治<sup>\*3</sup>、森智夫<sup>\*4</sup>、近藤隆一郎<sup>\*4</sup>

<sup>\*1</sup>宮崎大学農学部、<sup>\*2</sup>静岡大学農学部、<sup>\*3</sup>農業・食品産業技術総合研究機構東北農業研究センター、<sup>\*4</sup>九州大学大学院農学研究院

Woody biorefinery with functional microorganisms. ～Direct ethanol production from cellulosic materials by white-rot fungus *Phlebia* sp. MG-60～

Ichiro Kamei<sup>\*1</sup>, Yoshiyuki Hirota<sup>\*1</sup>, Sadatoshi Meguro<sup>\*1</sup>, Hirofumi Hirai<sup>\*2</sup>, Kenji Yamagishi<sup>\*3</sup>, Toshio Mori<sup>\*4</sup>, Ryuichiro Kondo<sup>\*5</sup>

<sup>\*1</sup>Faculty of Agriculture, University of Miyazaki, Miyazaki 889-2192, Japan, <sup>\*2</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*3</sup>National Agricultural Research Center for Tohoku Region, Fukushima, 960-2156, Japan, <sup>\*4</sup>Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

Abstract: Twelve strains of basidiomycetes were applied for ethanol fermentation. Silicon rubber plug was used to block the aeration for keeping semi-aerobic condition in flasks. When glucose was used as carbon source, *Phlebia* sp. MG-60 showed the high productivity of ethanol (over 70% of theoretical conversion rate). When *Phlebia* sp. MG-60 was cultured with in 20 g/l microcrystalline cellulose, 2.8 g/l ethanol, 25.3% of theoretical maximum was detected after 480 h incubation. When silico plug was used for keeping aerobic condition, there was no production of ethanol in the culture with glucose or cellulose. Hexoses; glucose, mannose, galactose and fructose were well assimilated by *Phlebia* sp. MG-60. In the case of pentoses, there was no production of ethanol from arabinose, however, good fermentability of xylose by *Phlebia* sp. MG-60 was observed. When *Phlebia* sp. MG-60 was cultured with in 20 g/l unbleached hardwood kraft pulp (UHKP), 64.3% and 70.3% ethanol of theoretical maximum were detected after 240 h and 480 h incubation respectively. When *Phlebia* sp. MG-60 was cultured with in 20 g/l softwood kraft pulp (USKP), 19.4% and 42.4% ethanol of theoretical maximum were detected after 240 h and 480 h incubation respectively. These results indicated that ethanol production is occurred simultaneously with hydrolysis of cellulose.

2011-206

高機能性微生物による木質バイオリファイナリー

～メタゲノムライブラリからの木材分解酵素獲得の試み～

森智夫<sup>\*1</sup>、平井浩文<sup>\*2</sup>、山岸賢治<sup>\*3</sup>、亀井一郎<sup>\*4</sup>、近藤隆一郎<sup>\*1</sup>

<sup>\*1</sup>九州大学大学院農学研究、<sup>\*2</sup>静岡大学農学部、<sup>\*3</sup>農業・食品産業技術総合研究機構東北農業研究センター、<sup>\*4</sup>宮崎大学農学部

Developments of wood biorefinery techniques with functional microorganisms. Functional screening of novel wood-degrading enzymes genes from metagenome libraries derived from soils.

Toshio Mori<sup>\*1</sup>, Hirofumi Hirai<sup>\*2</sup>, Kenji Yamagishi<sup>\*3</sup>, Ichiro Kamei<sup>\*4</sup>, Ryuichiro Kondo<sup>\*1</sup>

<sup>\*1</sup>Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan, <sup>\*2</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan, <sup>\*3</sup>National Agricultural Research Center for Tohoku Region, National Agriculture and Food Research Organization, Fukushima, 960-2156, Japan, <sup>\*4</sup>Faculty of Agriculture, University of Miyazaki, Miyazaki 889-2192, Japan

Abstract: Several metagenomic libraries were constructed from soils via short-term enrichment culture. The cultures for accumulation contained avicel, kraft pulp or cedar wood powder as carbon source and the cultures were incubated for a week. Bacterial cells were collected by centrifugation, and whole genomes were extracted. Partial digested (using *Sau3AI*) genomes were ligated into pUC19 plasmid, and then transformed into *Escherichia coli* DH5  $\alpha$  chemical competent cells. Recombinant cells were spread on LB agar medium containing RBBR-stained CMC. After incubation, CMCase-positive clones appeared with clear halo against blue culture color. DNA sequence analysis of the transformed inserts revealed that the sequence contained novel CMCase.

2011-207

高分子リグニン酸化能をもつ CWPO-C における基質酸化部位の同定

重藤 潤<sup>\*1</sup>、伊藤義隆<sup>\*2</sup>、堤 祐司<sup>\*1</sup>、近藤隆一郎<sup>\*1</sup>

<sup>\*1</sup>九州大学 大学院 農学研究院、<sup>\*2</sup>九州大学 大学院 生物資源環境科学府

Oxidation mechanism of cationic cell-wall-bound peroxidase (CWPO-C) toward lignin model compounds.

Jun Shigeto, Yoshitaka Itoh, Yuji Tsutsumi, Ryuichiro Kondo

Department of Forest and Forest Products Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581 Japan

Abstract: Cationic cell-wall-bound peroxidase (CWPO-C) has the capability to oxidize sinapyl alcohol, ferrocyclochrome *c*, and synthetic lignin polymers, unlike most peroxidases. It is extrapolated that the oxidation site is located on CWPO-C protein surface and homology modeling and chemically modified CWPO-C studies suggest Tyr-74 and/or Tyr-177 are possible participants in the catalytic site. The present study clarifies the importance of these tyrosine residues for substrate oxidation using recombinant CWPO-C and recombinant mutant CWPO-C with phenylalanine substitution(s) for tyrosine. Our results indicated that Tyr-74 and Tyr-177, instead of heme pocket, take a central role in the oxidation of guaiacol, 2,6-dimethoxyphenol and syringaldazine.

2011-208

シロイヌナズナ CWPO-C ホモログのダブルノックアウト変異体解析

伊藤義隆<sup>\*1</sup>、重藤 潤<sup>\*2</sup>、堤 祐司<sup>\*2</sup>、近藤隆一郎<sup>\*2</sup>

<sup>\*1</sup>九州大学大学院 生物資源環境科学府、<sup>\*2</sup>九州大学大学院 農学研究院

Function analysis of cationic cell-wall-bound peroxidase (CWPO-C) homolog double-knockout mutants on Lignin in *Arabidopsis thaliana*.

Yoshitaka Itoh, Jun Shigeto, Yuji Tsutsumi, Ryuichiro Kondo

Faculty of Agriculture, Kyushu University, 6-10-1, Fukuoka, 812-8581, Japan

Abstract: Cationic cell-wall-bound peroxidase (CWPO-C) oxidizes sinapyl alcohol and synthetic

lignin polymer, and Tyr-74 and -177 located on the protein surface are possible substrate oxidation sites for high molecular weight substrates. These characteristics imply that CWPO-C is related to lignification. Three CWPO-C homolog genes among 73 *Arabidopsis* peroxidases are also suggested to be involved in lignification by the analyses of *Arabidopsis* T-DNA insertion mutants. These results suggest that the Tyr located on the protein surface of peroxidase may play an important role in lignification. In this study, *Arabidopsis* double knockout mutants, in which CWPO-C homolog genes were ablated, were generated to clarify the function of three peroxidases in lignification. Also, protein structures of all *Arabidopsis* peroxidases were constructed by homology modeling, and possible substrate oxidation site locates on protein surface were analyzed *in silico*.

2011-209

*Sphingobium* sp. SYK-6 株由来の *ligD* 遺伝子を発現する組換え植物の解析

辻 幸子<sup>\*1</sup>, 石川靖之<sup>\*1</sup>, 高橋理恵<sup>\*1</sup>, 佐藤かな<sup>\*1</sup>, 片山義博<sup>\*3</sup>, 原 啓文<sup>\*4</sup>

菱山正二郎<sup>\*5</sup>, 政井英司<sup>\*2</sup>, 梶田真也<sup>\*1</sup>

<sup>\*1</sup> 東京農工大学大学院生物システム応用科学府、<sup>\*2</sup> 長岡技術科学大学工学部生物系、<sup>\*3</sup> 日本大学生物資源科学部森林資源科学科、<sup>\*4</sup> 岡山理科大学工学部生体医工学科、<sup>\*5</sup> 森林総合研究所バイオマス化学研究領域

Characterization of transgenic plants with *ligD* gene isolated from *Sphingobium* sp. SYK-6.

Yukiko Tsuji<sup>\*1</sup>, Yasuyuki Ishikawa<sup>\*1</sup>, Rie Takahashi<sup>\*1</sup>, Kanna Sato<sup>\*1</sup>, Yoshihiro Katayama<sup>\*3</sup>, Hirofumi Hara<sup>\*4</sup>, Shojiro Hishiyama<sup>\*5</sup>, Eiji Masai<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>

<sup>\*1</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan, <sup>\*2</sup> Department of Bioengineering, Nagaoka University of Technology, Niigata 940-2188, Japan, <sup>\*3</sup> College of Bioresource Sciences, Nihon University, Kanagawa 252-0880, Japan, <sup>\*4</sup> Department of Biomedical Engineering, Okayama University of Science, Okayama 700-0005, Japan, <sup>\*5</sup> Department of Biomass Chemistry, Forestry and Forest Products Research Institute, Ibaraki 305-8687, Japan

Abstract: *Sphingobium* sp. SYK-6, a gram-negative bacterium, can utilize various monomeric and dimeric aromatic compounds, which appeared in lignin biosynthetic pathway, such as cinnamic acids, cinnamaldehydes and  $\beta$ -O-4 dimers. In our previous studies, some genes involved in degradation of these compounds were isolated from the bacterium and characterized. One of them, *ligD* gene encoding C $\alpha$  dehydrogenase catalyzes the first step of cleavage reactions for ether bond of  $\beta$ -O-4 dimers. This enzyme oxidizes alcohol to carbonyl group at benzyl (C $\alpha$ ) position of the dimers. It has been known that the presence of carbonyl group at the benzyl position of aryl propane units in lignin speeds up the rate of cleavage of beta-aryl ether linkages during kraft pulping condition (Gierer et al., 1980; Gierer and Noren, 1982). Thus, we introduced the *ligD* gene into plant genome and try to generate transgenic plants whose lignin can be easy to remove from hollocellulose fraction under the alkaline pulping condition. The enhanced cleavage of beta-aryl ether linkages which are the most common bonds in lignin structure might contribute not only to pulp and paper industries but also to bioethanol production from lignocellulose materials. Characteristics of the transgenic *Arabidopsis* plants will be discussed as a preliminary step toward the molecular engineering of lignin.

2011-210

イネにおけるシリリングリグニン生合成経路の解明

小柴太一<sup>\*1</sup>、廣瀬孝江<sup>\*1</sup>、向井まい<sup>\*1</sup>、山村正臣<sup>\*1</sup>、坂本正弘<sup>\*2</sup>、鈴木史朗<sup>\*1</sup>、服部武文<sup>\*1</sup>、梅澤俊明<sup>\*1\*3</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> 京都大学大学院農学研究科地域環境科学専攻、<sup>\*3</sup> 京都大学生存基盤

## 科学研究ユニット

Elucidation of syringyl lignin biosynthetic pathway in rice plant.

Taichi Koshiba<sup>\*1</sup>, Norie Hirose<sup>\*1</sup>, Mai Mukai<sup>\*1</sup>, Masaomi Yamamura<sup>\*1</sup>, Masahiro Sakamoto<sup>\*2</sup>, Shiro Suzuki<sup>\*1</sup>, Takefumi Hattori<sup>\*1</sup> and Toshiaki Umezawa<sup>\*1\*3</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan, <sup>\*2</sup>Division of Environmental Science & Technology, Graduate School of Agriculture, Kyoto University, 606-8502, Japan, <sup>\*3</sup>Institute of Sustainability Science, Kyoto University, Kyoto, 611-0011, Japan.

**Abstract:** We have analyzed the physiological function of putative rice (*Oryza sativa*) caffeic acid *O*-methyltransferase 3 (OsCOMT3). Recombinant COMT3 catalyzed the 5-methylation of 5-hydroxyferulate (5-HFA) and 5-hydroxyconiferylaldehyde (5-HCAld) as substrates, and the methylation of 5-HFA was inhibited by 5-HCAld. The rice plant which was down-regulated in expression of *COMT3* exhibited a weakened staining with Wiesner reagent in the walls of vascular bundle cells and sclerenchyma tissue compared to wild-type plant. Lignin content of the transgenic shoot was decreased, and syringyl lignin content of those was reduced up to 87% than that of wild-type. These data indicate that the physiological function of COMT3 is to catalyze the 5-methylation in the biosynthetic pathway of syringyl lignin, and suggest that the biosynthetic pathway of syringyl lignin in rice is similar to those in dicyledonous plants.

2011-P01

シラカシモデル林における土壌形成過程での有機物の挙動

勝亦京子<sup>\*1</sup>、田中裕也<sup>\*1</sup>、宮崎毅<sup>\*2</sup>、松本雄二<sup>\*1</sup>

<sup>\*1</sup>木材化学研究室、<sup>\*2</sup>環境地水学研究室・東京大学大学院農学生命科学研究科

Changes of organic substances at *Quercus myrsinaefolia* forests during soil formation.

Kyoko S. Katsumata<sup>\*1</sup>, Yuya Tanaka<sup>\*1</sup>, Tsuyoshi Miyazaki<sup>\*2</sup>, Yuji Matsumoto<sup>\*1</sup>

<sup>\*1</sup>Laboratory of Wood Chemistry, Graduate School of Agricultural and Life Sciences, the University of Tokyo, <sup>\*2</sup>Laboratory of Soil Physics and Soil Hydrology, Graduate School of Agricultural and Life Sciences, the University of Tokyo, 113-8657, Japan

**Abstract:** Lignin is considered to play an important role in the fixation of organic carbon on the earth. On the other hand, it is difficult to trace quantitatively the behavior of lignin during soil formation. In this study, changes of organic substances during soil formation were investigated in terms of organic carbon content, extractability by various solvents and yield of Klason residue. Samples (living plant, litter and soil) were collected at *Quercus myrsinaefolia* forests at the University of Tokyo Tanashi Forest. Total organic carbon (TOC) of living wood and litter were among 43-47%. TOC of soils were 14-4% and was in a range of carbon (C) contents of Japanese forest soil. Any soil did not contain inorganic carbon. This means that C content is equal to TOC in Tanashi forest soil. Amounts of organic matter were estimated by assuming that the carbon content of organic matter was 50%. Yields of extractives on estimated organic matter were 10-38%, 3-11% and 1-3% in living wood, litter and soil, respectively. It was apparent that organic matter turns into hardly extractable materials during soil formation.

2011-P02

Chemical Components of Eccentric Grown Wood of Teak.

Ganis Lukmandaru

Department of Forest Product Technology, Faculty of Forestry, Universitas Gadjah Mada, 55281, Indonesia

**Abstract:** Chemical components of minimum and maximum ring width in the outer heartwood of

eccentric grown teak (*Tectona grandis*) were compared. The woods were sampled from 10 leaning trees of thinning activities. The values of chemical components of eccentric wood were in the range of normal teak woods. *T-test* analysis showed that no significant differences in extractive, ash, pentosan, and acid soluble lignin content levels. However, the difference was found in Klason lignin content, which the woods with maximum ring width showed higher values than those of minimum ring width.

2011-P03

植物の進化に伴うリグニン構造の多様化に関する考察

寺島 典二

名古屋大学 (名誉教授)

Speculations on the diversification of lignin structure during the evolution of plant.

Noritsugu Terashima

Nagoya University (Emeritus Professor)

Present address: 2-610 Uedayama, Tenpaku, Nagoya 468-0001, Japan

Abstract: Diversification of lignin structure occurred during evolution of plant, from *p*-hydroxyphenyl (H)-guaiacyl (G) lignin to syringyl (S)-G lignin. About 400 million years ago, the first vascular plants appeared on the earth. The vascular bundle performed various functions, conduction of aqueous material, mechanical support of plant, and defense against injuries and microbial attack by formation of supra-molecular complex composed of lignin and polysaccharides. Pteridophyta and gymnosperms were the first dominant vascular plant, but change of environment on the earth resulted in evolution of angiosperms, in which multifunctional tracheid differentiated to conduction-specialized vessel and support-specialized fiber. The strong defense function arising from the frequent condensed structures in H-G lignin in gymnosperms was weakened to moderate defense by less condensed S-G lignin in angiosperms. Adequate defense by S-G lignin and quick biodegradation after the plant death provided suitable environment for frequent alternation of generation and faster evolution to adapt environmental change on the earth.

2011-P04

針葉樹仮道管壁複合中間層におけるリグニン-多糖類-超分子複合体の形成に関する考察

寺島典二<sup>\*1\*4</sup>、福島和彦<sup>\*2</sup>、吉田正人<sup>\*3</sup>、Ulla Westermark<sup>\*1\*5</sup>

<sup>\*1</sup>STFI(Swedish Pulp and Paper Research Institute), <sup>\*2</sup>名古屋大学大学院農学研究科森林化学研究室, <sup>\*3</sup>名古屋大学大学院農学研究科生物材料物理学研究室, <sup>\*4</sup>現在: 自宅(468-0001,名古屋市天白区植田山 2-610), <sup>\*5</sup>Present address: Hörnåkers vägen 45, Täby, Sweden

Speculations on the formation of supramolecular complex of lignin and polysaccharides in the compound middle lamella region of softwood tracheid.

Noritsugu Terashima<sup>\*1\*4</sup>, Kazuhiko Fukushima<sup>\*2</sup>, Masato Yoshida<sup>\*3</sup>, Ulla Westermark<sup>\*1\*5</sup>

<sup>\*1</sup>STFI(Swedish Pulp and Paper research Institute), <sup>\*2</sup>Laboratory of Forest Chemistry, School of Bioagricultural Science, Nagoya University, Nagoya 464-8601, Japan, <sup>\*3</sup>Laboratory of Bio-material Physics, School of Bio-agricultural Science, Nagoya University, Nagoya 464-8601, Japan, <sup>\*4</sup>Present address: 2-610 Uedayama, Tenpaku, Nagoya 468-0001, Japan, <sup>\*5</sup>Present address: Hörnåkers vägen 45, Täby, Sweden

Abstract: Supramolecular structure of lignins in compound middle lamella (CML) and secondary wall (SW) of softwood tracheid differs partly due to higher content of condensed structures (5-5'-biphenyl, dibenzodioxocin and 4-O-5'-diphenyl ether) in CML lignin than in SW lignin. In an early stage of cell wall formation, random networks made up of cellulose microfibril, xyloglucan and

pectin are formed in CML. A large number of globular *p*-hydroxyphenyl-guaiacyl lignin grow on the network. The growing ends of folded chain molecules are on the surface of the globules, and successive addition of monolignols by  $\beta$ -O-4 and  $\beta$ -5 linkages are prevailed. When the space on the polysaccharide network is almost filled up, insufficient space for further monolignol addition causes frequent bonding between two growing ends by 5-5' or 4-O-5' linkages. The circadian rhythm of cell activity may accelerate closer contact of the globules, and supply of one monolignol after the 5-5' bonding to form dibenzodioxocin structure.

2011-P05

広葉樹の葉リグニンの DFRC 法による検出(1)

松井直之、大平辰朗

(独)森林総合研究所バイオマス化学研究領域

Detection of broad-leaf lignin in angiosperms by DFRC analysis. (1)

Naoyuki Matsui, Tatsuro Ohira

Forestry and Forest Products Research Institute, Wood Extractives Lab. Matsunosato 1, Tsukuba, 305-8687 Japan

Abstract: The DFRC analysis gives C6-C3 type degradation products from arylether linkages of lignin. Therefore this method can be used to detect lignin specifically from plant tissues, excluding other (poly)phenolic substances. To investigate the lignin composition in broad-leaves of angiosperms, DFRC analysis was employed. Many leaves gave both guaiacyl- and syringyl-type degradation products, which indicates the broad leaf lignin has common structural elements with xylem lignin of the same tree. However, results were not always the same among species and tissues. Syringyl / guaiacyl ratio of DFRC products of leaf lignin was apparently lower than that of xylem lignin. The leaves of persimmon and cherry gave only trace amount of degradation products. These results show the heterogeneous distribution of leaf lignin in angiospermous trees.

2011-P06

ニトロベンゼン酸化法によるリグニンのビフェニル型構造の定量的検討

玉井あかり、秋山拓也、松本雄二

東京大学大学院 農学生命科学研究科

Quantitative evaluation of biphenyl type structures in lignin by nitrobenzene oxidation method.

Akari Tamai, Takuya Akiyama, and Yuji Matsumoto

Laboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo, 113-8657, Japan

Abstract: Japanese cedar wood meals were subjected to alkaline nitrobenzene oxidation at different reaction temperature and for different period to investigate the yields of dehydrodivanillin, dehydrovanillinvanillic acid and dehydrodivanillic acid that are considered to be the products from biphenyl type structures (5-5 linkage type) in lignin. On the basis of the total yield of the products obtained in the optimized reaction condition, 170 °C for 2 hours, it was suggested that at least 5.2 % of phenylpropane units in the cedar lignin were involved in 5-5 linkage type structures.

2011-P07

パーム油由来のグリセリンを利用したポリウレタン複合材料及びエポキシ樹脂の熱的・機械的性質  
廣瀬重雄\*<sup>1</sup>、畠山立子\*<sup>2</sup>、畠山兵衛\*<sup>2</sup>

\*<sup>1</sup> 福井工業大学・工、\*<sup>2</sup> リグノセルリサーチ(株)

Thermal and mechanical properties of polyurethane composites and epoxy resins derived from glycerol from palm oil.

Shigeo Hirose<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup>, Hyoe Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui University of Technology, 3-6-1 Gakuen, Fukui-City, Fukui 901-8505, Japan, <sup>\*2</sup>Lignocel Research Co. Ltd., 391-5 Ofunato, Tsukuba, Ibaraki 300-1267, Japan

Abstract: Polyurethane composites were prepared using industrial by-products such as lignin (LS) obtained in pulping process, molasses (ML) obtained in sugar production process, crude glycerol (CG) obtained in bio-diesel fuel production process, cellulose and empty fruit bunches (EFB) of oil palm. Sodium lignosulfonate (LS), ML and CG were dissolved in polyethylene glycol 200 (PEG), and each of the above solutions, LSP, MLP and CGP were obtained. Cellulose powder with different particle size and EFB powder were mixed with the mixture of the above polyols, and then the obtained mixtures were allowed to react with poly(phenylene methylene)polyisocyanate (MDI) under a pressure of 20 MPa for 1 h, and then at 120 °C, for 2 h. The mechanical properties were studied by bending tests. The bending strength ( $\sigma$ ) was almost constant regardless of MLP contents (MLP content, % =  $W_{MLP} / (W_{MPL} + W_{LSP})$ ). Maximum value of  $\sigma_{max}$  was 23 MPa when fiber length was 28  $\mu$ m at MLP content of 80%, while  $\sigma_{min}$  was 11 MPa when fiber length was 37  $\mu$ m at MLP content of 50 %. The bending modulus  $E$  values also showed the similar tendency to those of  $\sigma$  values. Crude glycerol and pure glycerol were allowed to react with succinic anhydride, respectively. When the obtained poly acid derivatives of crude glycerol (CGPA) and GPA were allowed to react with glycerol diglycidyl ether (GDGE), the weight contents of CGPA [ $W_{CGPA} / (W_{CGPA} + W_{GPA})$ ] were change from 0 to 100 %. The glass transition temperatures were almost constant regardless of CGPA contents in epoxy resins.

2011-P08

工業リグニンを用いた新規セメント分散剤の開発

麻生知裕<sup>\*1\*2</sup>、幸田圭一<sup>\*1\*2</sup>、浦木康光<sup>\*1\*2</sup>、久保智史<sup>\*3</sup>、山田竜彦<sup>\*3</sup>、中嶋勇<sup>\*4</sup>

<sup>\*1\*2</sup>北海道大学大学院農学研究科、<sup>\*3</sup>森林総合研究所、<sup>\*4</sup>農業・食品産業技術総合研究機構農村工学研究所

Preparation of novel lignin-based cement dispersants from technical lignin.

Tomohiro Aso<sup>\*1</sup>, Keiichi Koda<sup>\*2</sup>, Yasumitsu Uraki<sup>2</sup>, Satoshi Kubo<sup>3</sup>, Tatsuhiko Yamada<sup>3</sup> and Isamu Nakajima<sup>4</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, 060-8589 Hokkaido, Japan, <sup>\*2</sup>Research Faculty of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, 060-8589 Hokkaido, Japan, <sup>\*3</sup>Department of Biomass Chemistry, Forest and Forest Products Research Institute, 1 Matsunosato, Tsukuba, 305-8687 Ibaraki, Japan, <sup>\*4</sup>National Institute for Rural Engineering, National Agriculture and Food Research Organization, 2-1-6 Kannondai, Tsukuba, 305-8609 Ibaraki, Japan

Abstract: We have developed amphiphilic lignin derivatives from technical lignin by the reaction with poly(ethylene glycol) derivatives. They obviously showed considerable surface activity. The utility of amphiphilic lignin derivatives were evaluated in terms of their dispersion capacity, as a cement admixture. Amphiphilic lignin derivatives (EPEG) prepared with monoepoxylated poly(ethylene glycol) gave higher dispersity to cement than lignosulfonate (LS), a commercially available lignin, at room temperature and 6°C. The cured cement mixed with amphiphilic lignin derivatives at both temperatures also revealed almost the same or slightly higher bending strength than those with LS and without lignin-based additive. In conclusion, EPEG-based amphiphilic lignin derivatives were proven to be a promising cement admixture that would be available even in the wintertime.

2011-P09

リグニン誘導体を用いた天然型有機系紫外線吸収剤

三亀啓吾<sup>\*1</sup>、大橋康典<sup>\*1</sup>、片平律子<sup>\*2</sup>、小澤佑<sup>\*3</sup>、片平正人<sup>\*3</sup>、渡邊崇人<sup>\*1</sup>、本田与一<sup>\*1</sup>、菅原智<sup>\*4</sup>、小池謙造<sup>\*4</sup>、渡辺隆司<sup>\*1</sup>

<sup>\*1</sup> 京都大学生存圏研究所、<sup>\*2</sup> 大阪大学蛋白質研究所、<sup>\*3</sup> 京都大学エネルギー理工学研究所、<sup>\*4</sup> 花王株式会社

Natural organic ultraviolet absorbers from lignin derivatives.

Keigo Mikame<sup>\*1</sup>, Yasunori Ohashi<sup>\*1</sup>, Ritsuko Katahira<sup>\*2</sup>, Yu Kozawa<sup>\*3</sup>, Masato Katahira<sup>\*3</sup>, Takahito Watanabe<sup>\*1</sup>, Yoichi Honda<sup>\*1</sup>, Satoshi Sugawara<sup>\*4</sup>, Kenzo Koike<sup>\*4</sup>, Takashi Watanabe<sup>\*1</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan. <sup>\*2</sup>Institute for Protein Research, Osaka University, Yamadaoka, Suita-shi, Osaka 565-0871, Japan. <sup>\*3</sup>Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan.

<sup>\*4</sup>Kao Corporation, 2-1-3 Bunka, Sumida-ku, Tokyo 131-8501, Japan.

Abstract: Currently, ultraviolet (UV) absorbers are becoming popular due to cosmetic and medical purposes. Exposure of skins to UV rays from the sun causes damage of the skins. Excessive exposure induces skin cancer and aging. Although the demand for UV absorbers with high safety and minimum environmental impacts is becoming increasing, most of the organic UV absorbers currently available are synthetic compounds from petroleum. Therefore, we started the research to develop UV absorbers from natural organic compounds. Natural aromatic polymer, lignin retain the potential to produce strong UV absorbers by oxidative degradation. By extensive screening of degradation products from lignin, we found the products having high absorbance in UV-A and UV-B regions.

2011-P10

フェルラ酸およびカフェ酸をモノマーとするポリエステルの高分子量化

石井大輔, 前田拓希, 河村奈々絵, 林久夫  
龍谷大学工学部物質化学科

Molecular weight enhancement of polyesters from ferulic or caffeic acids.

Daisuke Ishii, Hiroki Maeda, Nanae Kawamura, Hisao Hayashi

Department of Materials Chemistry, Faculty of Science and technology, Ryukoku University, Shiga 520-2194, Japan

Abstract: Enhancement of molecular weight was attempted for polyesters prepared from ferulic (FA) or caffeic (CA) acids, both of which are lignin-related aromatic hydroxyl acids. Polymerization of these acids was performed by ester exchange reaction in sodium acetate/acetic anhydride system followed by polycondensation at different temperatures and reaction time under reduced pressures. Molecular weight (MW) of poly(caffeic acid) (PCA) as estimated by GPC (relative to polystyrene standard) increased up to  $1.0 \times 10^6$  by polycondensation at 160 °C for 16 h. On the other hand, MW of poly(ferulic acid-co-glycolic acid) (PFG) increased only up to  $8.0 \times 10^3$  after polycondensation at 180 °C for 26 h. These polyesters showed different thermal behaviors: PCA formed liquid crystalline (LC) phase under shear upon heating to 140–170 °C; PFG polymerized with the FA feed ratio of 30% spontaneously formed LC phase above 130 °C.

2011-P11

ポリビニルアルコールとの微視的複合化によるリグノスルホン酸のゲル化と機能発現

仲西雄亮, 寺本好邦, 西尾嘉之  
京都大学大学院農学研究科森林科学専攻

Composite gel formation and functionalization of lignosulfonic acid via microcompositions with poly(vinyl alcohol).

Yusuke Nakanishi, Yoshikuni Teramoto, and Yoshiyuki Nishio

Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University  
Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

Abstract: Utilization of isolated lignins as a solid material is constrained by poor film formability and insufficient moldability due to their low molecular weight and molecular structure. In the present study, we prepared lignosulfonic acid (LSA)/poly(vinyl alcohol) (PVA) composite hydrogels. Cross-linking moiety was introduced by thermal treatment or reaction with glutaraldehyde. By thermal cross-linking, an elution of LSA in aqueous media could be prevented by formations of hydrogen bonding and sulfonate ester between LSA and PVA, both of which were corroborated by FT-IR measurement. The thermal-treated composite hydrogels demonstrated a sustained-release behavior of nicotine in normal saline solution. On the other hand, pre-interlinking of LSA was performed using poly(ethylene glycol) diglycidyl ether as a linking agent, in order to improve the LSA content for the LSA/PVA composite hydrogel prepared via chemical cross-linking in aqueous media. Thereupon, the incorporation of linked-LSA achieved much improvement of water retentivity for the composite hydrogels, where the maximum retentivity of distilled water was > 500 times its own weight.

2011-P12

アルカリリグニンのアルミニウム毒性除去能に関する研究 —擬似酸性土壌を用いた系での検討—  
相見 光<sup>\*1</sup>、栗本康司<sup>\*2</sup>、山内 繁<sup>\*2</sup>、池田 努<sup>\*3</sup>、眞柄謙吾<sup>\*3</sup>

<sup>\*1</sup> 東京大学大学院農学生命科学研究科木材化学研究室、<sup>\*2</sup> 秋田県立大学木材高度加工研究所

<sup>\*3</sup> 森林総合研究所木材化学研究室

Studies on the ability of alkali lignin to reduce aluminum toxicity assayed using acidic soils.

Hikaru Aimi<sup>\*1</sup>, Yasuji Kurimoto<sup>\*2</sup>, Shigeru Yamauchi<sup>\*2</sup>, Tsutomu Ikeda<sup>\*3</sup>, Kengo Magara<sup>\*3</sup>

<sup>\*1</sup> Wood Chemistry Laboratory, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan,

<sup>\*2</sup> Institute of Wood Technology, Akita Prefectural University, Akita 016-0876, Japan,

<sup>\*3</sup> Department of Biomass Chemistry, Forestry and Forest Products Research Institute, 1 Tsukuba, 305-8687, Japan

Abstract: The ability of alkali lignin to reduce aluminum toxicity was assayed by plant growth tests using acidic soils. Acidic soils used in this study were prepared by adding aluminum chloride or hydrochloric acid to Akadama soil (loamy soil). Root elongations of radish were suppressed in these acidic soils, and addition of alkali lignin to these soils did not have any effect on recovery. This result indicates that alkali lignin was not effective at reducing aluminum toxicity when these acidic soils were employed. Preliminary experiment using saponified ozone-treated kraft lignin indicates that improvement of the ability of alkali lignin may need to become effective at reduce aluminum toxicity in these soils.

2011-P13

直パルス通電加熱による木質バイオマスの急速熱分解生成物

本間千晶<sup>\*1</sup>、畑 俊充<sup>\*2</sup>、大橋康典<sup>\*2\*3</sup>、渡辺隆司<sup>\*2</sup>

<sup>\*1</sup> 北海道立総合研究機構林産試験場、<sup>\*2</sup> 京都大学生存圏研究所、<sup>\*3</sup> 現 ハリマ化成株式会社

Products from fast pyrolysis of wood biomass by pulse current heating.

Sensho Honma<sup>\*1</sup>, Toshimitsu Hata<sup>\*2</sup>, Yasunori Ohashi<sup>\*3</sup>, Takashi Watanabe<sup>\*3</sup>

<sup>\*1</sup> Hokkaido Research Organization Forest Products Research Institute 1-10 Nishikagura,

Asahikawa, Hokkaido, 071-0198, Japan, <sup>\*2</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji City, Kyoto, 611-0011, Japan, <sup>\*3</sup>present address: Harima Chemicals Incorporated, Kakogawa Plant and Central Research Laboratory, 671-4 Mizuashi, Noguchi-cho, Kakogawa, Hyogo 675-0019, Japan

Abstract: Fast pyrolysis of wood biomass with pulse current heating in order to get useful co-products from bio-oil and to know the pyrolysis conditions on bio-oil compositions and properties and functions of co-products were examined. The maximum yield of bio-oil was shown at around 500°C. The relationships between the reaction temperature and mass balance, the chemical structure and bio-oil compositions, the organics and ammonia adsorbed on char were discussed. It was suggested about the potential of the catalyst on the yields and properties of the products from fast pyrolysis.

2011-P14

バクテリア由来ピノレジノール変換酵素遺伝子の単離と機能解析

福原優樹<sup>\*1</sup>、上村直史<sup>\*1</sup>、中島正博<sup>\*2</sup>、菱山正二郎<sup>\*3</sup>、笠 大輔<sup>\*1</sup>、原 啓文<sup>\*4</sup>、  
片山義博<sup>\*5</sup>、福田雅夫<sup>\*1</sup>、梶田真也<sup>\*2</sup>、政井英司<sup>\*1</sup>

<sup>\*1</sup>長岡技術科学大学・生物、<sup>\*2</sup>東京農工大学大学院・生物システム応用科学府、

<sup>\*3</sup>森林総合研究所、<sup>\*4</sup>岡山理科大学・生体医工学科、<sup>\*5</sup>日本大学・生物資源科学部

Isolation and Characterization of the Pinoreosinol Reductase Gene of *Sphingobium* sp. Strain SYK-6. Yuki Fukuhara<sup>\*1</sup>, Naofumi Kamimura<sup>\*1</sup>, Masahiro Nakajima<sup>\*2</sup>, Shojiro Hishiyama<sup>\*3</sup>, Daisuke Kasai<sup>\*1</sup>, Hirofumi Hara<sup>\*4</sup>, Yoshihiro Katayama<sup>\*5</sup>, Masao Fukuda<sup>\*1</sup>, Shinya Kajita<sup>\*2</sup>, Eiji Masai<sup>\*1</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188,

<sup>\*2</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, <sup>\*3</sup>Forestry and Forest Products Research Institute, Tsukuba, Ibaraki 305-8687, <sup>\*4</sup>Department of Biomedical Engineering, Okayama University of Science, Kita-ku, Okayama 700-0005, <sup>\*5</sup>College of Bioresource Science, Nihon University, Fujisawa, Kanagawa 252-0880, Japan

Abstract: Our group aims to control the lignin biosynthesis in plants by using lignin catabolic genes from bacteria. In this study, we isolated and characterized an enzyme gene involved in the transformation of pinoreosinol (8-8' dimer) from *Sphingobium* sp. SYK-6. A cosmid clone which conferred the pinoreosinol transformation activity to a host strain *Pseudomonas putida* was isolated. In the 3.5-kb SalI fragment of the cosmid, we found a 948-bp open reading frame (*pinZ*) which has 21% identity with pinoreosinol reductase of *Arabidopsis thaliana*. Purified His-tag fused PinZ produced in *Escherichia coli* completely converted a racemic mixture of pinoreosinol into lariciresinol and secoisolariciresinol in the presence of NADPH. These results indicated that *pinZ* encodes pinoreosinol reductase. Disruption of *pinZ* in SYK-6 demonstrated that this gene is essential for the transformation of pinoreosinol.

2011-P15

*Sphingobium* sp. SYK-6 株から単離されたピノレジノール変換酵素  
遺伝子 *pinZ* を発現する組換え植物の解析

田村尚之<sup>\*1</sup>、中島正博<sup>\*1</sup>、辻 幸子<sup>\*1</sup>、福原優樹<sup>\*2</sup>、上村直史<sup>\*2</sup>、佐藤かな<sup>\*1</sup>、片山義博<sup>\*3</sup>、原 啓文<sup>\*4</sup>、  
菱山正二郎<sup>\*5</sup>、政井英司<sup>\*2</sup>、梶田真也<sup>\*1</sup>

<sup>\*1</sup>東京農工大学大学院生物システム応用科学府、<sup>\*2</sup>長岡技術科学大学工学部生物系、<sup>\*3</sup>日本大学  
生物資源科学部森林資源科学科、<sup>\*4</sup>岡山理科大学工学部生体医工学科、<sup>\*5</sup>森林総合研究所バイ  
オマス化学研究領域

Analysis of transgenic plants with the bacterial gene for pinoreosinol reductase, *pinZ*, which has been

isolated from *Sphingobium* sp. SYK-6.

Masayuki Tamura<sup>\*1</sup>, Masahiro Nakajima<sup>\*1</sup>, Yukiko Tsuji<sup>\*1</sup>, Yuuki Fukuhara<sup>\*2</sup>, Naoto Kamimura<sup>\*2</sup>  
Kanna Sato<sup>\*1</sup>, Yoshihiro Katayama<sup>\*3</sup>, Hirohumi Hara<sup>\*4</sup>, Syoujiro Hishiyama<sup>\*5</sup>, Eiji Masai<sup>\*2</sup>, Shinya Kajita<sup>\*1</sup>  
<sup>\*1</sup>Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and  
Technology, Tokyo, 184-8588 Japan, <sup>\*2</sup>Department of BioEngineering, Nagaoka University of  
Technology, Niigata, 940-2188, Japan, <sup>\*3</sup>Department of Forest Science and Resources, Nihon  
University Collage of Biosource Sciences Kanagawa, 252-8510, Japan, <sup>\*4</sup>Department of Biomedical  
Engineering, Okayama University of Science, Okayama, 700-0005, Japan, <sup>\*5</sup>Forestry and Forest  
Products Research Institute, Ibaraki, 305-8687, Japan

Abstract: We try to modify lignan and lignin biosyntheses in transgenic plants by expression of various types of bacterial genes for catabolism of aromatic compounds. This study focused on one of the genes, *pinZ*, which encodes pinoresinol reductase that catalyzes the conversion of pinoresinol to lariciresinol. To overexpress the gene efficiency in transgenic plants, we modified codon usage of endogenous *pinZ* gene and constructed an expression vector with the resultant cDNA sequence. Generation of transgenic BY-2 cells and *Arabidopsis thaliana* plants have been performed by traditional *Agrobacterium* mediated transformation procedures. Appropriate level of PinZ activity as it is in recombinant *Escherichia coli* could be detected in crude enzymes prepared from both of the transgenic lines.

2011-P116

Quercus 属外樹皮におけるスベリン芳香族部分の化学構造と生合成

伊藤彰伸、松本匠哉、中林亮太、鈴木利貞、片山健至

香川大学農学部

Chemical structure and biosynthesis of poly phenolic domain of suberin in outre bark of Quercus family.

Akinobu Ito, Takuya Matsumoto, Ryota Nakabayashi, Toshisada Suzuki, Takeshi Katayama  
Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795

Abstract: Suberin is one of the main components in outer bark of woody plants, wound healing tissue of higher plants and periderm of underground organs. The insoluble biopolymer is composed of poly aliphatic domain and poly phenolic domain. Although the structure and composition of the poly aliphatic domain were well investigated, those of the poly phenolic domain were unclear. In this study, a  $\beta$ -O-4' enol ether dimer of methyl ferulate and its derivatives were isolated from methanolysis products of extractive free outer bark of Quercus suber and Q. variabilis. Dehydrogenative polymerization of feruloyloxy hexadecanoic acid with horseradish peroxidase and H<sub>2</sub>O<sub>2</sub> was carried out as a suberin model system. A 5-O-4' diaryl ether type dimer of the substrate and its derivatives were isolated together with a  $\beta$ -5' dimer. These results suggest that feruloyloxy fatty acid derivatives are dehydrogenatively polymerized by a peroxidase to give  $\beta$ -O-4' enol ether structures with  $\beta$ -5', 5-O-4' and the other coupling structures, which would form the poly phenolic domain of suberin in the outer bark of Quercus family. Dehydrogenative polymerization of feruloyloxy hexadecanoic acid with Q. variabilis bark crude enzyme is being examined.

2011-P17

シロイヌナズナ T-DNA 挿入変異体を用いたリグニン前駆物質輸送体の絞り込み

津山濯<sup>\*1</sup>、高部圭司<sup>\*1</sup>、尾形善之<sup>\*2</sup>

<sup>\*1</sup>京都大学大学院農学研究科、<sup>\*2</sup>理化学研究所植物科学研究センター

Seeking the candidates of lignin transporter using *Arabidopsis* T-DNA tagged mutants.

Taku Tsuyama<sup>\*1</sup>, Keiji Takabe<sup>\*1</sup>, Yoshiyuki Ogata<sup>\*2</sup>

\*<sup>1</sup>Graduate School of Agriculture, Kyoto University, Kyoto, 606-8502, Japan, \*<sup>2</sup>RIKEN Plant Science Center, Yokohama, Kanagawa, 230-0045, Japan,

Abstract: Lignin biosynthesis proceeds in three steps; biosynthesis, transport, and polymerization of lignin precursors. Though many researches have elucidated the biosynthesis and the polymerization of lignin precursors, their transport mechanism has not been investigated except coniferin transport into vacuole. To identify the transporter of lignin precursor, we selected candidates of transporter genes in *Arabidopsis thaliana* by co-expression analysis. Mature stems of T-DNA tagged mutants of candidate genes were harvested and analyzed their lignin distribution. A T-DNA mutant showed weak Mäule color reaction in iterfascicular fiber. Although lignin content of the mutant was not different from Col-0, S/V ratio was decreased. The candidate of transporter gene may be involved in transport of S lignin precursors.

2011-P18

サリチル酸投与によってシラカンバ幼植物体に誘導される植物免疫に係わるペルオキシダーゼの解析

鈴木 拓, 石栗 太, 飯塚和也, 吉澤伸夫, 横田信三  
宇都宮大学農学部

Analysis of plant-immunity-related peroxidases induced in Japanese birch plantlets by administration of salicylic acid.

Hiromu Suzuki, Futoshi Ishiguri, Kazuya Iizuka, Nobuo Yoshizawa, Shinso Yokota  
Faculty of Agriculture, Utsunomiya University, Utsunomiya 321-8505, Japan

Abstract: Salicylic acid (SA) is known to induce immunity in plants against pathogens through systemic acquired resistance. The present study investigated localization of peroxidase induced in Japanese birch plantlets by administration of SA. Histochemical observation of peroxidase revealed that SA induced peroxidases with higher activity in the wider area around the administered site compared to the controls, suggesting the involvement of these peroxidases in plant immunity. Proteomic analysis was also performed using protein samples prepared from the plantlets treated with SA. As the results, malate dehydrogenase and arginase were detected and identified as the proteins specific to SA treatment.

2011-P19

ファイトアレキシン生産時の *Cupressus lusitanica* 培養細胞のリグニン生成  
柴田久美子、Ransika De Alwis、藤田弘毅  
九州大学大学院農学研究院

Lignin formation at phytoalexin producing *Cupressus lusitanica* cultured cell.

Kumiko Shibata, Ransika De Alwis, Koki Fujita

Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

Abstract: The lignin formation with water stress, mechanical stress, elicitor stress on *Cupressus lusitanica* cultured cell was investigated. By analysis of acidolysis and pyrolysis method on the cells at the incubation time same as phytoalexin production (up to 5 days), only the trace amount of lignin degradation products were detected. No significant change of lignin content was observed on Klason lignin content. Therefore, the cells would response at first for protection from elicitor stress in short time (several days) with low molecular weight phytoalexin such like  $\beta$ -thujaplicin. And then at later phase, lignin formation was completed in the cell wall against various stresses including water stress, mechanical stress and so on.

## 第 57 回 (2012.10.17-18) アクロス福岡 国際会議場

2012-101

二段階半流通型加圧熱水処理不溶残渣のリグニン

鈴木信義、高田昌嗣、山内一慶、坂 志朗

京都大学大学院エネルギー科学研究科

Lignin in the residues as treated by two-step semi-flow hot-compressed water.

Nobuyoshi Suzuki, Masatsugu Takada, Kazuchika Yamauchi, Shiro Saka

Graduate School of Energy Science, Kyoto University, Japan

Abstract: Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*) were treated with two-step semi-flow hot-compressed water. The first stage was conducted at 230°C/10 MPa for 15min and the second stage at 270°C/10MPa for 15min. The residues at the first and second stages of Japanese cedar contained 59.7 and 43.1wt% of the original lignin, while these of Japanese beech 50.8 and 23.2wt%, respectively. As hot-compressed water treatment proceeds for the first and second stages, the cell wall was destructed for both species. However, the cell wall of the beech was remarkably destructed, compared with cedar, and in the residue of the second stage, only the middle lamella region remained for beech. On the other hand, for the cedar, the cell wall was not so destructed and its structure was comparatively retained. From these observations and the yield of alkaline nitrobenzene oxidation products, the fiber cell wall of the beech encrusted with syringyl lignin would be more likely to be composed of non-condensed type of lignin, while middle lamella and its cell corner region encrusted with guaiacyl lignin would be largely composed of condensed type of lignin. In the case of cedar, however, the middle lamella region remained even at the end of the second stage, thus must have mainly condensed type lignin. In addition, compared with the beech, the cell wall portion of the cedar must have more condensed type of lignin. Such a difference suggests that the topochemical difference in lignin exists in the residues as treated by hot-compressed water.

Keywords: hot-compressed water, topochemistry, lignin distribution, TEM, UV microscope

2012-102

バイオディーゼル燃料用植物ジャトロファから抗酸化活性を有するカテコール型リグナン・ネオリグナンの単離

江藤恭子<sup>\*1</sup>, 小池 悠<sup>\*1</sup>, 鈴木利貞<sup>\*1</sup>, 片山健至<sup>\*1</sup>, Tanachai Pankasemsuk<sup>\*2</sup>

<sup>\*1</sup>香川大学農学部, <sup>\*2</sup>チェンマイ大学農学部

Isolation of antioxidant catechol lignan/neolignans from *Jatropha curcas*, a shrub for biodiesel fuel production.

Kyoko Eto<sup>\*1</sup>, Yu Koike<sup>\*1</sup>, Toshisada Suzuk<sup>\*1</sup>, Takeshi Katayama<sup>\*1</sup>, Tanachai Pankasemsuk<sup>\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795, Japan

<sup>\*2</sup>Faculty of Agriculture, Chiang Mai University, Chiang Mai 50200, Thailand

Abstract: The ethyl acetate soluble fraction of the methanol extract obtained from the defatted seed residue of *Jatropha curcas* had the same potent antioxidant activities as Trolox. From the antioxidant fraction a catechol-type furofuran lignan, (+)-3,3'-bisdemethylpinoresinol; five catechol-type 1,4-benzodioxane neolignans, (-)-isoamericanol A, (+)-americanol A, 9'-O-methylisoamericanol A, 9'-O-methylamericanol A, and isoamericanin A; and two catechol-type sesqueneolignans with furofuran and 1,4-benzodioxane moieties, isoprincepin and princepin were isolated and identified. Potent antioxidant activities of these eight compounds were also confirmed. The ethyl acetate soluble fraction of the methanol extract was found to be more effective than  $\alpha$ -tocopherol by the tests for preventing oxidation of commercial salad oil and

Jatropha oil and the biodiesel fuels (BDF) derived from the two oils.

2012-103

リグニン性状とリグニン硬化エポキシ樹脂特性の相関

香川博之<sup>\*1</sup>、岡部義昭<sup>\*1</sup>、佐々木 千鶴<sup>\*2</sup>、中村 嘉利<sup>\*2</sup>

<sup>\*1</sup>(株)日立製作所日立研究所有機材料研究部

<sup>\*2</sup>徳島大学大学院ソシオテクノサイエンス研究部ライフシステム部門

Correlation between lignin properties and properties of epoxy resin hardened by lignin.

Hiroyuki Kagawa<sup>\*1</sup>, Yoshiaki Okabe<sup>\*1</sup>, Chizuru Sasaki<sup>\*2</sup>, Yoshitoshi Nakamura<sup>\*2</sup>

<sup>\*1</sup>Hitachi Research Laboratory, Hitachi, Ltd.,

7-1-1 Omika-cho, Hitachi-shi, Ibaraki-ken, 319-1292 JAPAN

<sup>\*2</sup>Department of Life System, Institute of Technology and Science, The University of Tokushima, 2-1 Minamijosanjima-cho, Tokushima-shi, Tokushima-ken, 770-8506 JAPAN

Abstract: We are currently researching the use of woody biomass, particularly the application of lignin extracted from steam-exploded woody biomass to epoxy resin, which is widely used in modern electric and electronic equipment. We have already reported that the weight-average molecular weight (Mw) of lignin after the steam explosion process decreased by setting a higher steam pressure and a longer process time, however, the hydroxyl equivalent of the lignin increased under those conditions. We report that the correlation between lignin properties and properties of epoxy resin hardened by lignin. Epoxy resins hardened by lignin with different Mw showed approximately the same glass transition temperatures (Tg), implying that the crosslink density of hardened resin is not much different in this range of Mw. We also prepared epoxy molding compounds using lignin as a hardener. Steam-explosion conditions of cedar chips were explored, and the molding compounds with lower water absorption were obtained for longer steam time, reflecting the properties of lignin. Mechanical and electrical properties of molding compounds were independent of the steam-explosion conditions.

Keywords: steam explosion, epoxy, resin, crosslink, mechanical property.

2012-104

グリコールエーテル系溶剤中での酸分解によるスギ木粉からのリグニン抽出および抽出リグニンのサーモトロピック液晶性ポリエステル化

石井大輔<sup>\*1</sup>、山崎昌男<sup>\*2</sup>、山太郎<sup>\*1</sup>、井林賢太<sup>\*1</sup>、白井伸明<sup>\*3</sup>、松本正<sup>\*3</sup>、中沖隆彦<sup>\*1</sup>、林久夫<sup>\*1</sup>

<sup>\*1</sup>龍谷大学理工学部物質化学科、<sup>\*2</sup>桜宮化学株式会社、<sup>\*3</sup>滋賀県東北部工業技術センター

Lignin extraction from Sugi (*Cryptomeria japonica* D. Don) woodmeal by acid-catalyzed solvolysis in glycolethers and preparation of thermotropic liquid crystalline polyester from the glycolether lignin. Daisuke Ishii<sup>\*1</sup>, Masao Yamazaki<sup>\*2</sup>, Ryotaro Yamamoto<sup>\*1</sup>, Kenta Ibayashi<sup>\*1</sup>, Nobuaki Shirai<sup>\*3</sup>, Tadashi Matsumoto<sup>\*3</sup>, Takahiko Nakaoki<sup>\*1</sup>, Hisao Hayashi<sup>\*1</sup>

<sup>\*1</sup>Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Otsu, Shiga 520-2194, Japan, <sup>\*2</sup>Sakuranomiya Chemical, Co. Ltd., Moriyama, Shiga 524-0044, Japan,

<sup>\*3</sup>Northeastern Industrial Research Center of Shiga Prefecture, Nagahama, Shiga 526-0024, Japan

Abstract: Extraction of Lignin from Sugi (*Cryptomeria japonica* D. Don) by acid-catalyzed solvolysis in glycolethers at 160 °C for 2 h has been performed. The glycol lignin, obtained by concentrating the soluble fraction in glycolethers, showed good solubility to acetone, 2-butanone and chloroform. Furthermore, it was found that the glycol lignin contains considerable amount of hydroxyl groups (0.677 mmol OH / g). Preparation of polyesters by esterification of the glycol lignin and diacid chlorides (adipoyl chloride, sebacoyl chloride, and terephthaloyl dichloride) was performed in acetone. The polyesters, obtained as the insoluble fraction in acetone, showed melting transitions

at 70 °C and 190–210 °C. The multiple melting transition implies that the glycol lignin polyester has the thermotropic liquid crystalline nature, which was shown by polarized optical microscopy.

Keywords: solvolysis lignin, glycoethers, sulfonic acid, liquifaction, liquid crystalline polyesters

#### 2012 特別講演

##### バイオエタノール製造で副生するリグニンの有効利用

坂西欣也<sup>\*1</sup>、松永興哲<sup>\*1</sup>、井上宏之<sup>\*1</sup>、スヤント<sup>\*2</sup>

<sup>\*1</sup> 産業技術総合研究所、<sup>\*2</sup> インドネシア BPPT

Utilization of lignin coproduced in the bio-ethanol production process.

Kinya Sakanishi<sup>\*1</sup>, Kotetsu Matsunaga<sup>\*1</sup>, H2iroyuki Inoue<sup>\*1</sup>, Suyanto<sup>\*</sup>

<sup>\*1</sup>National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8568, Japan,

<sup>\*2</sup>Agency for the Assessment and Application of Technology, Indonesia

Abstract: Lignocellulosic biomass resources, such as wood wastes and oil palm trunks(OPT), are expected to be feedstock for recovering lignin derivatives during 2<sup>nd</sup>-generation bioethanol production process. In the present study, OPT were thermally extracted with ethyleneglycol and phenol/ ethyleneglycol mixed solvent. The soluble fraction includes mainly lignin derived fraction (LDF), which exhibited the good plasticity and thermal stability. The plasticized fractions were processed to prepare green composites (biomass-derived carbon fibers and biomass plastics).

Keywords: lignocellulosic biomass, oil palm trunks, solvent extraction, ethanol fermentation, lignin

#### 2012-201

##### MWL 抽出残渣からの LCC 解析用フラクションの探索 (2) : 2 次元 NMR による分析

宮川泰幸、上高原浩、高野俊幸

京都大学大学院農学研究科

Fractionation of extracted residue of MWL for LCC analysis (2).

Yasuyuki Miyagawa, Hiroshi Kamitakahara, Toshiyuki Takano

Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract: The residual wood meal left after milled wood lignin (MWL) isolation (MWR) was fractionated several times to afford xylan-lignin fraction (X-L). X-L was extracted with lignin solvent 1, 4-dioxane/water (9: 1, v/v) to give a soluble fraction (X-L-Fraction-1 (XL-F1)) and an insoluble fraction (XL-F1-residue). XL-F1-residue was further extracted with xylan solvent (DMSO) to afford a soluble fraction (X-L-Fraction-2 (XL-F2)) with 43.0% yield based on XL-F1-residue. XL-F2 was mainly composed of xylan and some amount of lignin, and according to the 2D NMR analysis, it is suggested the existence of phenyl glycoside type LC linkages in XL-F2.

Keywords: *Eucalyptus globulus*, milled wood lignin (MWL); lignin-carbohydrate complex (LCC); gel permeation chromatography (GPC); hetero-nuclear single quantum coherence (HSQC)

#### 2012-202

##### <sup>13</sup>C 標識法と高分解能NMR を組み合わせたリグニンの構造解析

今村良教<sup>\*1</sup>、西村裕志<sup>\*2,\*5</sup>、寺島典二<sup>\*3</sup>、松下泰幸<sup>\*1</sup>、青木 弾<sup>\*1</sup>、片平正人<sup>\*4,\*5</sup>、福島和彦<sup>\*1</sup>

<sup>\*1</sup> 名古屋大学大学院生命農学研究科、<sup>\*2</sup> 京都大学生存圏研究所、<sup>\*3</sup> 名古屋大学名誉教授、<sup>\*4</sup> 都大学エネルギー理工学研究所、<sup>\*5</sup> JST-CREST

Structural analysis of lignin by a specific <sup>13</sup>C-enrichment technique combined with high resolution solution state NMR.

Yoshinori Imamura<sup>\*1</sup>, Hiroshi Nishimura<sup>\*2\*5</sup>, Noritsugu Terashima<sup>\*3</sup>, Yasuyuki Matsushita<sup>\*1</sup>, Dan Aoki<sup>\*1</sup>, Masato Katahira<sup>\*4\*5</sup>, Kazuhiko Fukushima<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioagricultural Science, Nagoya University, Nagoya 464-8601, Japan,

<sup>\*2</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Uji 611-0011, Japan,

<sup>\*3</sup>Emeritus professor, Nagoya University, Nagoya 464-8601, Japan, <sup>\*1</sup>Institute of Advanced Energy (IAE), Kyoto University, Uji 611-0011, Japan, <sup>\*5</sup>JST-CREST

**Abstract:** In order to analyze lignin structures, a technique of specific <sup>13</sup>C-enrichment of cell wall lignin combined with nondestructive analysis of the whole cell wall material by high-resolution 2D-NMR (HSQC) in solution-state has been developed. Additional technique of making difference NMR spectrum between <sup>13</sup>C-enriched lignin and unenriched lignin provided a simpler spectrum arising exclusively from the <sup>13</sup>C-enriched carbon. From the signal intensity of the simplified difference HSQC spectrum between <sup>13</sup>C- $\alpha$ -enriched and unenriched lignins, quantitative determination was made on the frequencies of major inter-unit bonds, and coniferyl alcohol, coniferaldehyde end groups.

2012-203

MALDI-FT-ICR MS/MSによる単離リグニンの精密構造解析

吉岡 康一<sup>\*1</sup>、丸本 真輔<sup>\*1</sup>、渡辺 隆司<sup>\*1, \*2</sup>

<sup>\*1</sup>京大生存圏研究所、<sup>\*2</sup>JST, CREST

Structural analysis of the isolated lignin by MALDI-FT-ICR MS/MS.

Koichi Yoshioka<sup>\*1, \*2</sup>, Shinsuke Marumoto<sup>\*1</sup>, Takashi Watanabe<sup>\*1, \*2</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere (RISH), Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan. <sup>\*2</sup>CREST, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

**Abstract:** MALDI-MS gives direct structural information in a wide range of molecular weight regions. However, structural analysis of lignin by MALDI-MS is still limited. Our group has analyzed isolated and synthetic lignin using MALDI-TOF and Fourier-transform ion cyclotron resonance (FT-ICR) MS. In this study, structure of the lignin isolated from *Eucalyptus globulus* and *Fagus crenata* was analyzed by MALDI-FT-ICR MS/MS. Comparative analyses of the mass spectra between the isolated lignin and synthetic lignin model compounds demonstrated existence of oligomeric structures including  $\beta$ - $\beta$  and  $\beta$ -O-4 linkages.

**Keywords:** interunit linkage, network structure,  $\beta$ -O-4 linkage, syringaresinol, *Eucalyptus globulus*, *Fagus crenata*

2012-204

Lignin released from spruce wood during hot-water extraction.

Ivan Sumerskiy, Andrey Pranovich, Bjarne Holmbom, Stefan Willför

Process Chemistry Centre, Laboratory of Wood and Paper Chemistry, Åbo Akademi University, FI-20500 Turku/Åbo, Finland.

**Abstract.** Ground spruce sapwood was extracted with pressurized hot water in an accelerated solvent extractor (ASE) at 170 °C during 20, 60 and 100 min. Dissolved aromatic substances in water extracts were isolated by sorption on XAD-7 resin and fractionated into lignin, oligomeric aromatic substances (OAS) and insoluble-in-methanol compounds (IMC). The extracted and separated fractions as well as the ground wood before and after extraction were analyzed by classical wet chemistry (Derivatization Followed by Reductive Cleavage (DFRC), Klason lignin and content of extractive substances) and instrumental physico-chemical methods (GC, RP-HPLC and SEC, and NMR, FT-IR, UV and mass spectrometry). The yield of dissolved lignin slightly increased during the

hot-water extraction. Simultaneously, the proportion of lignin in extracted total dissolve solids decreased to about the half. The physico-chemical characteristics of isolated lignins were considerably different compared to spruce MWL. The extracted lignin had a notably lower molar mass than MWL. During hot-water extraction the number of hydroxyl and especially carboxylic groups in lignins increased and the lignins became more condensed.

2012-205

アセチルブロミド法によるリグニン含有量の定量におけるタケパルプ中のキシラン含有量の影響(II)フルフラール生成量の検討

中川明子、張翼、大井洋

筑波大学大学院 生命環境科学研究科

Effect of xylan content in alkali bamboo pulp on determination of lignin content by acetyl bromide method (II) -Examination of furfural production -.

Akiko Nakagawa-izumi, Yi Zhang, Hiroshi Ohi

Graduate School of Life and Environmental Sciences, University of Tsukuba

Abstract: The xylan in hardwood pulp affects the acetyl bromide method due to UV absorption of the product. The maximum production of furfural from xylose in the acetyl bromide treatment was 8.5 %. During room temperature treatment, furfural decreased slightly, but UV absorbance of the resulting solution at 280nm increased. On the other hand, in this treatment with heating, furfural decreased remarkably but those of UV absorbance increased slightly. It shows that xylan produces furfural and it promptly changes to product which has UV absorption.

2012-206

リグニン  $\beta$ -O-4結合新規選択的開裂法( $\gamma$ -TTSA法)の検討(4)-天然リグニンへの適用-

安藤大将<sup>\*1</sup>、西村裕志<sup>\*2\*3</sup>、片平正人<sup>\*3</sup>、高野俊幸<sup>\*1</sup>、矢野浩之<sup>\*2</sup>、中坪文明<sup>\*2</sup>

<sup>\*1</sup>京都大学大学院農学研究科、<sup>\*2</sup>京都大学エネルギー理工学研究所、<sup>\*3</sup>京都大学生存圏研究所

Studies on the selective cleavage method for  $\beta$ -O-4 linkages of lignins ( $\gamma$ -TTSA method). (4) -Application to natural lignin-

Daisuke Ando<sup>\*1</sup>, Hiroshi Nishimura<sup>\*2\*3</sup>, Masato Katahira<sup>\*2</sup>, Toshiyuki Takano<sup>\*1</sup>, Hiroyuki Yano<sup>\*3</sup>, Fumiaki Nakatsubo<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

<sup>\*2</sup>Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan

<sup>\*3</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan

Abstract: Application of  $\gamma$ -TTSA method (consisted of four reactions; tosylation, thioetherification, sulfonation, alkali-treatment), which has been proposed as new selective  $\beta$ -O-4 cleavage method, to Milled Wood Lignin (MWL) from *Eucalyptus globulus*. HSQC-NMR spectra of the four reaction products suggested that the four reactions proceeded in MWL as well as in lignin model compounds. Especially, HSQC-NMR spectrum of the final product revealed that  $\beta$ -O-4 linkages were selectively cleaved with the retention of  $\beta$ - $\beta$  linkages in the last reaction.

Keywords: Cleavage of  $\beta$ -O-4 linkage,  $\beta$ -Elimination, *Eucalyptus globulus*, HSQC-NMR, LCC, Milled Wood Lignin

2012-207

TEMPOをメディエーターに用いたリグニンモデル化合物の電解酸化

三波 由実<sup>\*1</sup>、白石 匠<sup>\*2</sup>、高野 俊幸<sup>\*1</sup>、上高原 浩<sup>\*1</sup>

<sup>\*1</sup>京都大学大学院農学研究科、<sup>\*2</sup>京都大学生存圏研究所

TEMPO-mediated electro-oxidation of lignin model compounds.

Yumi Sannami\*<sup>1</sup>, Takumi Shiraishi\*<sup>2</sup>, Toshiyuki Takano\*<sup>1</sup>, Hiroshi Kamitakahara\*<sup>1</sup>

\*<sup>1</sup>Division of Forest & Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan, \*<sup>2</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

**Abstract:** The TEMPO-mediated electro-oxidation of monomeric lignin model compound **1G** (1-(4'-ethoxy-3'-methoxyphenyl) ethanol) in 70% CH<sub>3</sub>CN-H<sub>2</sub>O and 10% dioxane-carbonate buffer afforded the corresponding C  $\alpha$ -carbonyl compound **2G** in high yields, suggesting that the oxidation of C  $\alpha$ -hydroxyl group proceeded efficiently. On the other hand, in the TEMPO-mediated oxidation of dimeric compound **3G** (4-ethoxy-3-methoxyphenylglycerol- $\beta$ -guaiacyl ether) in 70% CH<sub>3</sub>CN-H<sub>2</sub>O, most of starting material **3G** was recovered, whereas in that of compound **3G** in 10% dioxane-carbonate buffer, the corresponding C  $\gamma$ -carbonyl compound **7G** was obtained as a main product in moderate yield, suggesting that the oxidation of C  $\gamma$ -hydroxyl group proceeded efficiently. As the result, it was found that the TEMPO-mediated electro-oxidation was significantly influenced by the solvent used.

**Keyword:** 2,2,6,6-tetramethylpiperidine-*N*-oxyl, electrolysis, mediator, lignin, C  $\alpha$ -carbonylation

2012-208

広葉樹リグニン熱分解における低分子シリンゴール類/グアイアコール類の生成挙動

小竹毅郎、河本晴雄、坂 志朗

京都大学大学院エネルギー科学研究科

Formation behaviors of monomeric syringols/guaiacols in pyrolysis of hardwood lignin.

Takeo Kotake, Haruo Kawamoto, Shiro Saka

Graduate School of Energy Science, Kyoto University

**Abstract:** Hardwood lignin gives monomeric syringols/guaiacols with various side-chains at 300-350° C, while their pyrolytic formation mechanisms are not well-known. To clarify it, pyrolytic reactivities of sinapyl alcohol (SA) and coniferyl alcohol (CA) were compared first under the condition of N<sub>2</sub>/200-350°C/5min. As a result, pyrolytic products from SA were similar to those from CA, which suggests similar reactions occurring for both compounds. Influences of the addition of a solvent (1,3-diphenoxybenzene) and an H-donor (1,2,3,10b-tetrahydrofluoranthene) on the reactivities of SA and CA suggested that the decomposition reactivity of SA dramatically increase at 350°C where radical intermediates play important roles. This characteristic feature reduced the monomeric syringols yields significantly at 350°C under neat condition and in solution from SA and buna milled wood lignin (MWL). The addition of the H-donor increased the monomeric syringols yields greatly, which is explained by the stabilization effect on the intermediate radicals. On the other hand, the monomeric syringols yields from buna wood at 350°C were much higher from those of buna MWL and sugi (MWL/wood) even without the addition the H-donor. These results indicate that the buna wood pyrolysis at 350°C produces some H-donors for stabilization of the intermediate radicals from buna lignin.

**Keywords:** lignin, pyrolysis, mechanism, sinapyl alcohol, monomer formation

2012-209

亜硫酸を用いた前加水分解化学パルプ化法

石 岩、横山朝哉、秋山拓也、松本雄二

東京大学大学院農学生命科学研究科

Prehydrolysis chemical pulping by the use of sulfurous acid.

Shi Yan, Tomoya Yokoyama, Takuya Akiyama, Yuji Matsumoto

Wood Chemistry Laboratory, Department of Biomaterials Sciences,  
Graduate School of Agricultural and Life Sciences, The University of Tokyo

**Abstract:** For the total utilization of wood polysaccharides, suitable combination of prehydrolysis stage and chemical pulping (delignification) stage was surveyed. Condition of prehydrolysis by the use of hydrochloric acid, sulfuric acid or sulfurous acid was adjusted so that majority of hemicellulose could be obtained as monosaccharides. Prehydrolysis residue was subjected to chemical pulping under various condition. Pulping of prehydrolysis residues obtained by hydrochloric acid or sulfuric acid were rather difficult under any conditions examined. On the other hand prehydrolysis residue obtained by sulfurous acid were found to be easily delignified by simple alkali cooking and give pulp in rather high yield (42% based on the original wood) with rather high purity as cellulose (about 92%). Monosaccharide yield from hemicellulose during prehydrolysis stage was close to 90%.

2012–210

Biodegradation behavior of petroleum hydrocarbons by *Pestalotiopsis* sp. NG007.

Dede Heri Yuli Yanto, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University, 3–5–7 Tarumi, Matsuyama, Ehime 790–8566, Japan

**Abstract:** The biodegradation of three different petroleum hydrocarbon samples, namely, heavy oil A, heavy oil C and asphalt by *Pestalotiopsis* sp. NG007 was examined under ligninolytic condition at pH 4.5 or under saline condition at pH 8.2. *Pestalotiopsis* sp. NG007 exhibited high activity for the biodegradation of all three petroleum hydrocarbon samples. However, the biodegradability was found to be highly dependent on the type of petroleum hydrocarbons and the environmental condition. The degree of biodegradation of petroleum hydrocarbon components differed according to the petroleum hydrocarbons, the aliphatic fraction being more susceptible to biodegradation than the aromatic, resin, and asphaltene fraction in all petroleum hydrocarbon samples. The extent of biodegradation by *Pestalotiopsis* sp. NG007 was found to be in the order of heavy oil A > heavy oil C > asphalt; the petroleum hydrocarbons with higher composition of aliphatic fraction being more susceptible to biodegradation. Regarding to environmental condition, aliphatic and aromatic fraction was preferentially degraded under saline condition at pH 8.2, particularly in asphalt, led to higher biodegradation rate compared with under ligninolytic condition at pH 4.5. The study shows that the dynamic ratio of aliphatic to other constituents in petroleum hydrocarbons affects the biodegradation behavior by *Pestalotiopsis* sp. NG007.

**Keywords:** biodegradation, heavy oil, asphalt, hydrocarbon, *Pestalotiopsis* sp., ligninolytic enzymes.

2012–2011

Enhancement of ligninolytic systems for degradation of DDT by *Trametes versicolor* U97 pre-grown in oil palm empty fruit bunch.

Ajeng Arum Sari<sup>\*1</sup>, Kazutaka Itoh<sup>\*2</sup>, Sanro Tachibana<sup>\*2</sup>

<sup>\*1</sup>The United Graduate School of Agricultural Sciences, Ehime University, 3–5–7 Tarumi, Matsuyama, Ehime 790–8566, Japan, <sup>\*2</sup>Department of Applied Bioscience, Faculty of Agriculture, Ehime University, 3–5–7 Tarumi, Matsuyama, Ehime 790–8566, Japan

**Abstract:** Oil palm empty fruit bunch (EFB) as agricultural waste is potentially used for pre-grown source of white-rot fungi (WRF) since it contains lignin, cellulose and hemicellulose. Enzyme activity secreted by WRF mainly depends on its additives such as metals and veratryl alcohol. This study aims to investigate the ability of EFB as pre-grown source of *Trametes versicolor* U97 to degrade DDT in liquid medium and soil including addition of several additives e.g.

CuSO<sub>4</sub>, MnSO<sub>4</sub>, and veratryl alcohol in soil. DDT in water, malt extract liquid medium, and soil was degraded 68%, 75%, and 54% during 30 d incubation period, respectively. Addition of CuSO<sub>4</sub> even in low concentration and MnSO<sub>4</sub> in high concentration have negative effect for DDT degradation. Furthermore, 0.5 mM of veratryl alcohol was optimum concentration to obtain the maximum degradation. Addition of EDTA as lignin peroxidase (LiP) inhibitor could reduce degradation of DDT, revealed lignin peroxidase plays a role in degradation of DDT.

Keywords: biodegradation, DDT, oil palm empty fruit bunch, *Trametes versicolor* U97, lignin peroxidase.

2012-212

Degradation of 2,4,8-trichlorodibenzofuran, a polychlorinated dibenzofurans, by *Cerrena* sp. F0607. Asep Hidayat, Kazutaka Itoh, Sanro Tachibana

Faculty of Agriculture, Ehime University, 3-5-7 Tarumi, Matsuyama, Ehime 790-8566, Japan

Abstract: *Cerrena* sp. F0607 was chosen as fungus degrader and degradation of 2,4,8-trichlorodibenzofuran (2,4,8-TCDF) was investigated. The degradation of 2,4,8-TCDF was above 40% after 30 day, the degradation per-unit biomass increased during the incubation period, and glucose consumption increased rapidly when 2,4,8-TCDF was present in the culture. It was evidence that fungus oxidized 2,4,8-TCDF as an alternative source of energy and carbon. The increasing of glucose consumption stimulated the growth of fungi that will couple to the degradation of 2,4,8-TCDF. The ligninolytic enzymes were detected and tent to increase their activity in the presence of 2,4,8-TCDF, especially laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP). The addition of various additives, such as MnSO<sub>4</sub>, CdSO<sub>4</sub>, CuSO<sub>4</sub>, 1-Hydroxybenzotriazole (HBT), NaN<sub>3</sub>, AgNO<sub>3</sub>, and Piperonyl Butoxide (PB) was investigated. The result showed that there were variation on both degradation and enzymatic activities. Through a *Partial Least Square* analysis, it could be clearly concluded that laccase has a role in the degradation of 2,4,8-TCDF. Whereas cytochrome P-450 monooxygenase could not be excluded from the degradation of 2,4,8-TCDF, since PB showed inhibition of the degradation without disturbing fungal growth.

Keywords: biodegradation, 2,4,8-TCDF, *Cerrena* sp., ligninolytic enzymes, oxygenase.

2012-213

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株における glyoxal oxidase 遺伝子高発現によるリグニン分解特性の改善

山田祐人<sup>\*1</sup>、平井浩文<sup>\*2</sup>、河岸洋和<sup>\*1\*2</sup>

<sup>\*1</sup>静岡大学農学部、<sup>\*2</sup>静岡大学創造科学技術大学院

Improvement of ligninolytic properties by high expression of glyoxal oxidase gene in hyper lignin-degrading fungus *Phanerochaete sordida* YK-624.

Yuto Yamada<sup>\*1</sup>, Hirofumi Hirai<sup>\*1</sup>, Hirokazu Kawagishi<sup>\*1\*2</sup>

<sup>\*1</sup>Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan

<sup>\*2</sup>Graduate School of Science and Technology, Shizuoka University, Shizuoka 422-8529, Japan

Abstract: Glyoxal oxidase (GLOX) is a radical copper oxidase that catalyzes the oxidation of aldehydes to carboxylic acids coupled to the dioxygen reduction to H<sub>2</sub>O<sub>2</sub>. GLOX is a source of the extracellular H<sub>2</sub>O<sub>2</sub> that is required for the oxidations catalyzed by the ligninolytic peroxidases. In the present study, GLOX gene (*glx*) of *Phanerochaete chrysosporium* was cloned, and the promoter of *bee2* cloned from *P. sordida* YK-624 was used to drive the expression of *glx*. The expression vector was transformed into a *P. sordida* YK-624 uracil auxotrophic mutant UV-64, and 16 clones were obtained as *glx*-introducing transformants. These transformants showed

higher GLOX activities than wild type of *P. sordida* YK-624 and control transformants into which only marker plasmid was introduced although manganese peroxidase activities of these transformants were hardly different from those of wild type and control transformants. Moreover, these transformants showed higher ligninolytic activity than wild type and control transformants. These results suggest that ligninolytic properties of white-rot fungi can be improved by high expression of *glx*.

2012-214

大腸菌によるポルフィリンの生産と、そのリグニン分解

岸川明日香<sup>\*1</sup>、福留裕文<sup>\*2</sup>、福留留美<sup>\*2</sup>、石橋徹<sup>\*2</sup>、近藤隆一郎<sup>\*3</sup>

<sup>\*1</sup>九州大学大学院生物資源環境学府、<sup>\*2</sup>シキソンパワー株式会社、<sup>\*3</sup>九州大学大学院農学研究院

Efficient production of porphyrin by *Escherichia coli* and lignin degradation by coproporphyrin.

Asuka Kishikawa<sup>\*1</sup>, Hirofumi Fukutome<sup>\*2</sup>, Rumi Fukutome<sup>\*2</sup>, Toru Ishibashi<sup>\*2</sup>, Ryuichiro Kondo<sup>\*3</sup>

<sup>\*1</sup>Department of Agro-environmental Sciences, Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, Fukuoka 812-8581, Japan, <sup>\*2</sup>SIXONPOWER Co., Ltd.

<sup>\*3</sup>Department of Agro-environmental Sciences, Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

Abstract: *Escherichia coli* carrying a deletion of *ypjD* gene produced red pigment, when it is cultivated in minimal A culture medium. This pigment was purified and analyzed by LC/MS, GC/MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and NOESY, and it was assumed to be coproporphyrin(III). In order to find a new way to use coproporphyrin, we tried to degrade lignin by photosensitization reaction of coproporphyrin. The absorbance of alkali lignin at 280 nm decreased after photo irradiation at 368 nm with coproporphyrin( I ).

Keywords: Coproporphyrin, *Escherichia coli*, Lignin degradation, Photosensitizer, Photo irradiation

2012-215

糸状菌ラッカーゼの至適pHおよび速度パラメーターに及ぼす緩衝液中のアミノ基の影響

池田 隆造<sup>\*1</sup>、平 修<sup>\*2</sup>、近藤 隆一郎<sup>\*3</sup>、後藤 秀幸<sup>\*1</sup>

<sup>\*1</sup>石川県立大学大学院生物資源環境科学研究科、<sup>\*2</sup>北陸先端科学技術大学院大学マテリアルサイエンス研究科、<sup>\*3</sup>九州大学大学院農学研究院環境農学部門サステイナブル資源科学講座

Effects of amino group in buffer systems on optimal pH and kinetic parameters of fungal laccase.

Ryuzoh Ikeda<sup>\*1</sup>, Shu Taira<sup>\*2</sup>, Ryuichiro Kondo<sup>\*3</sup>, Hideyuki Goto<sup>\*1</sup>

<sup>\*1</sup>Graduate School of Bioresources and Environmental Science, Ishikawa Prefectural University, 1-308 Suematsu, Nonoichi, Ishikawa 921-8836, Japan; <sup>\*2</sup>School of Material Science, Japan

Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan;

<sup>\*3</sup>Department of Agro-Environmental Sciences, Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Abstract: We found that the optimal pH of fungal laccase from the white rot fungus *Pycnoporus cinnabarinus* varies with buffer systems used in the enzyme reaction. Buffer systems containing amino group (glycine and aspartic acid, tris, and ammonium) caused the optimal pH shifting to alkaline side by 1.5 pH unit for ABTS and by 1.0 pH unit for DMP. There occurred an increase of  $K_m$  and a decrease of  $k_{cat}$  for ABTS and a decrease of  $K_m$  and  $k_{cat}$  for DMP in aspartate and tris-acetate buffer system containing amino group. Protonated amino group in the buffer systems seems to affect the optimal pH and kinetic parameters for the laccase.

Keywords: fungal laccase, optimal pH shifting, substrate specificity, substrate binding site, carboxylic acid

2012-216

アオモリヒバのリグナン生合成に関与する*O*-メチルトランスフェラーゼ遺伝子の取得

鈴木綾乃<sup>\*1</sup>、萩原迪子<sup>\*1</sup>、米田夕子<sup>\*1</sup>、河合真吾<sup>\*1</sup>、西田友昭<sup>\*1</sup>、サフェンドリ・コマラ・ラガムスタリ<sup>\*2</sup>、鈴木史朗<sup>\*2</sup>、梅澤俊明<sup>\*2</sup>

<sup>\*1</sup>静岡大学農学部、<sup>\*2</sup>京都大学生存圏研究所

Isolation of *Thujopsis dolabrata* var. *hondai* *O*-methyltransferase involved in the biosynthesis of lignans.

Ayano Suzuki<sup>\*1</sup>, Michiko Hagiwara<sup>\*1</sup>, Yuko Yoneda<sup>\*1</sup>, Shingo Kawai<sup>\*1</sup>, Tomoaki Nishida<sup>\*1</sup>, Safendri Komara Ragamustari<sup>\*2</sup>, Shiro Suzuki<sup>\*2</sup>, Toshiaki Umezawa<sup>\*2</sup>

<sup>\*1</sup>Department of Environment and Forest Resources Science, Faculty of Agriculture, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan, <sup>\*2</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto 611-0011, Japan

Abstract: *Thujopsis dolabrata* var. *hondai* (Aomori-hiba, Hinoki-asunaro) is one of the useful woods in Japan. Moreover, it is known that *T. dolabrata* var. *hondai* biosynthesizes anti-cancer lignans, such as deoxypodophyllotoxin,  $\beta$ -peltatin and so on. These lignans have 3,4,5-trimethoxyphenyl nuclei, but these oxidative modifications are not present in gymnosperm lignin. Comprehensive genetic analysis by a next generation sequencer is one of the most effective approaches to identify the whole expressed genes in a particular sample, which can help identify the genes involved in the methoxyl substitutions. The aim of this study is to isolate cDNAs which encode enzymes involved in the biosynthesis, especially *O*-methyltransferases (OMTs). As a result, we isolated six OMT genes, *TdOMT 1* to *TdOMT 6*. Currently, we are conducting the heterologous expression of these genes.

Keywords: *O*-methyltransferase; syringyl lignans; biosynthesis; heterologous expression; *Thujopsis dolabrata* var. *hondai*

2012-217

*O*-Methyltransferases involved in lignan biosynthesis in *Anthriscus sylvestris*.

Safendri Komara Ragamustari<sup>\*1\*2</sup>, Takefumi Hattori<sup>\*1\*3</sup>, Eiichiro Ono<sup>\*4</sup>, Shiro Suzuki<sup>\*1</sup>, Masaomi Yamamura<sup>\*1</sup>, and Toshiaki Umezawa<sup>\*1\*2</sup>

<sup>\*1</sup>Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan. <sup>\*2</sup>Institute of Sustainability Science, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

<sup>\*3</sup>Institute of Socio-Arts and Sciences, The University of Tokushima, Tokushima, 1-1, Minamijosanjima-cho, Tokushima 770-8502, Japan, <sup>\*4</sup>Institute for Plant Science, Suntory Business Expert Ltd. 1-1-1 Wakayamadai, Shimamoto, Mishima, Osaka 618-8503, Japan

Abstract: We report the isolation and characterization of two plant *O*-methyltransferases (OMTs) involved in lignan biosynthesis in *Anthriscus sylvestris*. The recombinant OMTs were overexpressed in *E. coli* expression systems and were tested for activity using a number of substrates. Both OMTs showed exclusive regio-specific activity towards dibenzylbutyrolactone lignans. AsOMT50 converted matairesinol into arctigenin, while AsOMT116 converted thujaplicatin into 5-methylthujaplicatin, and were thus renamed AsMROMT and AsTJOMT, respectively. In a phylogenetic tree generated from an alignment of plant OMT amino acid sequences, AsMROMT and AsTJOMT are located in a clade dominated by plant flavonoid and lignan OMTs. AsMROMT is closely related to the *Carthamus tinctorius* matairesinol OMT (CtMROMT). Gas Chromatography-Mass Spectrometry (GCMS)-based analysis of recombinant AsMROMT and AsTJOMT assays towards their respective substrates show that the two OMTs have comparable kinetic attributes with previously characterized plant OMTs, having  $k_{\text{cat}}/K_m$  values of  $0.0143 \mu\text{M}^{-1} \text{min}^{-1}$  and  $0.0763 \mu\text{M}^{-1}$

min<sup>-1</sup>, respectively. Gene expression of the OMTs in different organs show that *AsTJOMT* has highest expression levels in rhizomes, which is in line with previous reports indicating high amount of lignan in the mentioned organ. As for *AsMROMT*, we were unable to observe detectable amounts of its expression in the organs that we tested. To our knowledge, this is the first report of the isolation and characterization of plant OMTs involved in lignan biosynthesis in *A. sylvestris*.

2012-218

Fluorescence-tagged monolignols for delineating plant cell wall lignification.

Yuki Tobimatsu<sup>\*1</sup>, Armin Wagner<sup>\*2</sup>, Lloyd Donaldson<sup>\*2</sup>, Prajakta Mitra<sup>\*3</sup>, Dominique Loque<sup>\*3</sup>, Oana Dima<sup>\*4</sup>, Claudiu Niculaes<sup>\*4</sup>, Wout Boerjan<sup>\*4</sup>, Jeong Im Kim<sup>\*5</sup>, Nickolas Anderson<sup>\*5</sup>, Clint Chapple<sup>\*5</sup>, John H. Grabber<sup>\*6</sup>, John Ralph<sup>\*1\*7</sup>

<sup>\*1</sup>University of Wisconsin-Madison, Department of Biochemistry, USA, <sup>\*2</sup>Scion, Biotransformation Group, New Zealand, <sup>\*3</sup>Joint BioEnergy Institute (JBEI), Lawrence Berkley National Laboratory, USA, <sup>\*4</sup>VIB, Ghent University, Department of Plant System Biology, Belgium, <sup>\*5</sup>Purdue University, Department of Biochemistry, USA, <sup>\*6</sup>US Department of Agriculture, Dairy Forage Research Center, USA. <sup>\*7</sup>US Department of Energy, Great Lakes Bioenergy Center (GLBRC), USA

Abstract: Fluorescence-tagged monolignols, *p*-hydroxycinnamyl alcohols  $\gamma$ -linked to fluorogenic dyes such as aminocoumarin, nitrobenzofuran, or styrylpyridinium derivatives were synthesized and tested as photoprobes for *in vitro* and *in vivo* studies of cell wall lignification. To illustrate the use of the probes for analysis of monolignol-protein interactions, the complexation of each coumarin-tagged monolignol with horseradish apoperoxidase was monitored by Förster resonance energy transfer (FRET). In addition, to test an imaging approach, fluorescence-tagged monolignols were fed into various plant cell systems and the localization of incorporated probes was readily visualized by fluorescence microscopy.

Keywords: enzyme-substrate complex; fluorescence probes; Förster (fluorescence) resonance energy transfer (FRET); *in vivo* imaging; monolignol conjugate synthesis; peroxidase

2012-219

*Quercus*属の外樹皮におけるスベリン芳香族部分の化学構造と酵素的生成  
伊藤彰伸, 松本匠哉, 鈴木利貞, 片山健至  
香川大学農学部

Chemical structure and enzymatic formation of aromatic domain of suberin in outer bark of *Quercus* spp.

Akinobu Ito, Takuya Matsumoto, Toshisada Suzuki, Takeshi Katayama,

Faculty of Agriculture, Kagawa University, 2393 Ikenobe, Miki-cho, Kagawa 761-0795, Japan

Abstract: To clarify chemical structure of aromatic domain of suberin in outer bark of *Quercus* spp., basic methanolysis of the outer bark of *Quercus suber*, namely cork, with sodium methoxide was performed. From the methanolysis products previously an  $\alpha=\beta-O-4'$  enol ether dimers of methyl ferulate had been isolated and identified, and furthermore the other  $\alpha=\beta-O-4'$  enol ether dimer of a ferulate derivatives was isolated in this study. This ferulate-derivative moiety is presumed to be  $\omega$ -feruloyloxy(long-chain fatty acids) methyl ester whose the long-chain fatty acids were a mixture of the monologues. A dimeric ferulate bonding to  $\omega$ -hydroxy(long-chain fatty acids) was isolated for the first time as a methanolysis product, and is considered to be derived from the bonding sites between the aliphatic and aromatic domains. Isolation of a  $\beta-5'$  benzofuran dimer of methyl ferulate was also suggested. A biosynthetic approach, dehydrogenative dimerization of 16-(feruloyloxy)-hexadecanoic acid with cell-free extracts of *Q. variabilis* bark in the presence of hydrogen peroxide was carried out in order to support the elucidation of the chemical structure.

Formation of a 4-*O*-5' diaryl ether type dimer of the substrate was found for the first time.

Keywords: Cork, *Quercus suber*, *Quercus variabilis*, ferulic acid, 16-(feruloyloxy)-hexadecanoic acid

2012-220

改変型植物酸性peroxidaseの酵母での発現と精製(4)

吉中喬慈、川合伸也

東京農工大学大学院

Heterogeneous expression and purification of modified plant peroxidase (4)

Kyouji Yoshinaka, Shinya Kawai

Tokyo University of Agriculture and Technology, Japan

Abstract: Most of plant peroxidases can oxidize coniferyl alcohol efficiently, but not sinapyl alcohol. On the other hand, a few of plant peroxidases were reported to use sinapyl alcohol as preferred substrates. It is suggested that they have the additional active sites in the other positions than the heme pocket in the active site. We tried to introduce the additional catalytic sites of these peroxidases to PrxA3a, an anionic peroxidase of hybrid aspen, *Populus kitakamiensis*, for substrate specificity modifications and for certifications of the surface amino acid residue hypothesis. As a result, PrxA3a A165W and PrxA3a F77Y, PrxA3a F77Y A165W raised the oxidizing ability of cytochrome *c* which cannot enter into the heme pocket. Furthermore, PrxA3a F77Y, PrxA3a F77Y A165W, and PrxA3a F77Y L182Y gained sinapyl alcohol polymerizing activity. We analyzed shifts of Soret band absorption by H<sub>2</sub>O<sub>2</sub> treatment. The responses to the H<sub>2</sub>O<sub>2</sub> of Soret band absorption differed in mutated PrxA3a enzymes and wild type. Therefore, it is thought that electron transfer is occurred between heme and mutated amino acid residues.

2012-P01

カンバ類癌腫病菌カバノアナタケIO-U1株生菌体による非フェノール性β-O-4型リグニンモデル二量体の分解機構

土屋 慧, 石栗 太, 飯塚和也, 吉澤伸, 横田信三

宇都宮大学農学部森林科学科

Degradation mechanisms of a non-phenolic β-O-4 lignin model dimer by intact cells of birch canker-rot fungus *Inonotus obliquus* IO-U1 strain.

Satoshi Tsuchiya, Futoshi Ishiguri, Kazuya Iizuka, Nobuo Yoshizawa, Shinso Yokota

Department of Forest Science, Faculty of Agriculture, Utsunomiya University, 350 Mine-machi, Utsunomiya 321-8505, Japan

Abstract: The present study investigated the degradation mechanisms of a non-phenolic β-O-4 lignin model dimer, 1-(4-ethoxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol, by intact cells of birch canker-rot fungus *Inonotus obliquus* IO-U1 strain. In addition, extracellular ligninolytic enzyme activities of the fungus were assayed with culture liquid based on the modified Basal III medium. The degradation products by β-O-4 bond cleavage and by cleavage of Cβ-etherified aromatic ring were detected by GC-MS analysis of the metabolites from the lignin model dimer. The activities of laccase, Mn(II)-dependent peroxidase, and lignin peroxidase were detected as ligninolytic enzymes in the fungal culture liquid. It was suggested that β-O-4 bond cleavage and cleavage of Cβ-etherified aromatic ring of the lignin model dimer might have occurred by laccase and unidentified mediators from the fungus, because laccase activity was the highest in the culture liquid.

Keywords: canker-rot fungus, forest pathology, *Inonotus obliquus*, lignin biodegradation, ligninolytic enzyme

2012-P02

イオン液体溶媒系に溶解した植物細胞壁の分子量分布

曲琛, 岸本崇生, 濱田昌弘, 中島範行

富山県立大学工学部生物工学科

Molecular weight distributions of plant cell walls recovered from various ionic liquid systems.

QU Chen, KISHIMOTO Takao, HAMADA Masahiro, NAKAJIMA Noriyuki

Bioorganic chemistry Lab, Department of Biotechnology, Toyama Prefectural University

Abstract: A method for NMR analysis of entire plant cell walls without isolating their components was recently developed in our laboratory. The method consists of ball-milling of cell walls, dissolution in ionic liquids, in situ acetylation, and recovery of acetylated materials. However, dissolution in ionic liquids with relatively long ball-milling times may cause partial degradation of wood components. In order to clarify these points, molecular weight distributions of acetylated plant cell walls recovered from different ionic liquid systems were examined by gel permeation chromatography (GPC). The results showed that the molecular weight of the acetylated cell-walls recovered from 1-allyl-3-methylimidazolium chloride ([Amim]Cl) at 30°C–80°C and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) at 100°C for 2 h were comparable to or a little higher than that of N-methylimidazole (NMI)/DMSO system.

Keywords: molecular mass, SEC, size exclusion chromatography, lignin, cellulose

2012-P03

アセチル化リグニンを原料とする水酸基を持たないエポキシ樹脂硬化物の

合成と熱的性質

廣瀬重雄<sup>\*1</sup>、川崎淳貴<sup>\*1</sup>、島田幹夫<sup>\*1</sup>、畠山立子<sup>\*2</sup>、畠山兵衛<sup>\*2</sup>

<sup>1</sup>福井工業大学・工、<sup>\*2</sup>リグノセルリサーチ(株)

Thermal properties of cured epoxy resins without hydroxyl groups derived from O-acetyl lignin.

Shigeo Hirose<sup>\*1</sup>, Junki Kawasaki<sup>\*1</sup>, Mikio Shimada<sup>\*1</sup>, Tatsuko Hatakeyama<sup>\*2</sup> and Hyoe Hatakeyama<sup>\*2</sup>

<sup>\*1</sup>Fukui University of Technology, 3-6-1 Gakuen, Fukui-City, Fukui 901-8505, Japan, <sup>\*2</sup>Lignocel

Research Co. Ltd., 73-8 Yatsumata, Fukui 910-3558, Japan

Abstract: Cured epoxy resins without hydroxyl groups were prepared using O-acetylalcoholysis lignin (AcAL). AcAL, Bisphenol A diglycidyl ether (BPADGE) and a catalytic amount of 2-ethyl-4-methylimidazole (2E4MI) were dissolved in tetrahydrofuran (THF), and then THF was removed under a reduced pressure. The obtained reaction mixtures having various [EPOXY]/[PhOAc] mole ratios ranging from 0.8 to 1.2 were cured at 150 °C for 5 hr. Thermal properties of the obtained cured epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). The glass transition temperatures ( $T_g$ 's) showed a maximum at the [EPOXY]/[PhOAc] mole ratio of 1.0. The thermal decomposition temperatures ( $T_d$ 's) and mass residues at 500 °C were almost constant regardless of [EPOXY]/[PhOAc] ratios. It was found that 2E4MI acts as an effective catalyst for the curing reaction between PhOAc groups of AcAL and epoxy groups of BPADGE.

Keywords: O-acetyl lignin, cured epoxy resins, synthesis, thermal properties.

2012-P04

土壌炭素固定能評価のための植物リターの安定炭素同位体比分析におけるリグニンの影響

山田竜彦<sup>\*1</sup>、林 徳子<sup>\*1</sup>、世良 耕一郎<sup>\*2</sup>、酒井正治<sup>\*1</sup>

<sup>\*1</sup>森林総合研究所、<sup>\*2</sup>岩手医科大学

Effect of lignin to stable carbon isotopic analysis of plant litter for the evaluation of soil organic

matter accumulation.

Tatsuhiko Yamada<sup>\*1</sup>, Noriko Hayashi<sup>\*1</sup>, Kouichiro Sera<sup>\*2</sup>, Masaharu Sakai<sup>\*1</sup>

<sup>\*1</sup>FFPRI, Tsukuba Japan, <sup>\*2</sup>Iwate Medical University, Morioka Japan

Abstract: Stable carbon isotopic analysis of plant litter provides important information for the evaluation of soil organic matter accumulation. The carbon isotope ratio of  $^{13}\text{C}/^{12}\text{C}$  ( $\delta^{13}\text{C}$ ) shows around  $-14\text{‰}$  and around  $-28\text{‰}$  on the C4 plants and C3 plants, respectively. We have reported that the isotope ratio of soils under the C3 and C4 plants shows convergence to around  $-24\text{‰}$  with the depth of the soil increasing. Fresh leaves of the C4 and C3 plants were corrected and the each leaf samples were separated in 4 kinds of extractive fractions and Klason lignin fraction. The isotope ratio data of all Klason lignin fraction showed not much difference with that of original plant leaves. The data didn't support of the hypothesis of the leaf lignin that might be a difficult to degrade in soil was the main reason of the carbon isotope ratio convergence with the soil depth.

Keywords: soil analysis, carbon isotope, plant litter, leaf lignin

2012-P05

レジノール型モデル化合物の高圧水蒸気蒸留条件と構造変化の検討

鎌田将利、葭谷耕三、棚橋光彦

岐阜大学大学院 応用生物科学研究科

Examine of condition of high-pressure steam distillation and structural change of resinol model compounds.

Masatoshi Kamada, Kouzou Yoshitani, Mitsuhiko Tanahashi

Graduate School of Applied Biological Sciences, Gifu University, Gifu 501-1193, Japan

Abstract: For determination of high-pressure steam-distillation condition of resinol type compounds from wood, some resinol and dilactone type model compounds such as sesamin, pinoresinol, syringaresinol, dehydrodiferulic acid and dehydrodisinamic acid were synthesized and submitted to the high-pressure steam-distillation at  $110^{\circ}\text{C}$  to  $180^{\circ}\text{C}$  with a newly constructed apparatus. Sesamin was distilled at  $150^{\circ}\text{C}$  but pinoresinol and syringaresinol were not distilled under these conditions. Moreover, when these compounds were heated, these compounds partially changed to each epimers. By contrast dehydrodiferulic acid and dehydrodisinamic acid were not distilled. But 1,4-diphenolic butadiene derivative was distilled by high-pressure steam-distillation. 1,4-Diphenolic butadiene derivative that is degradation product was obtained by decarboxylation of dehydrodiferulic acid and dehydrodisinamic acid.

Keywords: furofuran, furoolacton, resinol, ferulic acid, vanillin

2012-P06

リグニンを原料としたポリエステル調製の調製

磯崎友史<sup>\*1</sup>、石崎光輝<sup>\*2</sup>、幸田圭一<sup>\*1</sup>、山田竜彦<sup>\*3</sup>、浦木康光<sup>\*1</sup>

<sup>\*1</sup>北大院農、<sup>\*2</sup>北大農、<sup>\*3</sup>森林総研

Preparation of polyester derived from lignin.

Tomofumi Isozaki<sup>\*1</sup>, Koki Ishizaki<sup>\*2</sup>, Keiichi Koda<sup>\*3</sup>, Tatsuhiko Yamada<sup>\*4</sup>, Yasumitsu Uraki<sup>\*3</sup>

<sup>\*1</sup>Graduate School of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, 060-8589 Hokkaido, Japan. <sup>\*2</sup>Faculty of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, 060-8589 Hokkaido, Japan. <sup>\*3</sup>Research Faculty of Agriculture, Hokkaido University, Kita 9 Nishi 9, Kita-ku, Sapporo, 060-8589 Hokkaido, Japan. <sup>\*4</sup>Department of Biomass Chemistry, Forest and Forest Products Research Institute, 1 Matsunosato, Tsukuba, 305-8687 Ibaraki, Japan

Abstract: We prepared lignin-based fibrous polyester, by using technical lignin and carboxylic chloride. Kraft lignin (KL) and soda lignin (SL) were used as a technical lignin, while terephthaloyl

chloride (TC) was used as a carboxylic chloride. Polyethylene glycol (PEG) 400 and PEG–lignin, an isolated lignin recovered from solvolysis process of cedar wood chip with PEG400, were also used to improve mechanical strength of the resulting products. KL– and SL–based polyesters were too fragile to measure the tensile strength, but addition of PEG 400 to SL, and introduction of PEG to lignin showed a little improvement of the tensile strength and lead to thinner diameters of polyester fiber.

Keywords: kraft lignin, soda lignin, PEG–lignin, polyester, tensile strength,

2012–P07

高圧水蒸気蒸留による針葉樹材成分の抽出

伊藤優作、棚橋光彦、葭谷耕三

岐阜大学大学院 応用生物科学研究科

Extraction of constituents from soft wood by high–pressure steam distillation.

Yusaku Ito, Mitsuhiko Tanahashi, Kouzou Yoshitani

Graduate School of Applied Biological Sciences, Gifu University, Gifu 501–1193, Japan

Abstract: Newly developed high–pressure steam distillation was conducted for *Thujaopsi dorabrate* wood chips by stepwise increasing steam–temperature at 120, 140, 160, 180, and 200°C. Thujopsene was mainly distilled at 120 and 140°C, on the other hand ferrginol was mainly distilled at 160 and 180°C and some degradation products from lignin or polysaccharide such as vanillin and 5–hydroxymethylfurfural were distilled at 200°C.

Keywords: high–pressure steam, steam distillation, extract, soft wood, biomass

2012–P08

*Sphingobium* sp. SYK–6株のdehydrodiconiferyl alcohol代謝系遺伝子の単離と解析

高橋 健司<sup>\*1</sup>、上村 直史<sup>\*1</sup>、笠井 大輔<sup>\*1</sup>、菱山 正二郎<sup>\*2</sup>、原 啓文<sup>\*3</sup>、片山 義博<sup>\*4</sup>、  
福田 雅夫<sup>\*1</sup>、梶田 真也<sup>\*5</sup>、政井 英司<sup>\*1</sup>

<sup>\*1</sup>長岡技術科学大学・生物、<sup>\*2</sup>森林総合研究所、<sup>\*3</sup>岡山理科大学・生体医工学科、

<sup>\*4</sup>日本大学・生物資源科学部、<sup>\*5</sup>東京農工大学大学院・生物システム応用科学府

Characterization of the dehydrodiconiferyl alcohol catabolic genes in *Sphingobium* sp. strain SYK–6.

Kenji Takahashi<sup>\*1</sup>, Naofumi Kamimura<sup>\*1</sup>, Daisuke Kasai<sup>\*1</sup>, Shojiro Hishiyama<sup>\*2</sup>, Hirofumi Hara<sup>\*3</sup>,  
Yoshihiro Katayama<sup>\*4</sup>, Masao Fukuda<sup>\*1</sup>, Shinya Kajita<sup>\*5</sup>, Eiji Masai<sup>\*5</sup>

<sup>\*1</sup>Department of Bioengineering, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940–2188, Japan, <sup>\*2</sup>Forestry and Forest Products Research Institute, Tsukuba, Ibaraki 305–8687, Japan, <sup>\*3</sup>Department of Biomedical Engineering, Okayama University of Science, Kita–ku, Okayama 700–0005, Japan, <sup>\*4</sup>College of Bioresource Sciences, Nihon University, Fujisawa, Kanagawa 252–0880, Japan, <sup>\*5</sup>Graduate School of Bio–Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184–8588, Japan

Abstract: A bacterial catabolic pathway of a phenylcoumaran–type compound, dehydrodiconiferyl alcohol (DCA), was proposed by Habu et al. in 1988. In that pathway, the first step was the oxidation of the alcohol group at the  $\gamma$ –position of the B–ring side chain of DCA into the carboxyl group. The resultant product was degraded to 5–formylferulate and vanillin through the release of  $\gamma$ –carbon and the cleavage of C $\alpha$ –C $\beta$  linkage of the A–ring side chain. In this study, we isolated and characterized a part of the DCA catabolic genes of *Sphingobium* sp. strain SYK–6. Three alcohol dehydrogenase (ADH) genes, which conferred the DCA oxidation activity on a host strain, were isolated. In a previous study, we isolated three aldehyde dehydrogenase (ALDH) genes from SYK–6, which showed oxidation activities toward a broad range of aromatic aldehydes. All these ALDH gene products oxidized DCA–L into DCA–C. These results suggest that multiple ADH

and ALDH genes are involved in the conversion of DCA into DCA-C. Identification of the metabolites of DCA-C suggests that DCA-C was oxidized to DCA-CL, and then DCA-CL was converted to DCA-S via DCA-CC. The enzyme activity to convert DCA-C into DCA-CL was inducible, and did not require any cofactor.

Keywords: dilignol,  $\beta$ -5, biodegradation, microorganism

2012-P09

ヤマモモおよびオオバヤシャブシの環状ジアリールヘプタノイド生合成遺伝子の検索

笠井美波、鈴木綾乃、斉藤太一、米田夕子、河合真吾、西田友昭

静岡大学農学部

Isolation of cyclic diarylheptanoid synthase genes from *Myrica rubra* and *Alnus sieboldiana*.

Minami Kasai, Ayano Suzuki, Taichi Saito, Yuko Yoneda, Shingo Kawai, Tomoaki Nishida

Department of Environment and Forest Resources Science, Faculty of Agriculture, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan

Abstract: We have investigated the biosynthesis of a cyclic diarylheptanoid myricanol in *Myrica rubra* by feeding experiments using  $^{13}\text{C}$ -labeled cinnamic acid derivatives. On the other hand, we isolated cyclic diarylheptanoids from *Alnus sieboldiana*, which have  $\alpha$ -glucosidase inhibitory activity. In the present study, to identify the cyclic diarylheptanoid synthases of *M. rubra* and *A. sieboldiana*, their total RNAs were isolated from young shoots, and analyzed by a next generation sequencer. EST sequences having 70~80% homolog with chalcone synthase (CHS) super family were selected. 5' - and 3' - RACE PCRs were performed using the EST sequences and cDNAs synthesized from total RNAs of *M. rubra* and *A. sieboldiana*.

Keywords: cyclic diarylheptanoids; biosynthesis; transcriptome; *Myrica rubra*; *Alnus sieboldiana*

2012-P10

グリコールエーテル系溶剤中での酸分解によりスギ木粉から抽出したリグニンの沈殿分別と特性化

井林賢太<sup>\*1</sup>, 山本涼太郎<sup>\*1</sup>, 石井大輔<sup>\*1</sup>, 山崎昌男<sup>\*2</sup>, 白井伸明<sup>\*3</sup>, 松本正<sup>\*3</sup>, 中沖隆彦<sup>\*1</sup>, 林久夫<sup>\*1</sup>

<sup>\*1</sup>龍谷大学理工学部物質化学科, <sup>\*2</sup>桜宮化学株式会社, <sup>\*3</sup>滋賀県東北部工業技術センター

Precipitation fractionation and characterization of lignin from sugi (*Cryptomeria japonica* D. Don) extracted by acid-catalyzed solvolysis in glycolethers.

Daisuke Ishii<sup>\*1</sup>, Masao Yamazaki<sup>\*2</sup>, Ryotaro Yamamoto<sup>\*1</sup>, Kenta Ibayashi<sup>\*1</sup>, Nobuaki Shirai<sup>\*3</sup>, Tadashi Matsumoto<sup>\*3</sup>, Takahiko Nakaoki<sup>\*1</sup>, Hisao Hayashi<sup>\*1</sup>

<sup>\*1</sup>Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Otsu, Shiga 520-2194, Japan. <sup>\*2</sup>Sakuranomiya Chemical, Co. Ltd., Moriyama, Shiga 524-0044, Japan.

<sup>\*3</sup>Northeastern Industrial Research Center of Shiga Prefecture, Nagahama, Shiga 526-0024, Japan

Abstract: Extraction of lignin from sugi woodmeal was performed by solvolysis in mixed glycolethers to which *p*-toluenesulfonic acid was added as catalyst. The solvolysis was performed under reflux at 160 °C for 2 h. Lignin was obtained by concentrating the liquified fraction at 110 °C for 4 h under vacuum. Structural analysis of the obtained lignin was performed by FT-IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. Furthermore, in order to recover the lignin as solid, precipitation fractionation of the liquified lignin was attempted.

Keywords: solvolysis lignin, glycolethers, sulfonic acid, liquifaction, precipitation fractionation

2012-P11

広葉樹ユリノキあて材の樹幹内におけるリグニンおよび多糖類の偏在性

秋山拓也、松本雄二

東京大学大学院農学生命科学研究科

Uneven distribution of lignin, cellulose and hemicellulose in the tension wood stem of yellow poplar (*Liriodendron tulipifera*).

Takuya Akiyama, and Yuji Matsumoto

The University of Tokyo, Graduate School of Agricultural and Life Sciences, 1-1-1 Yayoi, Bunkyo, Tokyo 113-8657.

Abstract: Neutral sugar analysis was applied to wood meal taken from various sapwood positions in the tension wood stem of yellow poplar (*Liriodendron tulipifera*), and the results were compared with those of lignin analyses previously reported. The yield of glucose was higher along the periphery of the stem toward the tension wood part. In contrast, the yields of xylose and mannose were lower in this direction. A high positive correlation was observed between mannose yield and Klason lignin content ( $R^2 = 0.92$ ). The xylose yield was also correlated with the methoxyl content of the Klason residue ( $R^2 = 0.93$ ) and the *erythro/threo* ratio of  $\beta$ -O-4 structures ( $R^2 = 0.95$ ).

Keywords: reaction wood, mannan, xylan, lignin content, arylglycerol- $\beta$ -aryl ether

2012-P12

深海沈木から単離したバクテリアの分類学的位置と芳香族モノマー代謝

大田ゆかり、西真郎、芳賀拓真、坪内泰志、丸山正、長谷川良一、秦田勇二

(独)海洋研究開発機構 (JAMSTEC)

Phylogenetic analysis of culturable bacteria from deep-sea sunken wood and their aromatic compounds metabolism.

Yukari Ohta, Shinro Nishi, Takuma Haga, Taishi Tsubouchi, Tadashi Maruyama, Ryoichi Hasegawa, Yuji Hatada

Japan Agency of Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho Yokosuka 237-0061, Japan

Abstract: Functional screenings of culturable bacteria isolated from sunken wood collected from the deep sea revealed the existence of capable of metabolizing lignin-related aromatic compounds. The isolates were classified into diverse phyla, including Firmicutes, Actinobacteria, Bacteroidetes, and Proteobacteria. Twenty-one unique 16S rRNA gene sequences were detected including marine lineage isolates. The metabolites of the isolates were analyzed using liquid chromatography/mass spectrometry (LC/MS) or gas chromatography/mass spectrometry (GC/MS). Most of the representative isolates non-oxidatively decarboxylated the substrates to produce the corresponding aromatic vinyl monomers, which are used as feed stocks for bio-based plastics production. Oxidative metabolism of the lignin-related compounds for assimilation was frequently observed. Our study showed that the deep-sea environment contains an abundance of microorganisms capable of both non-oxidative and oxidative bioconversion of lignin-derived aromatic compounds. The ability for bioconversion of aromatic compounds found in this study will facilitate the development of future biotechnological applications.

Keywords: aromatic compounds, bioconversion, deep-sea bacteria, phenolic acid, vinyl monomer