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Acidolysis of Bamboo Lignin III

Estimation of Arylglycerol-β-aryl Ether Groups in Lignins*

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Abstract——The amounts of both uncondensed and condensed types of arylglycerol-α, β-diaryl ether groups in a bamboo, beech and a conifer (*Thuja standishii*) MWL's were estimated by gas-liquid chromatography of arylacetones as acidolysis monomer and by spectral analysis of phenolic hydroxyl groups released after mild acidolysis and acidolysis of the MWL's, respectively. The experimental results showed that the amounts of α-aryl ethers were between 0.07 and 0.09 and those of β-aryl ethers were 0.56 (bamboo), 0.51 (beech) and 0.35 (*Thuja*)/C_6-C_3 of which uncondensed types amounted 0.25, 0.26 and 0.18, respectively. It was tentatively concluded that the polymeric system of the bamboo lignin is composed of about 10 : 68 : 22 of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol via similar linkages found in spruce lignin and *p*-coumaric acid (0.07/C_6-C_3) is esterified at the terminal γ-carbons of the side chains of the polymeric system.

Introduction

In previous papers[1,2] acidolysis products of a bamboo lignin have been identified by gas-liquid chromatography, mass spectrometry and NMR spectrometry, and 3-hydroxy-1-(4-hydroxy-3, 5-dimethoxyphenyl)-2-propanone, 2-hydroxy-1-(4-hydroxyphenyl)-1-propanone, 1-hydroxy-1-(4-hydroxyphenyl)-2-propanone, 1-(4-hydroxyphenyl)-2-propanone, DL-syringaresinol and DL-epi-syringaresinol were found as new additional compounds. These results, in addition to permanganate oxidation on methylated bamboo lignin[3] have suggested that the bamboo lignin is in principle a mixed polymer of guaiacyl-, syringyl- and *p*-hydroxyphenylpropanes connected through similar linkages found in spruce lignin. However, since it has been established[4,5] that *p*-hydroxybenzaldehyde produced by alkaline nitrobenzene oxidation of bamboo lignin is mostly ascribed to the esterified *p*-coumaric acid and that the amount of other *p*-hydroxyphenyl compounds as lignin degradation product is considerably small, the participated *p*-hydroxyphenyl component in the polymeric system of the lignin has been suggested to be quite small in amount and only a little more than that in conifer lignin.

ADLER et al.[6] found that the increase in terminal methyl groups during the acidolysis of spruce MWL was equivalent to 25-33% of arylglycerol-β-aryl ether groups in the lignin. SARKANEN and SCHUERCH[7] also found that the increase in phenolic hydroxyl groups during ethanolysis of a spruce lignin corresponded to 26% of the β-aryl ether groups. It has been generally known[8] that the arylglycerol-β-aryl ether groups in which the arylglycerol moiety is either an uncondensed unit with a free phenolic hydroxyl group or is linked through hydrolyzable α-0-4 or β-0-4 bonds with the rest of the lignin molecule give acidolysis monomers, whereas the other part of the groups linked through unhydrolyzable bonds is not converted

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to the acidolysis monomers.

No attempt has hitherto been carried out for the estimation of arylglycerol-β-aryl ether groups in the angiosperm lignin which is composed of both arylglycerol-α- and β-aryl ether groups with guaiacyl- and syringlpropanes. Thus, in the present investigation the amounts of both uncondensed and condensed types of the arylglycerol α-β-diaryl ether groups in a bamboo, beech and a conifer (*Thuja*) lignins have been estimated by gas-liquid chromatography of arylacetones as acidolysis monomer and by spectral analysis of phenolic hydroxyl groups released after acidolysis of the lignins, respectively. The results are discussed in connection with a current idea on structural model of spruce lignin.

Experimental

Synthesis of model compounds

Guaiacylglycerol-β-guaiacylether was synthesized from vanillin according to the method by MIKSCHE[9]. The product was acetylated in a mixture of pyridine-acetic anhydride (1 : 1) and identified by NMR spectrometry. The data were in good agreement with the chemical structure of the compound as shown. NMR [$CDCl_3$] δ; 1.98(3H, s), 2.05(3H, s), 2.28(3H, s), 3.78 (6H, s) 4.10-4.80(β-CH, γ-CH2, 3H, m), 6.08(α-CH, 1H, d, J=6), 6.70-7.00(7H, m). MS m/e : 446 (M^+).

Syringylglycerol-β-guaiacyl ether was synthesized from syringaldehyde by a similar method. The NMR spectrum of its acetate was in good agreement with the chemical structure of the compound. NMR [$CDCl_3$] δ; 1.11(3H, s), 2.00(3H, s), 2.28(3H, s), 3.74(3H, s), 3.77(6H, s), 4.25 (1H, dd, J=4.5, 11.0), 4.45(1H, dd, J=5.0, 11.0), 4.89(1H, m), 6.04(1H, d, J=5.4), 6.67(2H, s), 6.75-7.10(4H, m). MS m/e : 476(M^+).

p-Hydroxyphenylglycerol-β-guaiacyl ether was synthesized from *p*-hydroxyacetophenone according to the method of KRATZL et al.[10] and identified as its acetate by NMR spectrometry. NMR [$CDCl_3$] δ; 1.96(3H, s), 2.01(3H, s), 3.80(3H, s), 4.01(1H, dd, J=6.0, 12.0), 4.32(1H, dd, J= 4.3, 12.0), 4.64(1H, m), 6.14(1H, d, J=6.4), 6.75-7.00(4H, m), 7.06(2H, d, J=8.5), 7.43(2H, d, J= 8.5). MS m/e : 416(M^+). The data were consistent with the chemical structure of the compound.

Guaiacylglycerol-α-guaiacylpropyl-β-guaiacyl diether was synthesized from guaiacylglycerol-β-guaiacyl ether according to the method by JOHANSSON and MIKSCHE[11]. The β-guaiacyl ether (2 g) was dissolved in chloroform (200 ml), cooled with dry ice in methanol at about -60°C and saturated with HBr gas. The chloroform solution of the bromide thus formed was shaken with a saturated $NaHCO_3$ solution in a separatory funnel, an yellow chloroform layer which contains corresponding quinone methide was separated and it was dried over anhydrous Na_2SO_4. Guaiacylpropane (15 g) was added into the chloroform solution and the solution was kept at room temperature for several minutes. The chloroform was evaporated *in vacuo* and the reaction mixture was subjected to silicagel column chromatography. The column (30 mm $\times$60 cm) was eluted with chloroform, the eluate was collected as 10 ml fractions automatically, and the products in each fraction was tested by TLC (PF_{254}, $CHCl_3$) using a UV lamp. After the fractions containing guaiacylpropane the compound which absorbed shortwave ultraviolet light and was considered to be guaiacylglycerol-α, β-diaryl ether appeared. Then, the fractions containing the compound were combined, the solvent was evaporated *in vacuo* and the residue was crystallized from ethanol-hexane. Colorless crystal. M. P. 110-112°C (Erythro form; Ref.[11] Erythro. 113–114°C, Threo. 220-230°C). Yield, 1.2 g. NMR [$CDCl_3$] δ; 0.83(γ'-

CH_3, 3H, *t*, J=7), 1.50(β'-CH_2, 2H, m, J=7), 2.40(α'-CH_2, 2H, t, J=7), 3.71(3H, s), 3.74(3H, s), 3.80(3H, s), 3.99(γ-CH_2, 2H, m), 4.31(β-CH, 1H, m), 5.20(α-CH, 1H, d, J=8), 6.50-7.10(10H, m). Acetate [$CDCl_3$] δ ; 0.81(γ'-CH_3, 3H, t, J=7), 1.48(β'-CH_2, 2H, m, J=7), 1.82(3H, s), 2.14(3H, s), 2.36(α'-CH_2, 2H, t, J=7), 3.59(3H, s), 3.63(3H, s), 3.70(3H, s), 4.50-4.69(β-CH, γ-CH_2, 3H, m), 5.40(α-CH, 1H, d, J=6), 6.50-7.00(10H, m). MS (acetate) m/e : 552(M^+), 387(M^+-$0C_6H_3(OCH_3)CH_2CH_2CH_3$), 327(387-$CH_3COOH$), 285(327-$CH_2$=C=O), 166($C_6H_3(OH)(OCH_3)CH_2CH_2CH_3^+$), 123 ($^+OC_6H_4(OCH_3)$). These data were in good agreement with the chemical structure of guaiacylglycerol-α-guaiacylpropyl-β-guaiacyl diether.

Preparation of milled wood lignin (MWL)

Extractive-free wood powder (each 300 g) of a bamboo (*Phyllostachys pubesens*), beech (*Fagus crenata*) and *Thuja standishii* was milled for 100 hrs by using a vibratory ball mill. The MWL's were extracted from the milled wood with dioxane-water (9 : 1) and purified according to the standard method of BJÖRKMAN.[12]

Acidolysis

Each 5 mg of the model compounds or 10 mg of the MWL's was dissolved in 0.5 ml or 1.0 ml of a mixture solution of dioxane-water (9 : 1) containing 0.2 N HCl in a glass tube. The glass tube was sealed after flushing with nitrogen gas and heated at 120°C for various lengths of time. Two ml of water was added into the reaction mixture and it was adjusted to pH 3 with 0.4 N $NaHCO_3$ and extracted with chloroform. A minute drop of the chloroform extract was used for TLC analysis to check the amounts of acidolysis monomers formed and then the chloroform extract was dried over anhydrous Na_2SO_4 and evaporated to dryness *in vacuo*. The residue was dissolved in pyridine (0.1 ml) and then hexamethyl disilazane (0.1 ml) and trimethylchlorosilane (0.05 ml) were added, successively. The reaction mixture was shaken vigorously for 1 min. and after 5 min. keeping at room temperature, it was evaporated to dryness in a vacuum desiccator containing P_2O_5. The residue was dissolved in CCl_4 (0.5 ml) and analyzed by gas chromatography-mass spectrometry. Column, 3 % SE-52 on Chromosorb W, 2 m. Temperature, 195°C. The amounts of acidolysis monomers were calculated from the peak area on the chromatogram by using the calibration curves prepared previously for the respective authentic compounds.

Alternatively the reaction mixture in the acidolysis glass tube was used directly for determination of the phenolic hydroxyl groups according to the GOLDSCHMID method[13]. The amount of phenolic hydroxyl groups has been generally calculated based on the $\Delta\varepsilon$ value at 300 mμ. However, bamboo MWL gave a strong absorption around 330 mμ by the esterified *p*-coumaric acid which hindered from the calculation of the phenolic hydroxyl groups by $\Delta\varepsilon$ value at 300 mμ, and then $\Delta\varepsilon$ value at 250 mμ was used actually for calculation of the phenolic hydroxyl groups.

Mild acidolysis

The same condition and procedure as in acidolysis were used except that the reaction was carried out at 50°C for 24 hrs.

Method of analysis

NMR spectrum was recorded on a R 22 HITACHI high resolution NMR spectrometer with TMS internal standard. Mass spectrometry was conducted by using a SHIMAZU-LKB 9000 gas chromatograph-mass spectrometer.

Results and Discussion

Acidolysis of model compounds

To establish the experimental condition for estimating uncondensed type of arylglycerol-β-aryl ether groups in lignin, β-guaiacyl ethers of guaiacylglycerol, syringylglycerol and *p*-hydroxyphenylglycerol were subjected to acidolysis for various lengths of reaction time, and the acidolysis monomers formed were determined quantitatively by gas-liquid chromatography. Fig. 1 shows the amounts of acidolysis monomers formed from guaiacylglycerol-β-guaiacyl ether at respective reaction times. The β-guaiacyl ether in the reaction mixture was found to disappear completely after 1 hr. acidolysis. Concomitantly ω-hydroxyguaiacylacetone as the first acidolysis monomer appeared, increased to a maximum amount within 30 min. and then decreased rather rapidly. 1-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone and 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone were formed subsequently and decreased gradually. The amount of guaiacylacetone, a final product in acidolysis monomers increased progressively from the begining of the reaction, reached maximum after about 10 hrs. and then the maximum amount was kept for 36 hrs. Thus the compound was found to be a good indices for the progress of acidolysis and for the calculation of uncondensed β-0-4 linkage in lignin. A similar pattern of the progressive increase in amount was observed in another final product, vanilloyl methyl ketone. However, since vanilloyl methyl ketone gave a close retention time to that of vanillic acid and comparatively a small peak area on the chromatogram in the present experimental condition, it was not used as indices for the progress of acidolysis.

The acidolysis of syringylglycerol- and *p*-hydroxyphenylglycerol-β-guaiacyl ethers gave similar experimental results. In both cases, the amounts of syringyl- and *p*-hydroxyphenyl-acetones as final acidolysis monomers reached maximum after several hrs. and the maximum amounts were maintained for 36 hrs.

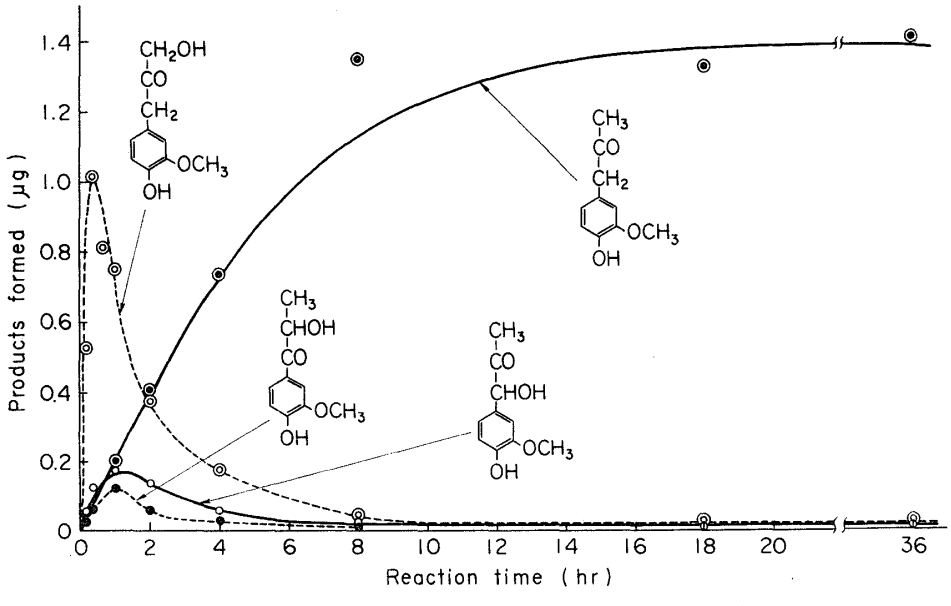

Fig. 1. Acidolysis of Guaiacylglycerol-β-guaiacyl Ether.

Fig. 2 shows the gas-chromatograms of the products from guaiacylglycerol-α-guaiacylpropyl-β-guaiacyl diether, which was used as a model compound for α, β-diaryl ethers in lignin,

by mild acidolysis and by acidolysis, respectively. As shown on the chromatogram, after mild acidolysis the peaks of guaiacylpropane released from α-0-4 linkage, and of guaiacylglycerol-β-guaiacyl ether, which were both identified by their retention times and mass spectrometry, but no peaks of the acidolysis monomers were detected. On the other hand, the peaks of guaiacol, guaiacylacetone and vanilloyl methyl ketone in addition to guaiacylpropane appeared after acidolysis. These results were consistent with the finding by ADLER et al.[15] who established that α-0-4 but not β-0-4 linkage was completely splitted by mild acidolysis.

Table 1 shows the amounts of guaiacyl- syringyl- and p-hydroxyphenylacetones obtained by acidolysis of the respective β-guaiacyl ethers for 24 hrs. The estimated amounts were about

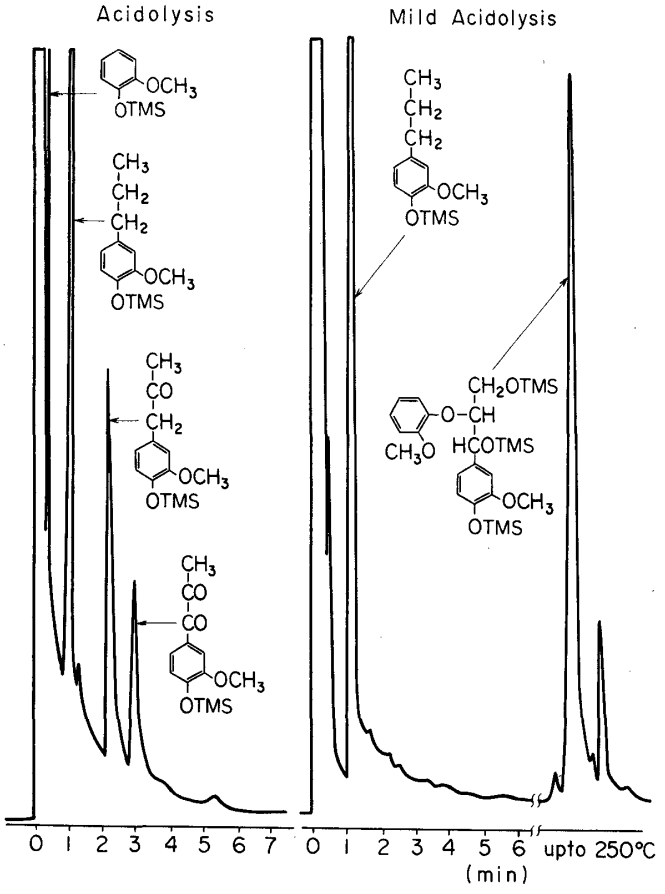

Fig. 2. Gas Chromatogram of TMS Derivatives of the Products from Guaiacylglycerol-α-guaiacylpropyl-β-guaiacyl Diether by Mild Acidolysis and Acidolysis. Column ; SE-52, 3 %, 2 m, 195°C.

Table 1. Estimation of Acidolysis Monomers by Gas Chromatography.

Starting material used (μ mol)		Arylacetone found (μ mol)	Factor*
p-Hydroxyphenylglycerol-β-guaiacyl ether	34.5	7.93	4.35
Guaiacylglycerol-β-guaiacyl ether	31.3	8.11	3.86
Syringylglycerol-β-guaiacyl ether	28.6	6.67	4.29

* Factors were calculated dividing the amounts of used materials by the amounts of arylacetones found.

half of the theoretical amounts, for which the arylglycerol moiety was supposed to be converted to the equal amount of arylacetone and diketone, suggesting not only the losses of the compounds during experimental procedure but also the occurrence of condensation reactions during acidolysis. However, repeated experiments gave reproducible results and it was possible to calculate the factors from the amounts of the respective arylacetones for the corresponding amounts of β-aryl ethers.

Fig. 3 shows the variation pattern of the acidolysis monomers during acidolysis of a bamboo lignin. The pattern in increase and decrease of the respective monomers during acidolysis

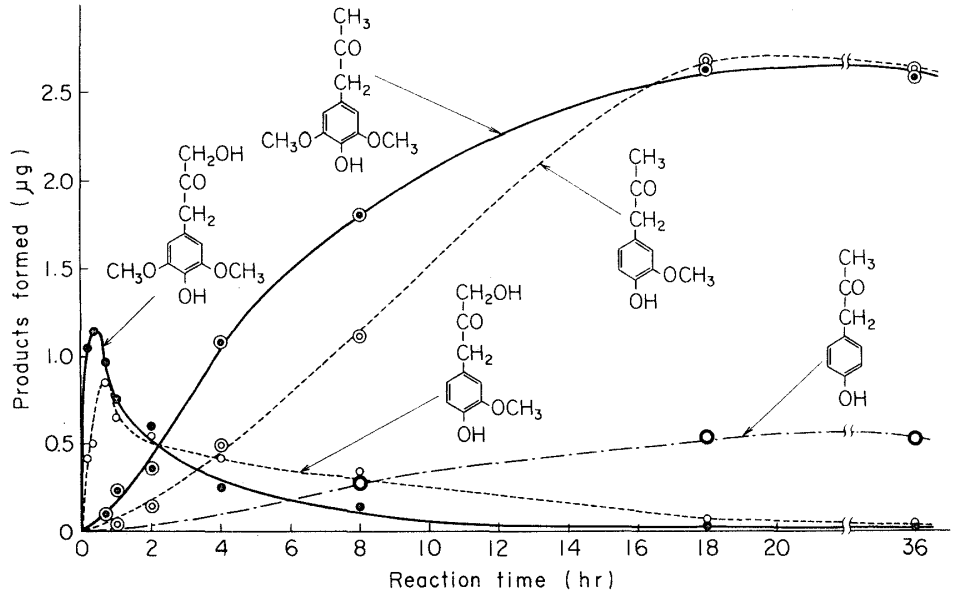

Fig. 3. Acidolysis of Bamboo Lignin.

Table 2. Amounts of Uncondensed Arylglycerol-β-aryl Ether Groups estimated from the Amounts of Arylacetones.

MWL (10 mg)		Found (μ mol)	Calculated (μ mol)	β-Aryl Ether (Mol./C_6-C_3)*
Bamboo	*p*-Hydroxyphenylacetone	0.35	1.51	0.02
	Guaiacylacetone	1.47	5.68	0.11
	Syringylacetone	1.25	5.35	0.11
Beech	*p*-Hydroxyphenylacetone	—	—	—
	Guaiacylacetone	2.14	8.26	0.16
	Syringylacetone	1.14	4.86	0.10
Thuja	*p*-Hydroxyphenylacetone	—	—	—
	Guaiacylacetone	2.41	9.29	0.18
	Syringylacetone	—	—	—
Bamboo** (hydrolyzed)	*p*-Hydroxyphenylacetone	—	—	—
	Guaiacylacetone	0.94	3.61	0.07
	Syringylacetone	0.91	3.89	0.08

* As average molecular weight of C_6-C_3 unit, 180 (*Thuja*) and 200 (beech and bamboo) were used, respectively.

** Bamboo MWL was hydrolyzed in 1 N NaOH at room temperature for 24 hrs.

was quite similar to those in the acidolysis of the model compounds, and the maximum amounts of guaiacyl-, syringyl- and *p*-hydroxyphenylacetones were maintained almost constantly after 18 hrs. reaction.

It was concluded from these results that the amounts of the respective arylacetones formed after 24 hrs. acidolysis of a given amount of the β-guaiacyl ethers of guaiacylglycerol, syringylglycerol and *p*-hydroxyphenylglycerol could be used for estimating uncondensed types of arylglycerol-β-aryl ether groups in lignins.

Table 2 shows the estimated amounts of the uncondensed arylglycerol-β-aryl ether groups in the lignins.

Estimation of phenolic hydroxyl groups released from model compounds after mild acidolysis and acidolysis

In parallel with the preceding experiment on the estimation of the uncondensed types of β-aryl ether groups total amounts of the α-0-4 and the β-0-4 linkages in the lignins have been estimated by the determination of phenolic hydroxyl groups after mild acidolysis and acidolysis of the lignins, respectively.

Table 3 shows the amount of phenolic hydroxyl groups/C_6-C_3 unit released from guaiacylglycerol-α-guaiacylpropyl-β-guaiacyl diether after mild acidolysis and acidolysis, respectively. In both reactions the amounts of phenolic hydroxyl groups released were about half of the theoretical values suggesting the occurrence of secondary condensation reactions, which lose phenolic hydroxyl groups, during acidolysis. It has been recognized that the condensation reactions leading to linkages between the benzylic carbon atoms and aromatic nuclei occur during acid hydrolysis of lignin. NIMZ[16] found that the treatment of guaiacylglycerol-β-guaiacyl ether with water at 100°C for several days gave dehydrodiconiferyl alcohol in yield of 32 % and thus it is conceivable that main parts of the phenolic hydroxyl groups loss during acidolysis of the β-aryl ethers should be ascribed to the formation of phenylcoumarane by rearrangement of the β-aryl ethers.

Table 3. Estimation of Phenolic Hydroxyl Groups released from Guaiacylglycerol-α, β-diaryl Ether after Acidolysis by UV Spectrum.

Optical Density 0.05 g/l, (250 mμ)		Increase in Opt. Density	Mol. OH/C_6-C_3	Factor
Guaiacylglycerol-α-guaiacylpropyl-β-guaiacyl diether	1.21	—	—	—
After mild acidolysis	1.64	0.43	0.45	2.22
After acidolysis	1.82	0.18	0.18	5.56

However, experimental results in the present condition gave the reproducible values and the factors correcting the results were calculated and applied for the estimation of the phenolic hydroxyl groups of the lignins after mild acidolysis and acidolysis, respectively.

Table 4 shows the amounts of the phenolic hydroxyl groups released from the β-guaiacyl ethers of *p*-hydroxyphenylglycerol, guaiacylglycerol and syringylglycerol after acidolysis. As in the case of Table 3, the amounts of the phenolic hydroxyl groups released from these compounds were all considerably small comparing with the theoretical values and thus factors for respective values found were calculated as described above.

Estimation of phenolic hydroxyl groups released from lignins after mild acidolysis and acidolysis

Table 4. Estimation of Phenolic Hydroxyl Groups released from Arylglycerol-β-guaiacyl Ethers after Acidolysis by UV Spectrum.

	Optical Density 0.05 g/l, (250 mμ)	Increase in Opt. Density	Mol. OH/C_6-C_3	Factor
p-Hydroxyphenylglycerol-β-guaiacyl ether	2.00	—	—	—
After acidolysis	2.98	0.98	0.43	2.32
Guaiacylglycerol-β-guaiacyl ether	1.36	—	—	—
After acidolysis	1.70	0.34	0.23	4.35
Syringylglycerol-β-guaiacyl ether	0.54	—	—	—
After acidolysis	0.94	0.40	0.74	1.35

Phenolic hydroxyl groups of a bamboo, beech and *Thuja* MWL's after mild acidolysis and acidolysis were determined by the same method, and α-0-4 and β-0-4 linkages/C_6-C_3 unit were calculated by correcting the amounts of the phenolic hydroxyl groups of these MWL's multiplying with the factors obtained from the respective model compounds. As shown in Table 5 the amounts of α-0-4 linkages in open ethers are between 0.07 and 0.09 which are not appreciable difference between gymnosperm and angiosperm lignins and in agreement with the value of spruce MWL hitherto been obtained[17]. However, the amounts of β-0-4 linkages in bamboo and beech (0.56-0.51) were much higher than that of *Thuja* lignin (0.35) indicating the additional participation of syringyl component to the β-0-4 linkages in former MWL's and it was consistent with the results in previous paper[1].

Table 5. Estimation of Phenolic Hydroxyl Groups released from MWL's after Acidolysis by UV Spectrum.

	Opt. Density 0.05 g/l, (250 mμ)	Mol. OH/C_6-C_3	Increase in Mol. OH/C_6-C_3	α-0-4*	β-0-4*
Bamboo MWL	0.49	0.24	—	—	—
After mild acidolysis	0.56	0.27	0.03	0.07	—
After acidolysis	0.96	0.47	0.20	—	0.56
Beech MWL	0.38	0.19	—	—	—
After mild acidolysis	0.45	0.22	0.03	0.07	—
After acidolysis	0.83	0.40	0.18	—	0.51
Thuja MWL	0.57	0.25	—	—	—
After mild acidolysis	0.68	0.29	0.04	0.09	—
After acidolysis	0.86	0.37	0.08	—	0.35
Bamboo MWL (hydrolyzed in 1 N NaOH)	0.41	0.22	—	—	—
After mild acidolysis	0.56	0.27	0.05	0.11	—
After acidolysis	0.83	0.46	0.19	—	0.53

* The values were calculated by correcting the amounts of phenolic hydroxyl groups of these MWL's multiplying with the factor obtained. As reference compounds, guaiacylpropane (ε, 9100), syringylpropane (ε, 8100) and *p*-hydroxyphenylpropane (ε, 8900) were used, respectively[14].

Possible distribution of α-0-4 and β-0-4 linkages in open ethers in lignins

The amounts of the uncondensed type of β-0-4 linkages were estimated from the amounts of guaiacyl- syringyl- and *p*-hydroxyphenylacetones from the lignins by multiplying with the respective factors, and then from the total amounts of β-0-4 linkages calculated from the amounts

Table 6. Possible Distribution of Arylalkyl Ethers in Bamboo, Beech and *Thuja* MWL's.

	Bamboo	Beech	*Thuja*	Bamboo* (hydrolyzed)
Phenolic hydroxyl/C_6-C_3	0.24	0.19	0.25	0.22
α-0-4	0.07	0.07	0.09	0.11
β-0-4	0.56	0.51	0.35	0.53
Uncondensed type	0.24	0.26	0.18	0.15
p-Hydroxyphenyl	0.02	—	—	—
Guaiacyl	0.11	0.16	0.18	0.07
Syringyl	0.11	0.10	—	0.08
Condensed type	0.32	0.25	0.17	0.38
Condensed type (except β-0-4)	0.13	0.23	0.31	0.14

* Bamboo MWL was hydrolyzed in 1N NaOH at room temterature for 24 hrs.

of the phenolic hydroxyl groups released by acidolysis the amounts of the condensed type of β-0-4 linkages were subsequently calculated. The results were shown in Table 6.

It is shown that the amounts of the condensed type of β-0-4 linkages is little higher than that of the uncondensed type in bamboo MWL but the ratio of both types of the ether is about the same in *Thuja* and beech MWL's. Furthermore the amounts of the condensed types other than β-0-4 linkages such as 5-5', β-5' and 4-0-5' were much higher in *Thuja* MWL than bamboo and beech MWL's indicating the greater participation of guaiacyl component than that of syringyl component to these condensed units in the lignins and the results are in good harmony with the fact that syringyl nucleus can not take 5-5' and β-5' linkages.

The amount of γ-O-CO- linkages with *p*-coumaric acid in the bamboo MWL was calculated to be 0.07 from the yield (5.5 %) of *p*-coumaric acid by alkaline hydrolysis of the MWL[18].

It was established in previous paper[19] that the DHP of *p*-coumaryl alcohol gave *p*-hydroxybenzaldehyde and acidolysis monomers in about the same yield as vanillin and the corresponding acidolysis monomers from the DHP of coniferyl alcohol, and that the DHP of *p*-coumaryl alcohol gave *p*-anisic-, 4-methoxyisophtalic and 5-5'-dehydrodianisic acids in the ratio of 1 : 0.26 : 0.41 which corresponded completely to the ratio of veratric-, isohemipinic and 5, 5'-dehydrodiveratric acids from the DHP of coniferyl alcohol. Recent investigation[20] further established that the ratio of dilignols of *p*-coumaryl alcohol such as dehydro-di-*p*-coumaryl alcohol, *p*-coumaryl resinol and *p*-hydroxyphenylglycerol-β-*p*-coumaryl ether formed by enzymic dehydrogenation is quite similar to that of dilignols of coniferyl alcohol obtained in a similar experiment.

Since acidolysis monomers composed of guaiacyl-, syringyl and small amounts of *p*-hydroxyphenyl nuclei, dimers such as *dl*-syringaresinol, *dl*-episyringaresinol, and 2, 3, 2'-trimethoxybiphenyl-5, 5'-dicarboxylic acid, 2, 3-dimethoxydiphenylether-5, 4'-dicarboxylic acid and 2, 2-dimethoxyphenylether-5, 4'-dicarboxylic acid as well as other degradation products in permanganate oxidation[3] have been obtained from bamboo MWL, assuming that 90 % of syringyl and 30 % of guaiacyl- and *p*-hydroxyphenyl glycerol-β-aryl ether groups in the MWL give acidolysis monomers, respectively then it should be reasonable to conclude that the polymeric system of the bamboo lignin is composed of about 10 : 68 : 22 of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol via similar linkages found in spruce lignin, and *p*-coumaric acid ($0.07/C_6$-C_3) is esterified at the terminal γ-carbons of the side chains of the polymeric system giving the final compositiom of 20 : 60 : 20 of *p*-hydroxyphenyl (including *p*-coumaric acid), guaiacyl- and syringyl components[18].

SIMIONESCU and ANTON[21] presented a structural scheme of the BRAUNS native lignin of reed. They assigned the absorption band at 320-322 mμ in UV spectrum of the lignin to the carbonyl groups conjugated to the aromatic nucleus. However, it was clearly established that the grass lignin contains 5-10 % of *p*-coumaric acid esterified and the absorption at this region is completely ascribed to the ester. Their structural scheme of the reed lignin was made up from 8 syringyl, 4 guaiacyl and 2 *p*-hydroxyphenyl units based on simply the ratio of the amounts of aromatic aldehydes obtained by nitrobenzene oxidation and on analyses of functional groups. The scheme, then contradicts with the empiric formula $C_9H_{8.25}O_3(OCH_3)_{1.35}$ of the lignin.

As previous paper[4] established, two third of *p*-hydroxybenzaldehyde produced in nitrobenzene oxidation is ascribed to the *p*-coumaric acid esterified and also it is generally known that angiosperm lignins consisting with about the same amount of guaiacyl and syringyl units give much higher amounts of syringaldehyde than those of vanillin in nitrobenzene oxidation, which is due to the uncondensed type structures of syringyl groups substituted with methoxyl groups at C_5, and then that the ratio of syringaldehyde to vanillin does not reflect the ratio of syringyl to guaiacyl units in lignin itself.

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