# Abstracts

S. HAYASHI, K. TSUNODA and K. NISHIMOTO: Anatomy and Properties of Tropical Woods. Manual II-Anatomy of 11 Ghanaian Wood Species, Mokuzaikenkyushiryo (Wood Research Review), No. 11, 48 (1977). (in Japanese)

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

Eleven Ghanaian 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).

T. ITOH and K. SHIMAJI: Orientation of Microfibrils and Microtubules in Cortical Parenchyma Cells of Poplar during Elongation Growth, Bot. Mag., Tokyo, 89, 291~308 (1976).

Three types of microfibrillar orientation, namely parallel, perpendicular and oblique to the main cell axis were found not only in the innermost surface of but also throughout the developing wall. Furthermore, three types of microtubule orientation, namely parallel, perpendicular and oblique to the main cell axis, were found, coinciding with those of microfibrils. As a whole, the wall was shown to be a crossed polylamellate structure.

These observations suggest that the orientation of microfibrils is determined at the time of wall formation, and not influenced by the extension of the wall.

K. SHIMAJI, T. ITOH and T. MITSUTANI: Anatomical Identification of Wooden Tools Excavated from Fujiwara Imperial Palace Site, Mokuzaikenkyushiryo (Wood Research Review), 11, 36 (1977). (in Japanese)

15 pieces of important wooden tools excavated from Fujiwara Imperial Palace Site (excavated time of some pieces are corresponding to Hakuho period and that of others to Yayoi period) are studied anatomically.

Identified wood species are: Torreya nucifera ARN., Cryptomeria japonica D. DON, Chamaecyparis obtusa SIEB. et ZUCC., Cyclobalanopsis sp., Morus bombycis KOIDZ., Camellia japonica L., Distylium racemosum SIEB. et ZUCC., Diospyros kaki var. silvestris MAKINO, Dicalyx sp. and Osmanthus heterophyllus GREEN.

F. TANAKA and K. OKAMURA: Measurement of Pole Figures and Orientation Functions for Valonia Cellulose, J. Polymer Sci., 15, 897 (1977)

The x-ray pole-figure technique has been applied to the study of orientation in *Valonia* cellulose. It is found that the maximum of the orientation distribution of the  $(2\overline{2}0)$  poles of crystallites in *Valonia* cell walls is precisely normal to the cell wall surface, and the pole population is denser in the longitudinal direction than in the transverse direction. The orientation is interpreted as a typical uniplanaraxial orientation after Heffelfinger and Burton's classification: a uniplanar orientation in  $(2\overline{2}0)$ , and two types of uniaxial orientation in the (220) and (400) planes based on the unit cell parameters for *Valonia* cellulose. The degree of biaxial orientation of the  $(2\overline{2}0)$ , (220), and (400) plane normals as well as three principal crystallographic axes are shown by Desper's equilateral triangle plots.

H. FUJIMOTO and T. HIGUCHI: Lignans from the Bark of Yellow Poplar (*Liriodendron tulipifera* L.), Mokuzai Gakkaishi (J. Japan Wood Res. Soc.), 23, (1977).

Three lignans and liriodendrin [(+)-syringaresinol-di- $\beta$ -D-glucoside] were isolated from the ethanolic extract of yellow poplar (*Liriodendron tulipifera* L.) by silica gel column chromatography. The lignans were identified as (+)-syringaresinol, (+)pinoresinol and a new bisepoxylignan, which is constituted of syringyl and guaiacyl units, (+)-medioresinol.

Acid hydrolysis of the water soluble fraction of the ethanolic extract showed the occurrence of the mono- and diglucosides of the three resinols.

Discussion was held on the low optical rotation value of the syringaresinol in relation to the biosynthesis of lignin.

T. HIGUCHI, M. SHIMADA, F. NAKATSUBO and M. TANAHASHI: Differences in Biosyntheses of Guaiacyl and Syringyl Lignins in Woods, Wood Science and Technology, 11, 153 (1977).

Metabolic differences in the formation of guaiacyl and syringyl lignins were explained in terms of the different functions of O-methyltransferases and reducing enzymes which participate in methylation and reduction of the hydroxycinnamic acid intermediates in the biosynthetic pathway of these two types of lignins. Sinapyl alcohol was dehydrogenated with peroxidase and  $H_2O_2$  under various reaction conditions. Chemical properties of the dehydrogenation polymers (DHPs) formed were characterized, and the possible occurrence of syringyl lignin in hardwood was discussed. DHP and dimers of *p*-coumaryl alcohol were also characterized and discussed in relation to the formation of grass lignin which contains *p*-hydroxyphenyl propane as an additional lignin monomer.

T. HIGUCHI, M. SHIMADA, M. TANAHASHI, F. NAKATSUBO and T. YAMASAKI: Biochemistry of Lignin Formation in Wood, Tappi Conference Papers/Forest Biology Wood Chemistry Conference, 31 (1977).

It is known that lignification is initiated in the differentiated wood cells from the primary walls adjacent to the cell corner and then extended to the intercellular

layer, primary wall and secondary wall, and that lignin is synthesized from p-hydroxycinnamyl alcohols derived from sugars via shikimate-cinnamate pathways. Biosynthetic differences of guaiacyl and syringyl lignins between gymnosperms and angiosperms have been elucidated in relation to the different functions of enzymes, especially O-methyltransferases (OMTs) and reducing enzymes which participate in methylation and reduction of hydroxycinnamic acids as lignin intermediates. Sinapyl alcohol was dehydrogenated with peroxidase and  $H_2O_2$  in various conditions and the polymers (DHPs) formed were characterized related to the possible occurrence of syringyl lignin in hardwoods. The reaction of the quinonemethide of guaiacylglycerol- $\beta$ -guaiacyl ether (GCE) with D-glucuronic acid or D-glucose as model experiments of the formation of lignin-carbohydrate complex (L.C.C.) has shown that the carboxyl or primary hydroxyl groups at C<sub>6</sub> of the sugars is linked to C $\alpha$  of GCE, respectively. Significance of the complex compounds is discussed in connection with biosynthesis of L.C.C. in plant cell walls.

F. NAKATSUBO, A. J. COCUZZA, D. E. KEELEY and Y. KISHI: Synthetic Studies toward Mitomycins. I. Total Synthesis of Deiminomitomycin A, J. Amer. Chem. Soc., 99, 4835 (1977).

The mitomycins (la-e) are a class of antibiotics with activity against grampositive 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. It seemed to us that the most difficult problem in synthesizing the naturally occurring mitomycins is related to introducing the 9a methoxy group since this is known to be the most labile functionality present in the target molecules. In this communication, we wish to report a total synthesis of deiminomitomycin A (13). This synthesis involves two key cyclizations: the intramolecular Michael reaction used to construct the eight-membered ring of 8 and the trans-annular cyclization of 10 to 11 under conditions mild enough to introduce and preserve the 9a methoxy group.

M. SHIMADA and E. CONN: The Enzymatic Conversion of *p*-Hydroxyphenylacetaldoxime to *P*-Hydroxymandelonitrile, Arch. Biochem. Biophys., 180, 199 (1977).

2-Hydroxy (p-hydroxyphenyl)-acetaldoxime, the alternative precursor to phydroxyphenylacetonitrile in dhurrin biosynthesis, was synthesized and its effectiveness as a substrate was examined in microsomal enzyme system from sorghum seedlings. The hydroxyaldoxime was slowly converted to p-hydroxymandelonitrile when compared with p-hydroxyphenylacetonitrile and p-hydroxyphenylacetaldoxime. More-

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over, radioactivity from  $[U^{-14}C]$  tyrosine was efficiently incorporated by trapping experiments into both the nitrile and aldoxime, but not into the hydroxyaldoxime. The reaction products formed on hydroxylation of the nitrile by the microsomal enzyme were identified as *p*-hydroxybenzaldehyde, HCN, and H<sub>2</sub>O. Under anaerobic conditions, the nitrile was produced from the aldoxime and accumulated without undergoing hydroxylation. These results establish *p*-hydroxyphenylacetonitrile and not 2-hydroxy (*p*-hydroxyphenyl)-acetaldoxime as the intermediate in the conversion of *p*-hydroxyphenylacetaldoxime to *p*-hydroxymandelonitrile in dhurrin biosynthesis.

T. Аокі and T. YAMADA: Creep of Wood During Decrystallization and of Decrystallized Wood, Mokuzai Gakkaishi (J. Japan Wood Res. Soc.), 23, 10 (1977). (in Japanese)

It has been reported that wood is decrystallized markedly with the mixture of diethyl amine, sulfur dioxide and dimethyl sulfoxide (DMSO) and decrystallized wood is easily recrystallized by immersing in water. There are, however, few studies on the rheological behaviors of wood during decrystallization. In this paper, the temperature dependence of torsional creep of wood during decrystallization and of the decrystallized wood were examined. The results obtained were as follows:

1) Creep compliance increased in proportion to degree of decrystallization.

2) A relaxation process occurred in the untreated wet Hinoki in the temperature range of 55° to 75°C and this location moved to the lower temperature range as the degree of crystallinity decreased. This process also took place in the untreated wet ramie and did not in the depolysacchride wood, so the process would result from a molecular motion of cellulose and hemicellulose due to the scission of hydrogen bonds in the amorphous region.

3) Another relaxation process occurred in DMSO swollen Hinoki and in depolysaccharide Hinoki at the higher temperature. This process would be due to a molecular motion of lignin, because lignin was remarkably softened by DMSO and the process did not take place in untreated wet Ramie.

4) When creep measurements of the decrystallized wood were performed in water, the behavior analogous to a cross-linking reaction was observed, and this would be attributed to the structure changes due to the regeneration of hydrogen bonds.

T. AOKI and T. YAMADA: Chemorheology of Wood I. Stress Relaxation of Wood during Acid Hydrolysis, Mokuzai Gakkaishi (J. Japan Wood Res. Soc.), 23, 107 (1977). (in Japanese)

The effect of temperature and sulfuric acid concentration on torsional stress relaxation during hydrolysis for wood was investigated. The results obtained were as follows:

1) During hydrolysis a relaxation process occurred in the temperature range of 45° to 75°C. This process was similar to that in the untreated wet Hinoki, and it was considered that the process would result from a molecular motion in the amorphous region of both cellulose and hemicellulose (Physical Relaxation). The apparent activation energy in this process was 23.7 kcal/mol. And the relaxation time  $\tau_1$  was represented by the following empirical equations:

or

 $1/\tau_1 = 7.41 \times 10^{11} \times C^{2.34} \times \exp\{-23700/(RT)\}, \text{ (from } \log 1/\tau_1 - \log C)$ 

 $1/\tau_1=2.40\times 10^{14}\times \exp\{0.0671C-23700/(RT)\}$ . (from log  $1/\tau_1-C$ ) where, C is acid concentration (%) and T is temperature (°K).

2) Another relaxation process occurred in the higher temperature range. From the observation on the scission of native ramie fiber by sulfuric acid, it was considered that the process would be due to the scission of glucosidic bonds (Chemical Relaxation). The apparent activation energy in this process was 14.0 kcal/mol., corresponding to heterogeneous reaction process. And the relaxation time  $\tau_2$  was represented by the following equation:

 $1/\tau_2 = 1.86 \times 10^6 \times C^{1.04} \times exp\{-14000/(RT)\}$ .

T. AOKI and T. YAMADA: Chemorheology of Wood II. Torsion of Wood during Acid Hydrolysis, Mokuzai Gakkaishi (J. Japan Wood Res. Soc.), 23, 125 (1977). (in Japanese)

The intermittent torsional stress measurements of wood during hydrolysis with sulfuric acid were carried out, and the mechanism of stress change was discussed from the results of the measurements on X-ray diffraction, I. R. spectra and thermal softening for wood treated with sulfuric acid. The results were as follows:

1) The stress increased at first and then decreased in two stages with logarithmic time. These processes, however, were dependent remarkably on acid concentration. The relative stress y(t), which is the ratio of stress at time t to the initial stress, was represented approximately by

 $y(t) = -A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3),$ where  $A_1$ ,  $A_2$ ,  $A_3$  and  $\tau$  ( $\tau_1 < \tau_2 < \tau_3$ ) are constants.

2) In the region of the stress increase, the intensity of the characteristic I. R. absorption bands due to hemicelluloses decreased and the softening temperature shifted to lower range and the degree of crystallinity increased. It was considered that the generation of hydrogen bond occurred with the disolution of hemicelluloses in this region.

3) In the first stage of the stress decrease, the crystallinity remained almost unchanged. It was assumed that the scission of glucosidic bond in amorphous region occurred in this range. On the other hand, in the second stage of the stress

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decrease, the degree of crystallinity decreased and the intensity of crystalline-sensitive band (1110, 1060, 1040 cm<sup>-1</sup>) decreased. It was considered that the scission of glucosidic bond in crystalline region occurred in this range.

M. NORIMOTO and T. YAMADA: Dielectric Behaviour of Water Adsorbed on MWL, Mokuzai Gakkaishi (J. Japan Wood Res. Soc.), 23, 99 (1977). (in Japanese)

In order to make clear the state and the dielectric relaxaen mechanism of water adsorbed on MWL, the dielectric constant and loss factor for Hoonoki MWL having different moisture contents over the frequency range of 3 MHz to 50 Hz and temperature range of 20°C to -50°C as well as the sorption isotherm of water vapor on MWL at 20°C were measured. The results obtained were as follows:

1) Applying the HAILWOOD and HORROBIN solution theory to the sorption isotherm, the coefficients were calculated  $(K_1=29.0, K_2=0.865, M=514 \text{ g})$ , and from these values the amounts of the adsorbed water components, i.e. the hydrated water and the dissolved water, as functions of relative humidity were determined.

2) With increasing moisture content, the dielectric loss factor due to the adsorbed water increased in magnitude and the peak shifted rapidly to higher frequency range. On the other hand, the peak shifted to lower frequency range with decreasing temperature. From the frequency-temperature locations of loss factor maxima, the activation free energy, enthalpy and entropy for the relaxation due to the adsorbed water were determined, and the mechanism of reorientation for the adsorbed water MWL was discussed.

3) To estimate the specific polarization of the adsorbed water, the intrinsic dielectric constant for MWL having different moisture contents was calculated by the extrapolation. The specific polarization for the dissolved water was found to be 8.00 cc/g at 1 MHz and 20°C. Moreover, it was shown that the intrinsic dielectric constant at a given moisture content can be estimated from the specific polarization values for the adsorbed water, i.e. 1.11 cc/g for the hydrated water and 8.00 cc/g for the dissolved water.

M. NORIMOTO and T. YAMADA: Effect of Interior Boards on Indoor Humidity of Prefabricated Wooden House, Wood Research Review, No. 11, 17 (1977)., Humidity Conditioning by Wooden Materials II, Mokuzai Kogyo (Wood Industry), 32, 160 (1977). (in Japanese)

In order to make clear the function of humidity conditioning in a house by interior board, the climate in the prefabricated wooden houses which were lined with various kinds of interior boards was observed over a period of three years. From the results it was confirmed that wooden materials surpass generally the other

materials in the function of humidity conditioning.

T. OHGAMA, M. MASUDA and T. YAMADA, Stress Distribution within Cell Wall of Wood Subjected to Tensile Force in Transverse Direction, J. Soc. Mater. Sci. Japan, 26, 433 (1977). (in Japanese)

The stress distributions within the cell wall subjected to a tensile force in the tangential direction were discussed on the basis of a Finite Element Solution for the late-wood cell model. The values of YOUNG's modulus and POISSON's ratio of the cell obtained from this analysis were also compared with the experimental ones reported by BOUTELJE on the samples consisting of isolated latewood from Swedish pine-wood.

The model structure was constructed by considering the geometrical parameters representing the anatomical features of Hinoki-wood and the distribution of chemical constituents in the cell wall layer. Using the elastic constants and the volume fractions of framework and matrix components given by MARK and adopting two methods analysis for estimating the elastic parameters of a laminated system, the material constants of each cell wall layer were calculated. Furthermore, the other values for the material constants, which are obtained as the intersection of Young's modulus-specific gravity curves in radial and tangential directions, were used to compare the mechanical behaviour of the model mentioned above with that of the model without considering the fine structures in the cell wall.

The results were as follows;

(1) The maximum stress occurred in the lumen side of cell wall, and the stresses in S1, which are considered to be the initiation point of failure by MARK, and the stresses in S2 were considerably low. These results were different from those on the isotropic material with a circular hole.

(2) It was proposed that a large amount of intrawall failure, which is the separation of two adjacent tracheids, might result from the failure in M+P or S3. The failure in M+P occurs when the strength of matrix is near or less than 600 kg/cm<sup>2</sup> and the failure in S3 occurs when the tensile strength of fibril is near or less than  $1.1 \times 10^4$  kg/cm<sup>2</sup>. The former is more possible.

(3) Young's modulus of late-wood cell was calculated with the consideration of the distribution of framework and matrix and a good agreement between the calculated value and the experimental one was obtained.

M. HATA, K. KOMATSU and H. SASAKI: Structural Analysis of Wood Shelf as a Semi-rigid Jointed Frame, Mokuzai Gakkaishi (J. Japan Wood Res. Soc.), 23, 434 (1977). (in Japanese)

Structural analysis of wood shelf by Finite Element Method was conducted as

a two-dimensional frame with semi-rigid joints. Three joint factors were introduced first to express mechanical characteristics of semi-rigid joint, and determined experimentally on actual joints of beech with dowels.

Deformation of basic shelf structures with dowel joints subjected to the diagonal compressive force was calculated by use of these joint factors. Good coincidence was found on comparison between the calculated and the observed deformations.

M. MASUDA and T. MAKU: Mechanical Characteristics of Orthotropic Shallow Shells—Influence of the Restraint of Sliding or Expansion of the Roller Supported Edges, J. Soc. Mater. Sci., Japan, 26, 446 (1977). (in Japanese)

The mechanical characteristics of plywood shallow shells were analysed by means of the finite difference method. The influence of the restraint of sliding on the deformation rigidity of the shells is greater in the case of Ortho. 45° (the cross laminated shells with face grain incline 45° to x-edge) than in the case of Ortho. 0° and 90°. When the sliding along the edges is restrained, the rigidity of Ortho. 45° is nearly equal or a little higher than that of the isotropic shells, and much higher than that of Ortho. 0° and 90°. The rigidity of the parallel laminated shells is lower than that of the cross laminated shells, and the parallel laminated cylindrical shells are destroyed by the tensile membrane stress under a considerably low load (the numerical analysis and experiments). In the case of the rectangular shells, the more the ratio of the side lengths, the less the influence of the edge restraint of the Ortho. 45° shells becomes. The maximum deflection under a central concentrated load is about 3 times larger than that under the uniformly distributed same load, and in the case of Ortho. 45° and the isotropic cylindrical shells, the ratio is much larger. However, the deflection of Ortho. 45° shells under a central concentrated load is about a half of that of Ortho.  $0^{\circ}$  and  $90^{\circ}$ .

Z. NAM and T. MAKU: Thermal Degradation of Phenol-formaldehyde Resin extended with Thiolignin (I). Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) of the cured resin. Mokuzaikenkyushiryo (Wood Research Review), No. 11, 11 (1977). (in Japanese)

The thermal degradation course of phenol-formaldehyde resin extended with thiolignin was investigated in air at atmospheric pressure by means of thermoanalytical methods.

The DTA curves of the cured phenol-formaldehyde resins extended with thiolignin showed two peaks of exothermal reactions at lower temperatures than 550°C. The first exothermal peak  $(310 \sim 340^{\circ}C)$  was attributed to thermooxidation of thiolignin, and the second  $(510 \sim 450^{\circ}C)$  was done mainly to thermooxidation of phenol-

formaldehyde resin. The temperature at first exothermal peak was as follows; PF: L>PF-L>PLF>LF-P

H. SASAKI and P. F. WALSH: Cleavage Fracture Toughness of Wood-Epoxy Resin Bond System, J. Soc. Mater. Sci. Japan, 26, 453 (1977). (in Japanese)

This paper concerns with evaluation of cleavage fracture toughness of a woodepoxy resin bond system using a double cantilever type specimen. With consideration for the inhomogeneous distribution of elastic constants in wood, recommendable formulae to determine cleavage fracture toughness (GIC) were derived. As these formulae include the observed deflection of the cantilevers (opening), the variation of elastic constants existing among adherents is compensated and GIC obtained by these formulae has less variation than that by ordinary method.

The factors affecting on GIC for a wood-epoxy resin bond system as the thickness and flexibility of glueline and the strain rate were discussed experimentally.