

Abstracts

T. IKEDA, M. TAKAHASHI and K. NISHIMOTO: **Antitermitic Components of Kaya Wood, *Torreya nucifera* SIEB. et ZUCC.**, Mokuzai Gakkaishi (J. Japan Wood Res. Soc.), **24**, 262 (1978).

The antitermitic components of Kaya wood, *Torreya nucifera* SIEB. et ZUCC., against subterranean termites, *Coptotermes formosanus* SHIRAKI, were investigated. From the ether soluble fraction were isolated four antitermitic compounds, dendrolasin, nuciferal, torreyal and *o*-methoxycynnamic aldehyde. It is noticeable from the view point of the chemical structure-activity relationship that three aldehyde compounds were responsible for the resistance of Kaya wood against the termites. Torreyal and *o*-methoxycynnamic aldehyde, particularly, showed both termicidal and repellent activities.

K. NISHIMOTO: **Effect of Preservative Treatment of Timber on Wet-Vacuum System**, Mokuzai Kogyo (Wood Industry), **33**, No. 374, 23 (1978). (in Japanese).

Effect of new wood preservation process, coined as "wet vacuum system", is discussed. This process differs from the dry vacuum system, exemplified by the BETHELL process, in that timber is dipped immediately in preservative solution without preliminary vacuum of timber in immersion tank. It was found that wet vacuum process is the preferred commercial approach of lauan and other *Lyctus*-susceptible hardwoods because of its greater and uniform penetration of preservatives and shorter time of treatment.

K. NISHIMOTO: **Control of Wood-Boring Insects (15), Plywood Treated with Insecticide Mixed with Glue**, Mokuzai Kogyo (Wood Industry), **33**, No. 376, 41 (1978). (in Japanese).

The manufacturing process of plywood treated with insecticide mixed with glue was described. In addition, selection of insecticides fit for the process, analytical method of them diffused into each layer of plywood, and insecticidal effect of treated plywood are discussed briefly.

K. NISHIMOTO: **Control of Wood-Boring Insects (16), Control Measures of Termites**, Mokuzai Kogyo (Wood Industry), **33**, No. 377, 42 (1978). (in Japanese).

Practical design and construction practices for building construction to protect again termite attack are outlined. As to the several methods for controlling termite attack, their merits and demerits are discussed briefly.

S. HAYASHI, K. TSUNODA and K. NISHIMOTO: **Anatomy and Properties of Tropical Woods. Manual III-Anatomy of 10 Argentine Wood Species**, Mokuzaikenkyushiryō (Wood Research Review), No. 12, 29 (1978). (in Japanese)

The third report of a series of the research on anatomy and properties of tropical woods to supply the basic informations for reasonable utilization of woods.

Ten Argentine wood species are briefly mentioned on their distribution, uses, characters (color, hardness, specific gravity, grain and figure), and anatomical features with color pictures of appearance and microscopic pictures of cross-, radial- and tangential sections (40x).

K. TSUNODA and K. NISHIMOTO: **Distribution of the Teredinidae along the coasts of Japan, with a review of all named forms from Japan**, Mokuzaigakkaishi, 24, 127 (1978).

The classification of the Japanese teredinids is fairly confused, and the geographic distribution of the species has not been confirmed so far. Therefore, teredine specimens were collected at 33 localities, and were identified according to the new Turner's systematics to discuss the pattern of distribution of the teredinids along the coasts of Japan in conjunction with the results of early works reviewed.

Of 24 species that appeared in the early papers, only 9 species were found in the present investigation: *Teredo navalis* LINNAEUS, *Teredo furcifera* VON MARTENS, *Lyrodus pedicellatus* (QUATREFAGES), *Bankia carinata* (GRAY), *Bankia campanellata* MOLL and ROCH, *Bankia johnsoni* BARTSCH, *Bankia bipennata* (TURTON), *Teredora princesae* (SIVICKIS) and *Nototerodo edax* (HEDLEY).

Teredo navalis and *Lyrodus pedicellatus* are widely distributed in Japanese waters. *Bankia carinata* is relatively common, but the distribution is restricted to south-western parts of Japan. *Bankia johnsoni*, *Bankia bipennata* and *Teredora princesae* are found only in southern parts. For *Teredo furcifera*, *Bankia campanellata* and *Nototerodo edax*, the pattern of distribution is not evident because of insufficient locality records. The species which are not found in the present investigation but recorded before are generally distributed in southern areas with an exception of *Bankia setacea* (TRYON) in Hokkaido.

T. KOSHIJIMA, M. YONEDA, R. TANAKA and F. YAKU: **Chelating Polymers Derived from Cellulose and Chitin. II. Variation of the Amounts of Combined Metallic Ions with Functional Group Densities of Cellulosic Chelating Polymers**, Cellulose Chem. Technol., 11, 431 (1977).

The amounts of metallic ions combined to cellulose thiosemicarbazones carrying different densities of the thiosemicarbazono group were determined on Cu^{2+} , Hg^{2+} , Pb^{2+} and Ag^+ ions. By using chelating polymers having 97.3 (I), 78.7 (II), 57.5 (III)

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and 39.6% (IV) functional group ratios introduced, it was found that the maximum amounts of combined metallic ions were observed with (III) in Cu^{2+} , with (II) in Pb^{2+} and Hg^{2+} and with (I) in Ag^+ ion. These facts imply that the cellulosic chelating polymers having sparse functional group densities will preferentially coordinate to metallic ions with larger effective ionic radii in water while dense functional groups in chelating polymer tend to catch the ions with smaller ionic radii.

Cellulose semicarbazone was also synthesized and the combined metallic ions were analyzed under the condition where two kinds of transition metallic ions co-exist in a single solution. Abnormally high exchanging capacities of precious metallic ions were characteristic for these chelating polymers.

H. KAJITA, M. YONEDA, T. KOSHIJIMA, J. MUKUDAI and S. YATA: **Heat of wetting of the Constituents of Wood in Water**, J. Soc. Material Sci. Japan, **26**, No. 284, 417 (1977).

The total heat of wetting in water has been determined calorimetrically on extractive-free wood (red pine and beech) as well as on the major components derived from it. The major components used for the present tests were; holocellulose, α -cellulose, hemicelluloses, lignin-carbohydrate complex, and lignin. Especially, acetyl glucomannan and acetyl glucuronoxylan were used in order to get informations on the native state of hemicellulose in wood.

The results obtained are as follows:

(1) The total heat of wetting of extractive-free red pine and beech wood in water are 20.49 cal/g and 19.67 cal/g, respectively.

(2) The total heat of wetting of α -cellulose is almost the same as those of the wood.

(3) Of the materials tested, hemicelluloses had the highest total heat of wetting; acetyl glucomannan: 26.80 cal/g, arabinoglucuronoxylan: 30.18 cal/g and acetyl glucuronoxylan: 24.42 cal/g.

(4) The total heat of wetting of lignin is markedly affected by the method used for the preparation of samples. The values for lignin such as milled wood lignin and alcohol lignin, are lower than those of the other major components. The value for Klason lignin is somewhat larger than those for lignin mentioned above.

(5) From these results it is possible to estimate the relative contributions of its three major components to the total heat of wetting of wood. The proportion of contributions of the three components to the total heat of wetting of extractive-free red pine wood is 0.43 for cellulose, 0.38 for hemicelluloses and 0.19 for lignin. values for beech wood are 0.36, 0.48 and 0.16, respectively.

T. KOSHIJIMA, F. YAKU, and R. TANAKA: **Fractionation of Bjorkman LCC from *Pinus densiflora***, Applied Polymer Symposium No. 28, 1025 (1976).

Using DEAE Sephadex, Björkman LCC was fractionated into acetyl glucomannan (C-1-M, 50~55%), an acidic polysaccharide fraction (C-1-A, 24~26%) and a lignin-rich fraction containing carbohydrates (C-1-R, 3.5~4.5%). The last fraction was subjected to enzymic degradation with refined "cellulysin" to give the precipitate, which was further resolved by using an ethanol-water (2:1) mixture as solvent into a soluble (LCP-1E) and an insoluble (LCP-1) part. Repetition of the enzymic degradation and fractionation in the same manner as above gave fractions II and IIE. Fraction LCP-IIE with \bar{M}_n 3700 migrated electrophoretically to the anode as a single spot. It contained about 80% lignin and 8.4~9.4% neutral sugar units composed of D-mannose, L-arabinose, D-galactose, D-xylose, and D-glucose in the molar ratio of 3(2):1:3(2):1:1. Methylation and hydrolysis of IIE gave 2,3,4,6-tetra-O-methyl-D-galactose, 2,3,5-tri-O-methyl-L-arabinose, 2,3,4-tri-O-methyl-D-xylose, 2,3,4-tri-O-methyl-D-xylose, 2,3,6-tri-O-methyl-D-mannose, and 2,3,6-tri-O-methyl-D-glucose. It is believed from those results that D-galactose, L-arabinose, and D-xylose are bound glycosidically to the lignin in IIE, which involves two sugar residues for every lignin fragment.

F. YAKU, E. MURAKI, K. TSUCHIYA, Y. SHIBATA, and T. KOSHIJIMA: **The Preparation of Glucosamine Oligosaccharide and Its Cu(II) Complex**. Cellulose Chem. Technol., **11**, 421 (1977).

Chitosan was partially degraded by using nitrous acid. The degraded product was fractionated by means of fractional precipitation using aqueous ethanol solution of different concentrations containing a small amount of hydrochloric acid. Three fractions were obtained (F-1, F-2, and F-3) and purified by gel filtration on Sephadex G-15 column. Analysis indicated that all the fractions obtained were 2,5-anhydromannose glycoside of glucosamine oligosaccharide which contained 9~17 glucosamine units. The water soluble Cu(II) complex of glucosamine oligosaccharide was prepared. The molar ratio of Cu(II) to glucosamine unit in complex was determined from the visible spectrum of the aqueous solution to be 1:4.

T. KOSHIJIMA: **Chemical Conversion of Lignin for Practical Utilization**, J. Soc. Material Sci. Japan, **25**, No. 279, 1143 (1976).

Chemical conversion of lignins are surveyed from the view point of practical utilization. Hydrogenolysis products, grafting of hydrochloric acid lignin under irradiation of gamma ray, graft copolymerization of methyl methacrylate onto lignosulfonate by H_2O_2 -Fe(II) redox system and physical properties of the grafted lignins are described.

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T. KOSHIJIMA: **Chelating polymers Derived from Dialdehyde Cellulose**, Wood Research Review No. 11, 1 (1977).

Synthesis, characteristics, and metal-capturing ability of the chelating polymers derived from dialdehyde cellulose are described in relation to their selectivity for metallic ions.

J. AZUMA, N. KASHIMURA and T. KOMANO: **Studies on Pig Serum Lipoproteins V. Optical Properties of Low Density Lipoproteins**, J. Biochem., **83**, 1533 (1978).

The circular dichroism (CD), optical rotatory dispersion (ORD), and fluorescence emission spectra of two subfractions of pig serum low density lipoproteins (LDL₁ and LDL₂) were compared. The contribution of the carbohydrate moiety to the CD and ORD spectra was estimated on the basis of data obtained from isolated glycopeptides and the constituent monosaccharides. The carbohydrate moiety had no effect on the conformation of the protein moieties of LDL₁ and LDL₂ (apoLDL₁ and apoLDL₂). However, the intensities of the observed extrema in the CD and ORD spectra of the glycopeptides were greater than those expected from the monosaccharide composition. This suggests the existence of secondary structure in the carbohydrate moiety. In contrast to the carbohydrate moiety, the contribution of the lipid moiety to the CD and ORD spectra could not be neglected. When the effect of the lipid moiety was subtracted from the CD and ORD spectra, the spectra due to apoLDL₁ and apoLDL₂ were quite similar. Delipidation in the presence of sodium dodecyl sulfate (SDS) induced an increase in the content of disordered structure and α -helix accompanied by a decrease in the β -structure. In the presence of SDS, marked quenching occurred in the fluorescence emission spectra with a blue shift of the maximum emission wavelength from 332 to 326 nm. ApoLDL₁ and apoLDL₂ showed quite similar SDS-induced conformational transitions. The secondary structures of apoLDL₁ and apoLDL₂ in the native lipoproteins were stable to changes of pH and temperature. However, this stability was lost in the presence of SDS. These results suggest the importance of the lipid moiety in maintaining the native secondary structures of LDL₁ and LDL₂. From the overall similarity of the optical properties of apoLDL₁ and apoLDL₂, we conclude that the secondary structures of apoLDL₁ and apoLDL₂ are identical.

J. AZUMA and T. KOMANO: **Studies on Pig Serum Lipoproteins VI. Surface Charge of Very Low Density Lipoprotein**, J. Biochem., **83**, 1789 (1978).

The surface electric charge of pig serum very low density lipoprotein (VLDL) is described. By isoelectric focusing VLDL was separated into at least 3 fractions having different isoelectric points and polypeptide distributions. The ultracentrifugal

and electron microscopic results indicate that the VLDL was not drastically denatured by Ampholine.

T. YAMASAKI, K. HATA and T. HIGUCHI: **Separation of s-DHP from a Mixture of c-and s-DHPs with Special Reference to the Isolation of Syringyl Lignin**, *Holzforschung*, **32**, 20 (1978).

A mercurated 1 : 1 mixture of s-DHP and c-DHP was fractionated by the difference of solubility in acetic acid, and s- and c-DHP rich fractions were separated, respectively. This method must be used as an effective means to isolate syringyl lignin from hardwoods.

T. YAMASAKI, K. HATA and T. HIGUCHI: **Isolation and Characterization of Syringyl Component Rich Lignin**, *Holzforschung*, **32**, 44 (1978).

Mercurated MWLs of beech, Yamamomo (*Myrica rubra* Sieb. et Zucc.), and Kiri (*Paulownia tomentosa* Steud.) and a mercurated dioxane lignin of beech were fractionated by the difference of solubility in acetic acid, and the syringyl component rich lignins were separated and characterized analytically.

T. FUKUYAMA, F. NAKATSUBO, A. J. COCUZZA and Y. KISHI: **Synthetic Studies toward Mitomycins. III. Total Syntheses of Mitomycins A and C**. *Tetrahedron Letters* **49**, 4295 (1977).

The mitomycins (*la-e*) are a class of antibiotics with activity against Gram-positive and Gram-negative bacteria and also against several kinds of tumors. Since their structures were first elucidated in 1962, numerous synthetic approaches to the mitomycins have been reported. We have recently reported the first total synthesis of porfiromycin (*ld*), one of the naturally occurring mitomycins. In this communication, we wish to describe the first total syntheses of mitomycins A (*la*) and C (*lc*) by a synthetic route similar to the one we have used for the synthesis of porfiromycin (*ld*).

F. NAKATSUBO, T. FUKUYAMA, A. J. COCUZZA and Y. KISHI: **Synthetic Studies toward Mitomycins. 2. Total Synthesis of *dl*-Porfiromycin**, *J. Amer. Chem. Soc.*, **99**, 8115 (1977).

The mitomycins(*la-e*) are a class of antibiotics with activity against Gram-positive and Gram-negative bacteria and also against several kinds of tumors. Since their structures) were first elucidated in 1962, numerous synthetic approaches to the mitomycins have been reported. However, the mitomycins themselves have not yet been synthesized. In this communication, we wish to report the first total synthesis of *dl*-porfiromycin (*ld*) by the synthetic route that we recently used for the synthesis of deiminomitomycin A.

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A. SATO: **Some Aspects of Wood Utilization in Papua New Guinea and Philippines.** Mokuza Kenkyushiryō (Wood Research Review), No. 12, 102, (1978). (in Japanese)

The author visited several forest products laboratories, forestry stations, timber mills and wild bushes in Philippines and Papua New Guinea for a month from July to August in 1976.

In this report from above travels, following places were introduced and described mainly about forest products and wood extractives; FOPRIDECOM(Philippines), Forest Products Research Center, Keravat Forest Station, New Ireland Island, New Ireland Industry, Madang and JANT Lty. and Bulolo Valley (Papua New Guinea).

T. AOKI and T. YAMADA: **Chemorheology of Wood III. Diffusion Controlled Stress Relaxation in Wood,** Mokuza Gakkaishi (J. Japan Wood Res. Soc.), 24, 380 (1978). (in Japanese)

The diffusion controlled torsional stress relaxation for untreated Hinoki and Hinoki treated with DMSO and the DEA-SO₂-DMSO mixture was investigated and the following results were obtained.

- 1) Two relaxation processes were observed in wet and DMSO swollen conditions. The values of activation energy E_{act} in these processes were 23.7 kcal/mole (Physical Relaxation I) and 21.6 kcal/mole (Physical Relaxation II), respectively. It was considered that physical relaxation I would result from a molecular motion in the amorphous region of both cellulose and hemi-cellulose, while physical relaxation II from that of lignin. On the other hand, in the diffusion controlled process of Hinoki which was initially in dry condition, these E_{act} values decreased to about one-half.
- 2) A relaxation process (Physical Relaxation D) occurred in the diffusion controlled relaxation of Hinoki which was initially in dry condition and its E_{act} value was 12.4 kcal/mole. It was suggested that it would be due to changes in the microstructure such as inter- and intra-molecular networks. In the diffusion controlled relaxation, the value of chemical relaxation of Hinoki which was initially in dry condition was almost equal to those of physical relaxation I, II and D.
- 3) The E_{act} value of the chemical relaxation process in sulfuric acid solution for Hinoki which was initially in wet condition was about 1/2~1/3 of that obtained from the measurements of viscosity and weight loss under the homogeneous reaction. On the other hand, those of Hinoki which was initially in DMSO swollen condition and treated with the DEA-SO₂-DMSO mixture were 28.5 kcal/mole and 34.7 kcal/mole, respectively, and these values were almost equivalent to those obtained under the homogeneous chemical reaction. In this connection, it may be suggested that the values of 28.5 kcal/mole and 34.7 kcal/mole correspond to the activation energies

due to the scission of a glucosidic bond in amorphous region and in crystalline region of cellulose treated with DEA-SO₂, respectively.

K. SUMIYA: To Measure the Plant Cell—Extensibility and Rheological Measurement, Kagaku to Seibutsu, **16**, 236 (1978). (in Japanese)

The extension of plant cell wall is a rheological and biochemical phenomenon. The application of rheological and chemorheological measurement for plant is described.

A. YASUDA, M. MASUDA and T. MAKU: Studies on the Visual Characteristics of Wood Base Materials—Factor Analysis on the Visual Image of the Interior Wall Materials—, Mokuzaikenkyushiryō (Wood Research Review), No. 12, 81 (1978). (in Japanese)

In this study the semantic space of the visual or psychological image of the interior wall materials was analysed by means of an improved SD (semantic differential) method. The primary solution obtained by the principal factor analysis was rotated by means of the normal varimax method. The following five factors were obtained—(i) lightness or purity, (ii) naturalness or warmth, (iii) pleasantness or gorgeousness *i.e.* evaluation factor, (iv) roughness, (v) movement. Using this solution of semantic space, the factor score of the various materials were also calculated and the psychological profiles of the materials were represented by the shape of quadrangular whose diagonal length shows each factor score. The wood base materials which are often used for interior walls of reception rooms or living rooms have good estimation in the third factor. The value or lightness of the materials is closely related to the first factor, and the chroma has weak correlation to the third factor. The third factor score is related to complicated combinations of color and pattern of the materials, and finding the correlation formulae is the subject for a future study.

Z. NAM, S. TAKINO, S. ISHIHARA and T. MAKU: Properties of Board made from Asplund Pulp-Methyl Methacrylate Graft Copolymer. I. Preparation of Graft Copolymer by H₂O₂-Fe²⁺ Initiation System, Mokuzaikenkyushiryō (Wood Research Review), No. 12, 41, (1978). (in Japanese)

Graft copolymerization of methyl methacrylate onto Asplund pulp (AKAMATSU, *Pinus densiflora*) was investigated and the following results were obtained;

- (1) H₂O₂-Fe²⁺ initiation system was very effective for the grafting.
- (2) Alcohol-benzene extraction of Asplund pulp gave no effects on the total conversion ratio of MMA in the concentration range of H₂O₂ more than 1.8 × 10⁻² mole/liter.
- (3) Asplund pulp itself was found to accelerate the rate of polymerization of MMA.

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(4) The weight of PMMA branches grafted onto carbohydrate moieties was much more than the weight of the branches onto lignin, remarkably in the early stage of graft copolymerization.

S. ISHIHARA, H. KANEDA, Z. NAM, T. MAKU, M. GOTODA and N. TAKE-SHITA: **Note on Wood-plastic Composite by Ionizing Radiation. I. —Some Mechanical and Physical Properties and Flame-Retardancy of Wood-Polyvinylidene Chloride Composite—**, Mokuzaikenkyushiryō (Wood Research Review), No. 12, 53 (1978). (in Japanese)

Specimens of Buna (*Fagus crenata* BLUME) and Akamatsu (*Pinus densiflora* SIEB. et ZUCC.) were impregnated with vinylidene chloride monomer and exposed to the ^{60}Co source under dry and wet conditions.

The treated specimens were tested as to their static and dynamic bending strength, dynamic modulus of elasticity in bending and internal friction, surface hardness, hygroscopicity, dimensional stabilities, and their flame-retardancy.

The specific gravity, surface hardness and dynamic bending strength of the composite were apparently increased with an increase in the polymer loading, but the polymerization of the vinylidene chloride monomer in wood by-radiation had negligible effect on the bending strength, modulus of elasticity in bending and internal friction. A reduction in apparent moisture absorption and volumetric swelling as compared with untreated controls and an increase slightly in the efficiencies of the flame-retardancy and the fire-extinguishment were observed.