Investigations on Lignin and Lignification. XXV. Hydrogenation of Milled-Wood Lignins from White Pine and Blue Spruce

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To elucidate further the differences between the hydrogenation products of deciduous and coniferous milled-wood lignins, the latter were subjected to copper chromite-catalyzed high pressure hydrogenation under conditions that have been applied to such lignins derived from hardwoods. From the distillable hydrogenation products (b.p. 40–180°/1 mm.), which amounted to 30% of the isolated lignin, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-*n*-propylguaiacol, and dihydroconiferyl alcohol were isolated and identified by vapor phase chromatography and infrared spectroscopy. In addition to the above phenolic compounds, a mixture of neutral oils, an acid, and a white amorphous powder were separated by means of chemical prefractionation of the hydrogenation products. To assist in the characterization of certain unidentified compounds that were isolated by vapor phase chromatography, their infrared spectra were obtained and compared with those of model compounds that might be expected to result from lignin hydrogenation under these conditions.

Gas chromatography is being used increasingly in organic chemistry for the separation as well as the identification and quantitative determination of various compounds. The identities of compounds separated by this method are often realized by comparison of their retention times with those of previously described compounds. Infrared and mass spectroscopy are frequently applied to supplement gas chromatography, but identification can be accomplished by the latter alone by a comparison of retention times on the three different stationary phases—*viz.*, electron donor, electron acceptor, and nonpolar.[2]

In the previous communication of this series[3] the high pressure copper chromite-catalyzed hydrogenation of the milled-wood lignins of oak and birch were reported. Gas chromatography and infrared spectroscopy were used for the separation and identification of the hydrogenation products. These hydrogenation studies are here extended to two soft woods, namely white pine and blue spruce, as a means of comparison of the lignins of deciduous and coniferous wood species.

Results and Discussion

Hydrogen consumption during the copper chromite-catalyzed hydrogenation of the milled-wood lignins of blue spruce (OCH_3, 14.79%) and white pine (OCH_3, 14.36%) was 0.02–0.03 mole of hydrogen per gram of lignin. However, these may not represent the real values of hydrogen consumption by lignin *per se*. For, it must be noted that during the catalytic hydrogenation of lignin, the catalyst itself underwent a change in color from black to red, indicating hydrogen absorption by the catalyst, resulting in the reduction of the cupric oxide to metallic copper.

The four fractions that were obtained upon distillation of the viscous brown hydrogenation mixture were subjected to gas-liquid chromatography. Guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-*n*-propylguaiacol, and dihydroconiferyl alcohol were isolated and identified by their retention times and infrared spectra (Table I).

TABLE I
YIELDS AND MOLAR RATIOS OF LIGNIN HYDROGENATION PRODUCTS

	Blue Spruce			White Pine		
Compounds	Distillable, %	Lignin, %	Molar Ratios[a]	Distillable, %	Lignin, %	Molar Ratios[a]
Guaiacol	1.0	0.3	1.0	1.0	0 3	1.0
4-Methylguaiacol	11.5	3.5	10.4	10.2	2.9	9.1
4-Ethylguaiacol	7.0	2.1	5.7	6.5	1.9	5.4
4-*n*-Propylguaiacol	19.9	5.9	14.9	18.3	5.3	13.7
Dihydroconiferyl alcohol	27.0	8.1	18.4	25.0	7.3	16.6
Total	66.4	19.9		61.0	17.7	

[a] Guaiacol assigned a value of unity.

The relative concentrations of these compounds in the hydrogenation mixtures are almost identical for the two softwood species, indicating, along with infrared,[4] ultraviolet spectra, and elementary analyses, the essential similarity of these milled-wood lignins. These identified compounds represent about 60% of the weight of the distillable fractions and 20% of the weight of the lignin, while in case of hardwoods, guaiacol and syringol derivatives account for 20% of the weight of the lignin. In both cases, the molar ratios increase in the same way, and the relative amounts of *n*-propyl, ethyl, and methyl derivatives of guaiacol

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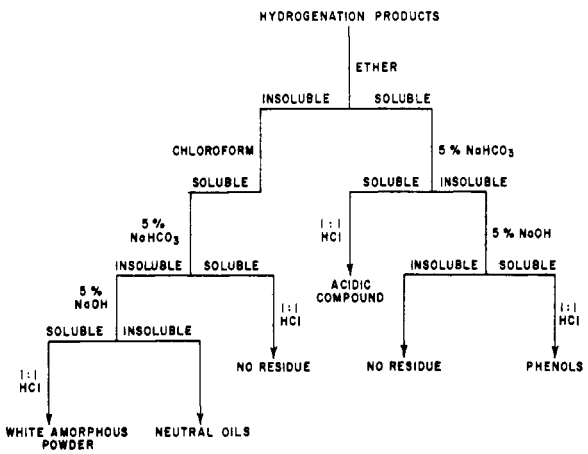
from the softwood lignins are equal to the sum of the guaiacyl and syringyl derivatives from the hardwood lignins.

After prefractionation of the lignin hydrogenation products by distillation *in vacuo*, a black-colored resin was obtained, amounting to 30% of the weight of the original material. To characterize this residue, a prefractionation of the hydrogenation products was accomplished by chemical methods (see Scheme I in Experimental). On

PREFRACTIONATION OF HYDROGENATION PRODUCTS OF SOFTWOOD LIGNINS



Scheme I

acidification of the chloroform-soluble, sodium hydroxide-extracted fraction, a creamy white, amorphous powder was obtained which represented 60% of the weight of the original lignin. Its infrared absorption spectrum was similar to that of the unhydrogenated milled-wood lignin except for the absence of an absorption band at 6 μ (ascribed to coniferyl aldehyde and α-ketone groups).[5] However, the unconjugated carbonyl or ester band at 5.8 μ remained.

The ultraviolet spectra of the residue and of unhydrogenated milled-wood lignin exhibit minima and maxima at 262 and 281 mμ, respectively. There was no hypsochromic shift of the minima, as was the case with the spectra of the distillable material. Moreover, between 290–300 mμ the absorption curve exhibits a sharper decrease than the original lignin, but not as sharp as in the case of the curve of the distillable hydrogenation products (Fig. 1). These observations indicated the hydrogenation and elimination of chromophoric groups and of aromatic ring-conjugated systems.

Elementary analysis of the residue reveals essentially the same C, H, and methoxyl contents as for the untreated lignin (Table II).

The chloroform-soluble, neutral fraction (representing 10% of the original lignin) exhibits a strong C—H stretching band at 3.5 μ, and a carbonyl

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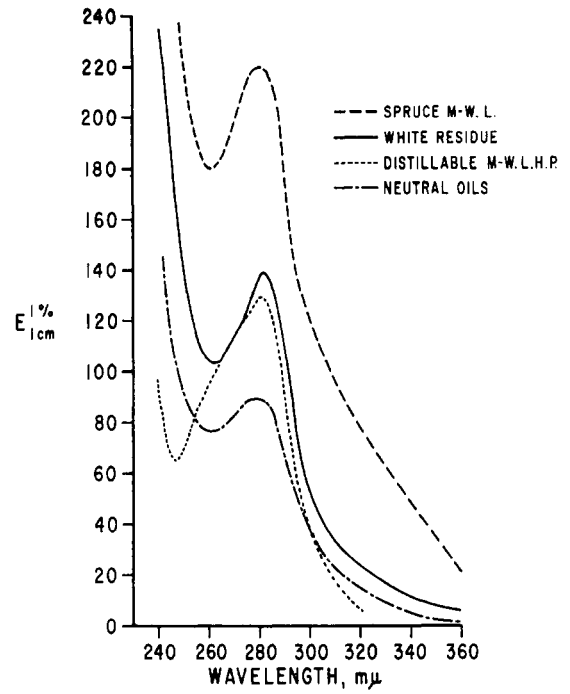

Figure 1

TABLE II
ELEMENTARY ANALYSES OF MILLED-WOOD LIGNIN AND ITS HYDROGENATION RESIDUE

	C, %	H, %	OCH_3, %
Unhydrogenated milled-wood lignin	61.94	5.90	14.77
Residue after hydrogenation	62.36	6.18	14.95

band at 5.8 μ, in addition to the characteristic bands of unconjugated guaiacols at 6.2 and 6.6 μ, thereby indicating that it contains carbonyl or carboxyl groups and aliphatic side chains. However, this component could not be volatilized for vapor phase chromatography studies.

The sodium bicarbonate-soluble fraction was obtained in an amount too small for identification. On the basis of its infrared spectrum, this material possesses a nonaromatic character.

The ether-soluble, sodium hydroxide-extracted fraction was subjected to gas-chromatographic analysis. Guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-*n*-propylguaiacol, and dihydroconiferyl alcohol were identified and isolated in the same concentrations as in the case of the distilled hydrogenation products. Furthermore, the same unidentified compounds were also present in similar ratios in the reaction mixtures which were prefractionated by distillation or by chemical means.

In addition to the above phenols, four other compounds were separated. Their infrared spectra exhibit bands at 6.2 and 6.6 μ, characteristic of an unconjugated guaiacol nucleus. The spectrum of one of these compounds also contains a band at 5.8 μ, representative of an unconjugated ketone.

Mass spectroscopy of the fourth fraction indi-

cates the presence of compounds of molecular weight higher than dihydroconiferyl alcohol.

In an attempt to characterize the unidentified components, model compounds which might result from the hydrogenation of lignin were prepared. Since the existence of 20% of a phenylcoumaran type dimeric structure in lignin has been reported,[6] a study of the products of the hydrogenolysis of this type of linkage was also made. If hydrogenolysis of benzylhydroxyl groups does not occur during the hydrogenation of the phenyl coumaran system but, rather, C—C bond cleavage does occur, then 4,6-dialkylguaiacols can result, along with methylguaiacol. A closed ring system might favor this cleavage. To test this possibility, 4,6-dimethylguaiacol and 4-methyl-6-ethylguaiacol were synthesized, and their retention times and infrared spectra determined. The results indicated that these compounds differed from the unidentified lignin hydrogenation products. Furthermore, none of the hydrogenation products exhibited an infrared spectrum with absorption bands characteristic of tetrasubstituted benzene derivatives. This indicates either that no such linkages exist in lignin, or that the phenylcoumaran system does not undergo hydrogenolysis under these conditions.

Conclusion

The similarity of the ratios of guaiacols present in the softwood lignin hydrogenation products to the guaiacyl and syringyl derivatives in the hardwood lignin hydrogenation products suggests the presence of the same type of C—C and C—O linkages between arylpropane monomers in the two kinds of lignins.

The high proportion of dihydroconiferyl alcohol provides further evidence for the presence of guaiacyl-glycerol-β-guaiacyl ether type linkages in the structure of lignin.

The presence of 4-*n*-propylguaiacol in a relatively high amount can result from the hydrogenolysis of γ-aryl ether type linkages activated by α-carbonyl groups, as explained previously.[3]

Methylguaiacol could be derived under these conditions from either the hydrogenolysis of structures containing phenylcoumaran or pinoresinol, or from lignin building stones in which arylpropane units are linked through a β,β'-carbon-carbon linkage on the side chain. However, the absence of 4,6-dialkylguaiacols indicates the greater probability of the latter type structure over the former. Further work on model compounds is expected to elucidate this question.

Experimental

The isolation of milled-wood lignins from white pine and blue spruce were conducted according to the reported procedure.[7]

Hydrogenation of these milled-wood lignins was carried out according to the procedure used earlier for the hydrogenation of hardwood lignins.[8] A solution of 5 g. of lignin in 200 ml. anhydrous dioxane was mixed with 5 g. of copper chromite catalyst, and subjected to hydrogenation at 1970 p.s.i. initial hydrogen pressure and 225° for 47 hr. The reaction mixture was centrifuged and filtered to remove the catalyst. Dioxane and all other compounds boiling below 100° were removed by distillation at atmospheric pressure. The dark residue was subjected to fractional distillation *in vacuo* at 1 mm., and four fractions were collected over the ranges 45°, 45–80°, 80–140° and 140–180°.

Vapor Phase Chromatography.—The separation of compounds from each fraction was accomplished using a standard Aerograph Model 110-C, equipped with a 130-disk integrator attachment. The disk integrator, mounted on a 1 mv. one-second pen-speed Brown recorder, was used for the peak area measurements. Higher separation factors for the guaiacols were obtained with a 5-ft. DEGS column (15% diethylene glycol succinate coated on 60/80 mesh firebrick at 168°, flow rate of 77 ml./min.), while for dihydroconiferyl alcohol, a 5-ft. carbowax 20/*M* column coated on 60/80 mesh firebrick at 239° was utilized. The carrier gas was helium, and the flow rate was 63 ml./min.

Infrared spectra were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer. Spectra were obtained on Nujol mulls or smears deposited from chloroform.

Ultraviolet spectra were measured with a Zeiss PM QII spectrophotometer. Anhydrous dioxane solutions (5 mg./100 ml.) were used.

Prefractionation of Hydrogenation Products.—The oily residue obtained after the removal of dioxane (at 60°, 20 mm.) was fractionated according to Scheme I.

The white amorphous residue was suspended in 200 ml. of water, centrifuged, and dried *in vacuo* over phosphorus pentoxide. It was purified by dissolving in a mixture of ethylene chloride and absolute ethanol (2:1), and precipitated into absolute ether. The residue recovered after centrifugation was washed twice with ether and once with petroleum ether and dried, first in a stream of dry air, and then *in vacuo* over phosphorus pentoxide.

Preparation of Model Compounds. 4-Ethylguaiacol.—Acetovanillone (4 g.) was dissolved in 50 ml. of absolute ethanol and treated with 0.2 g. of palladium chloride, 1 g. of charcoal, and 1 ml. of concd. hydrochloric acid, and the mixture was subjected to hydrogenation at 48 p.s.i. hydrogen pressure at room temperature. After filtration of the catalyst, the solvent was removed, and the residue was extracted with ether. 4-Ethylguaiacol distilled at 60°/1 mm; yield, 90%. The melting point of the 3,5-dinitrobenzoate of this compound is 127°. A mixed melting point with a sample of the 3,5-dinitrobenzoate obtained from 4-ethylguaiacol prepared by an alternate procedure[9] did not show a depression.

4,6-Dimethylguaiacol.—A 1.66-g. sample of 2-hydroxy-3-methoxy-5-methylbenzaldehyde[10] was dissolved in 30 ml. of glacial acetic acid; 0.75 g. of 5% palladium-on-charcoal was added and the mixture hydrogenated at 89 p.s.i. initial hydrogen pressure and room temperature. After removal of the solvent, the residue distilled at 74–76°/1 mm. After 2 days in the refrigerator, the oil crystallized, m.p., 34–35°.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.05; H, 7.89. Found: C, 71.02; H, 8.01.

4-Methyl-6-ethylguaiacol.—A 4 g. sample of 2-hydroxy-

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3-methoxy-5-methylacetophenone[11] was reduced by the Clemmensen method[12] with 75 g. of amalgamated zinc in 75 ml. of concd. hydrochloric acid and 75 ml. of water, and refluxed for 8 hr. The reaction mixture was extracted with ether. After removal of the ether, the residue distilled at 90–92°/1 mm., yield, 65%.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.28; H, 8.43. Found: C, 72.04; H, 8.28.

The 3,5-dinitrobenzoate melted at 161–162°.

Anal. Calcd. for $C_{17}H_{16}O_7N_2$: C, 56.66; H, 4.41; N, 7.77. Found: C, 56.85; H, 4.40; N, 7.53.

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Acetylation of Alginic Acid. I. Preparation and Viscosities of Algin Acetates

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Alginic acid can be completely acetylated with acetic anhydride and catalytic amounts of perchloric acid. Partially acetylated products may be obtained by removing samples during the controlled reaction. To keep the alginic acid in an activated form, 10–20% of water has to be retained in the fiber. If the viscosity of aqueous solutions of ammonium acetyl alginates is plotted against the degree of acetylation (D.A.), a maximum of the viscosity is obtained between a D.A. of 0.5 and 0.8. In the same range the rate of acetylation increases faster than expected. The results give strong support to the assumption of hydrogen bridge bondings between the vicinal hydroxyl groups in the uronic acid units as the reason for the low reactivity of alginic acid and alginates.

The acetylation or, generally, esterification of hydroxyl groups is one of the most important chemical procedures for changing properties of polysaccharides and other carbohydrates. Products of great commercial value such as cellulose acetate, starch acetate, etc., have thus been developed. The usual methods applied are the catalytic reaction with acetic anhydride or acetic acid, the reaction with acetyl chloride in the presence of an organic base, and a few others, all of them being applied in an anhydrous medium.

In contrast to most polysaccharides alginic acid, a glycuronoglycan of presumably β-(1→4) linked D-mannuronic acid units[1,2] and in a minor percentage[3] of L-guluronic acid units[4,5] cannot be acetylated by the classical methods.[6] Attempts to acetylate alginic acid by the reaction with ketene[7] seemed to be more successful but only about one acetyl group per uronic acid unit could be introduced.

Chamberlain, Cunningham, and Speakman reported the diacetate of alginic acid for the first time in 1946 using a water swollen alginic acid fiber in their experiments.[8,9] However, the degradation during the reaction was too severe to do any viscosity studies with sufficient accuracy. Takahashi reported the diacetate also[10] obtained by treatment of alginic acid with acetic anhydride vapor.

The present work provides information on a method by which fully as well as partially acetylated alginic acid may be obtained. The degradation is reduced to a minimum as indicated by the fact that the end products retain a high viscosity. The study of the variation of viscosity with D.A. gives information on the reactivity of alginic acid.

It is essential for a successful reaction to use a wet alginic acid fiber as starting material with as low an ash content as possible. The following partial dehydration has to be carried out in a way which permits an even distribution of the residual water. For this reason drying at elevated temperature is not suitable. A complete dehydration is disadvantageous because it inactivates the alginic acid. The favorable influence of the presence of some water probably is due to the association of the water molecules with the hydroxyl groups of the uronic acid units which otherwise form hydrogen bridge bondings to a larger extent. When hydrogen bridge formation is favored a substitution of the hydroxyl groups involved becomes very difficult.

If the reaction is performed at moderate temperatures, products with degrees of acetylation of up to 1.85 are obtained. The theoretical D.A. of 2 based upon the assumption that an alginic acid of 100% purity is fully acetylated and that the presumed structure of alginic acid is correct cannot be reached

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