TABLE II

Time, Min.	Concentration, M	
	Quinone V	HNO_2
0	0	0.001
4	0.020	0.018
10	0.048	0.048
20	0.070	0.072
40	0.074	0.070

*p*H 12 differential absorbance of the quinone at 290 mμ is nearly zero.

One mole of nitrous acid/mole quinone was also produced when the reaction was carried out in chloroform–acetic acid or methylene chloride. Titration of the reaction products in the latter solvent with aqueous sodium hydroxide indicated that V and nitrous acid were the only acidic products. Gas chromatography at room temperature of the reaction mixtures in acetic acid, chloroform–acetic acid, and methylene chloride disclosed the presence of methyl nitrite; although methyl acetate and methanol could have been detected in yields as low as 10%, these compounds were not found. Methyl nitrite was identified as follows: A solution of 0.274 g. of III (0.0015 mole) in 9 ml. of methylene chloride was treated with 1 ml. of 3*N* fuming nitric acid in methylene chloride. After 15 min., a 1-ml. sample of the reaction solution was separated by preparative gas chromatography at room temperature, using the Perkin-Elmer preparative-scale "K" column (polyethylene glycol on firebrick) and nitrogen as the carrier gas. The desired volatile product was collected in a liquid nitrogen trap and then transferred to a 7.5-cm. gas cell with sodium chloride windows. The obtained infrared spectrum was identical with the published[18] spectrum of pure methyl nitrite. After withdrawal of the sample for gas chromatography, the remaining solution of the reaction products was immediately put under vacuum and evaporated at low temperature. One recrystallization of the residue from ether–petroleum ether gave the quinone, m.p. 112–116°, in 66% yield.

In order to determine whether methyl acetate could form from methyl nitrite by transesterification, an oxidation of III in pure acetic acid was carried out with similar reagent concentrations as in the preceding experiment. After a reaction time of 10 min., the quinone V was essentially the only colored compound present in solution (determined by paper chromatography). Gas chromatography again indicated a high yield of methyl nitrite, but no methyl acetate or methanol. To 6 ml. of product solution was added 1 ml. of 70% reagent grade nitric acid. After 1 hr., gas chromatography showed that the concentration of methyl nitrite had decreased more than 50%, while methyl acetate had formed in a yield of at least 30%, based on the initial concentration of III. In a control experiment involving addition of water in place of 70% nitric acid, the concentration of methyl nitrite was reduced less than 10% (after correcting for dilution); methyl acetate was not detected.

The formation of water as a product of the oxidation of III to V in organic solvents was confirmed by gas chromatography on a number of different columns; no quantitative data were obtained, however.

Methyl nitrite from methanol and nitrous acid. A solution of 2.76 g. (0.04 mole) of sodium nitrite in 5 ml. of water was added to 90 ml. of acetic acid containing 0.80 ml. of methanol (0.02 mole), and the volume was made up to 100 ml. by addition of acetic acid. After 10 min., a sample was analyzed by gas chromatography; methyl nitrite was detected in approximately the same concentration as obtained from the oxidation of 0.2*M* solutions of III by 0.4*N* fuming nitric acid in acetic acid.

Acknowledgment. The author is indebted to Drs. J. K. Hamilton and H. L. Hergert for many helpful discussions, and to Mr. J. K. Anderson for the determination of spectra.

SHELTON, WASH.

(18) P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).

[CONTRIBUTION NO. 377 FROM THE LABORATORY OF ORGANIC CHEMISTRY AND ENZYMOLOGY, FORDHAM UNIVERSITY]

Investigations on Lignins and Lignification. XXIV.[1a,b] The Application of Hydrogenation, Hydrogenolysis, and Vapor Phase Chromatography in the Study of Lignin Structure

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Birch and oak milled-wood lignins were subjected to high pressure copper "chromite"-catalyzed hydrogenation and hydrogenolysis under conditions favoring cleavage over reduction. From the hydrogenation reaction mixture, there were isolated and identified by vapor phase chromatography retention times, and infrared spectra: 4-methyl guaiacol, 4-ethyl guaiacol, and 4-*n*-propyl guaiacol, their syringyl analogs, dihydroconiferyl alcohol, and dihydrosinapyl alcohol. Interpretation of these results in terms of C—O and C—C bond hydrogenolysis provides evidence for the presence of arylglycerol β-aryl ether, α-arylhydracrylic aldehyde γ-aryl ether, phenylcoumaran, and β,β'-carbon-carbon type linkages in lignin.

Considerable progress has been made in lignin chemistry since the first hydrogenations[2,3] were carried out on this natural polymer. In addition to increasing our knowledge of its structure,[4] investi-

(1) (a) For paper XXIII see C. J. Coscia, W. J. Schubert, and F. F. Nord, *Tappi*, **44**, 360 (1961). (b) For paper XXII see S. N. Acerbo, W. J. Schubert, and F. F. Nord, *J. Am. Chem. Soc.*, **82**, 735 (1960). Presented before the Division of Cellulose, Wood, and Fiber Chemistry at the Autumn Meeting of the American Chemical Society, 1961.

(2) E. E. Harris, J. D'Ianni, and H. Adkins, *J. Am. Chem. Soc.*, **60**, 1467 (1938).

(3) L. M. Cooke, J. L. McCarthy, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 3056 (1941).

(4) F. E. Brauns and D. A. Brauns, *The Chemistry of Lignin*, Supplement Volume, Academic Press Inc., New York, N. Y., 1960, Chapter 24.

gators have isolated preparations—*e.g.*, enzymically liberated,[5] native,[6] and milled-wood[7] lignins—which surpass earlier forms in their usefulness and resemblance to lignin in its natural environment. The difficulties involved in these isolations and the low yields obtained, however, necessitate hydrogenation studies of these lignins on a scale smaller than formerly utilized. Further, the standard techniques applied in earlier isolations and identifications of products must be abandoned in favor of more refined procedures. Thus, for the investigation of volatile hydrogenation products of milled-wood lignins, the versatility of gas-liquid chromatography was exploited. The rapid and simple techniques reported here may facilitate hydrogenation studies in various other phases of lignin research.

The isolation of cyclohexylpropane derivatives from lignin hydrogenation reaction mixtures[2] has provided evidence for the presence of a phenylpropane structure in lignin; and, since this has been established, lignin research has become concerned with the types of linkages which join these moieties together in lignin, as well as with the functional groups present in this polymer. The present study proceeded in the former direction—*i.e.* to establish the nature of the bonds connecting the lignin "building stones." To enable us to understand the types of reactions which occur during lignin hydrogenation and hydrogenolysis, we chose conditions to which many oxygenated alkylaromatic compounds have already been subjected.[8a,9,10] The wide variety of compounds which ensue under such conditions, however, poses both an advantage and a disadvantage. The former is the fact that the products, retaining their aromatic character, are closely related to the original lignins.[1a] The latter is the problem of isolation and identification.

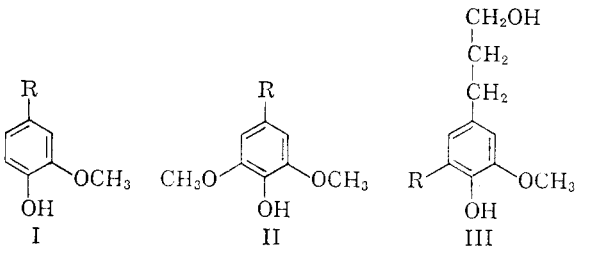
RESULTS

Birch and oak milled-wood lignins were subjected to hydrogenation in the presence of copper "chromite"; 0.03 mole of hydrogen per gram of lignin was absorbed, and the main products of the reaction were viscous liquids which were distilled *in vacuo*. Preliminary studies involving paper chromatography and mass spectroscopy of a sample of the hydrogenation products from a small scale run indicated that these liquids consisted of a complex mixture of phenolic compounds with molecular weights as high as 212.[1a] Because of this complexity, paper chromatographic studies were discontinued, and the more sensitive method of vapor phase chromatography was applied. On passing the high boiling fraction of distillable lignin hydrogenation products through a column of diethylene glycol succinate (DEGS) on firebrick at various temperatures, it was possible to separate the homologous series of guaiacyl and syringyl derivatives listed in Table I. The 4-methyl, 4-ethyl, and 4-*n*-propyl derivatives of guaiacol (I) and syringol[11] (II) were identified by their retention times and infrared spectra. Using a carbowax 20M column at higher temperatures, dihydroconiferyl alcohol (IIIa) was also isolated and identified. Finally dihydrosinapyl alcohol (IIIb) was separated on a silicone rubber column at 177°.

From the data recorded in Table II, it can be recognized that these compounds represent approximately 50% of the high-boiling components. Many of the remaining high-boiling components were present in such a low concentration that they defied identification. The main fraction of distillable material amounted to 40% of the original

TABLE I

RETENTION TIMES (MIN.) OF MILLED-WOOD LIGNIN HYDROGENATION PRODUCTS



Compound	DEGS at 168°	DEGS at 192°	Carbowax 20M at 239°	Silicone Rubber at 177°
4-Methyl guaiacol (I. R = CH_3)	9.4	3.4	1.8	—
4-Ethyl guaiacol (I. R = C_2H_5)	11.3	3.9	2.0	—
4-*n*-Propyl guaiacol (I. R = *n*-C_3H_7)	13.6	4.6	2.4	—
4-Methyl syringol (II. R = CH_3)	—	11.8	4.1	—
4-Ethyl syringol (II. R = C_2H_5)	—	13.1	4.8	—
4-*n*-Propyl syringol (II. R = *n*-C_3H_7)	—	15.0	5.6	—
Dihydroconiferyl alcohol (IIIa. R = H)	—	—	18.2	2.5
Dihydrosinapyl alcohol (IIIb. R = OCH_3)	—	—	—	6.0

(5) W. J. Schubert and F. F. Nord, *J. Am. Chem. Soc.*, 72, 3835 (1950).
(6) F. E. Brauns, *J. Am. Chem. Soc.*, 61, 2120 (1939).
(7) A. Bjørkman, *Svensk Papperstidn.*, 59, 477 (1956).
(8) (a) H. Adkins, *Reactions of Hydrogen*, University of Wisconsin Press, Madison, Wis., 1937. (b) Pp. 69–70. (c) P. 103. (d) P. 106.
(9) J. Entel, C. H. Ruof, and H. C. Howard, *J. Am. Chem. Soc.*, 73, 4152 (1951).
(10) S. B. Baker and H. Hibbert, *J. Am. Chem. Soc.*, 70, 63 (1948).
(11) Hereinafter, 2,6-dimethoxy phenol will be referred to as syringol.

TABLE II

YIELDS AND MOLAR RATIOS OF MILLED-WOOD LIGNIN HYDROGENATION PRODUCTS

Compounds	Birch			Oak		
	% of distillable	% of lignin	Molar ratio[a]	% of distillable	% of lignin	Molar ratio[a]
4-Methyl guaiacol	2.8	1.1	1.4	3.7	1.0	1.9
4-Ethyl guaiacol	2.3	0.9	1.0	2.2	0.6	1.0
4-*n*-Propyl guaiacol	5.8	2.3	2.4	9.5	2.6	4.1
4-Methyl syringol	5.1	2.0	2.1	11.4	3.1	4.8
4-Ethyl syringol	2.8	1.1	1.0	2.6	0.7	1.0
4-*n*-Propyl syringol	9.8	3.9	3.4	26.9	7.3	9.8
Dihydroconiferyl alcohol	5.1	2.0	1.9	2.1	0.6	0.8
Dihydrosinapyl alcohol	20.0	7.9	6.4	2.9	0.8	1.0
Totals	53.7	21.2		61.3	16.7	

[a] Molar ratios: 4-ethyl syringol assigned value of unity.

lignin, while the undistillable residue represents 20%. This accounts for 60% of the lignin hydrogenation products, excluding water and other materials which distilled below 100°.

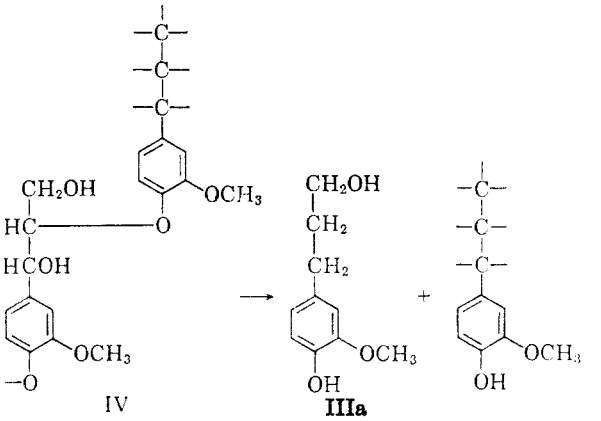
DISCUSSION

It has been reported that milled-wood lignin is a phenylpropane-derived polymer containing free phenolic hydroxyl groups, *p*-hydroxybenzyl alcohol moieties, aromatic ring-conjugated carbonyls, and possibly ethylenic double bonds.[1a,7] The sharpness of the absorption bands of its infrared spectra points to a homogeneity of such lignin. Upon catalytic hydrogenation and hydrogenolysis of this material, under the conditions chosen for this study, ethylenic double bonds and aromatic ring-conjugated carbonyl groups are reduced. Hydrogenolysis, which is greatly facilitated by copper "chromite" in the presence of aromatic systems, occurs readily for alpha and beta C—O bonds on a phenylpropane side chain.[8b]

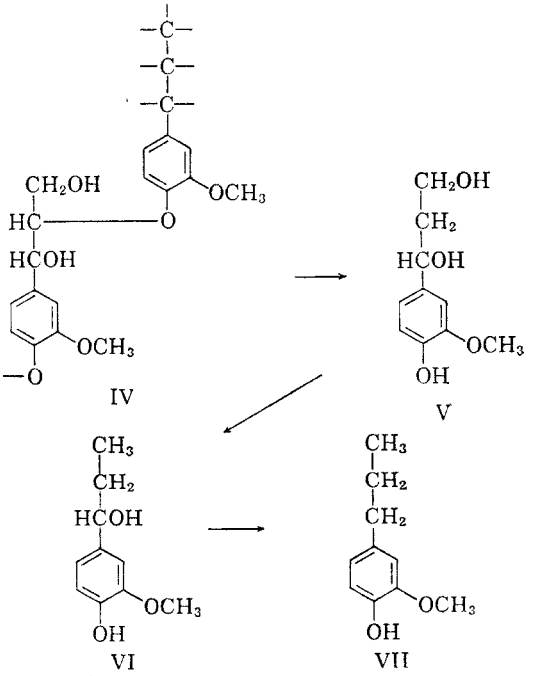
However, a most important aspect of the investigation is that under these experimental conditions, reactions of hydrogenation and hydrogenolysis can compete with one another. If hydrogenation takes place first, a subsequent hydrogenolysis is extremely limited. If the opposite sequence occurs, then one observes both bond cleavage and reduction. Therefore, the nature of the products will depend upon the relative rates of the two competing reactions. As indicated by the products obtained in these studies, we were able to restrict hydrogenation, and thereby achieve a prevalence of hydrogenolysis reactions.

In addition, it has been demonstrated[7] that milled-wood lignin contains a relatively large proportion of *p*-hydroxybenzyl alcohol moieties when compared with other lignin preparations. Although such groups are very labile themselves during catalytic hydrogenation, they may also contribute to the hydrogenolysis of other groups, as will be discussed below.

The hydrogenolysis of C—O bonds alpha and beta to an aromatic ring can readily explain the

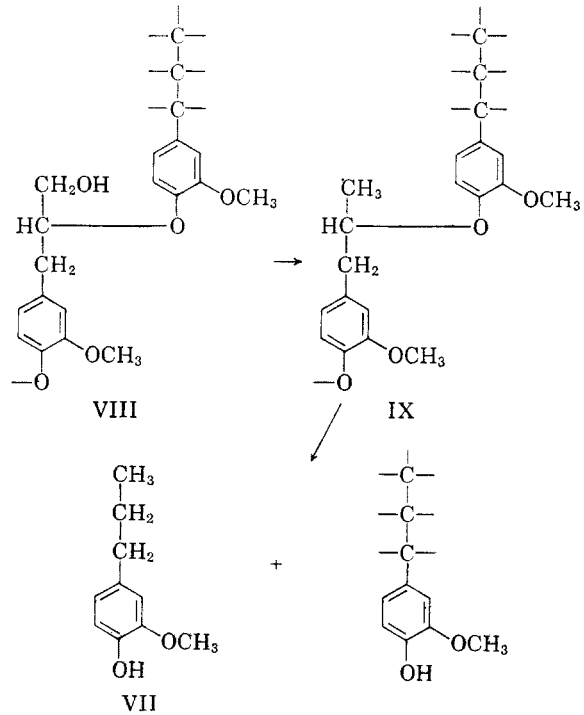


formation of dihydroconiferyl alcohol (III), if lignin contains linkages of the guaiacylglycerol β-aryl ether type (IV) as has been proposed.[12] It has also been demonstrated[2] that hydrogenolysis of a

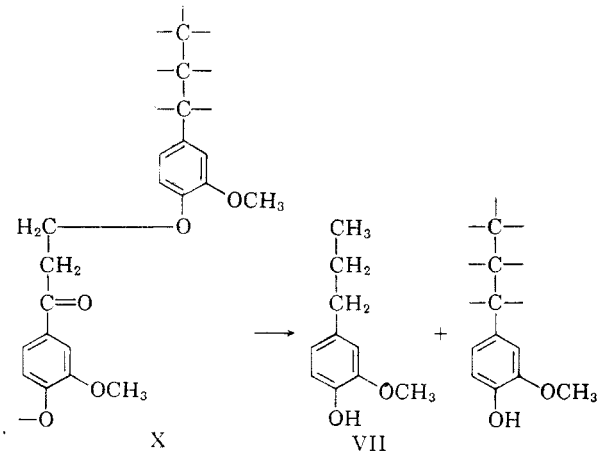


(12) E. Adler and S. Yllner, *Svensk Papperstidn.*, 55, 238 (1952).

C—O bond is induced by the presence of another C—O bond *beta* to it, and this arylglycerol β-aryl ether linkage could give rise to arylpropane derivatives by the following sequence of cleavages. As the benzyl C—O bond is far more labile than one gamma to the aromatic ring, this would provide only a relatively small amount of arylpropane derivatives in competitive reactions. Although an alpha C—O bond will induce hydrogenolysis of another C—O linkage and increase the yield of arylpropanes, it would appear that the relatively high proportion of



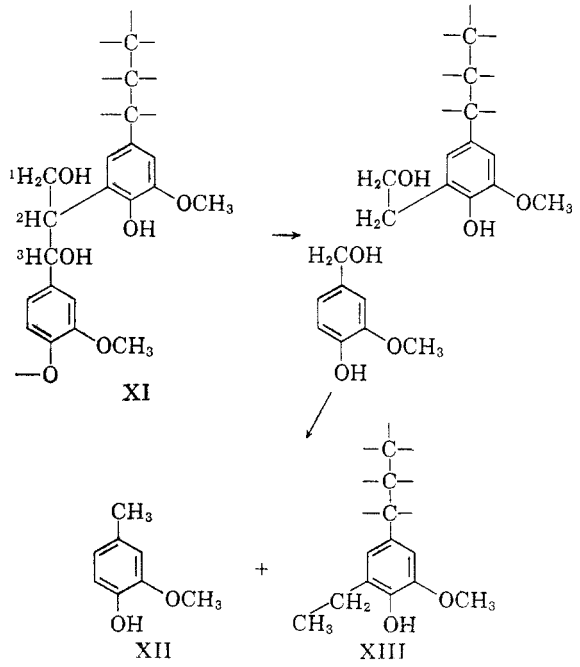
n-propyl derivatives obtained warrants a more satisfactory explanation. The fact that 3-phenylpropanol-1 has been found stable to hydrogenolysis under the present experimental conditions for as long as eight hours[8c] renders it unlikely that the primary alcoholic hydroxyl of dihydroconiferyl alcohol is being cleaved. It is possible, therefore, that lignin contains "building stones" linked through a γ-C—O aryl ether with an α-carbonyl group. This type structure, proposed to explain acetovanillone formation on lignin oxidation,[13] provides an α-carbonyl which can activate the hydrogenolysis of a γ-C—O ether. Hibbert, studying the copper "chromite"-catalyzed hydrogenolysis of certain dimers, had shown that an α-carbonyl is necessary to activate phenylpropyl β-alkyl aryl ether cleavage at lower temperatures.[10] Finally, the possibility that lignin contains terminal C—CH_3 groups is remote, and this explanation would appear least likely.[14]



These considerations have been expressed in terms of the guaiacyl derivatives but they pertain to the syringyl components as well.

Assuming that lignin contains a phenylpropane structure from which the isolated phenylmethane and phenylethane components are derived, the reaction in which this study differs principally from earlier work is in the cleavage of carbon-carbon bonds.

If the 2 and 3 carbons of a 1,3-primary, secondary glycol are alkylated, it will undergo cleavage at the 2,3-carbon-carbon bond[8d]; it has been proposed that lignin contains such glycols. Whether or not lignin is partially constituted of phenylcoumaran systems is debated,[13] but we have found evidence supporting their existence in milled-wood lignin. The open phenylcoumaran XI is a 1,3 primary, secondary glycol with phenyl substituents in the 2 and 3 positions. Although hydrogenolysis of the benzyl C—O bond would predominate under the present experimental conditions, it is possible that C—O and C—C bond cleavages would compete

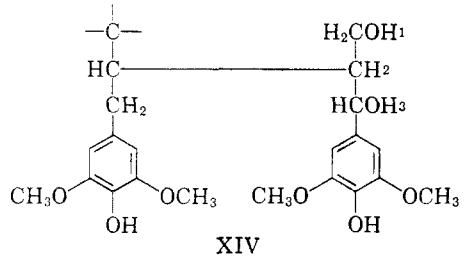


(13) E. Adler, *Ind. Eng. Chem.*, **49**, 1377 (1957).

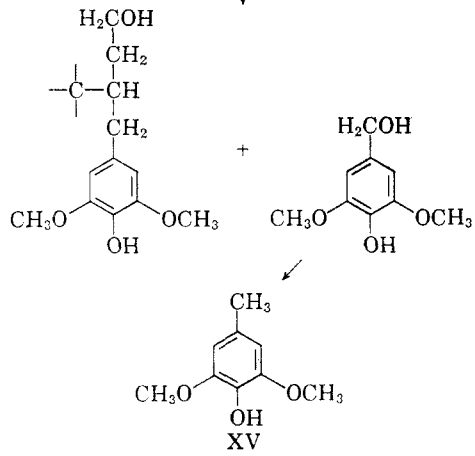
(14) F. E. Brauns, *The Chemistry of Lignin*, Academic Press, Inc., New York, 1952, p. 259.

with each other, and thereby some methylguaiacyl (XII) derivatives would be formed. The closed system would have a less labile α-C—O bond, and might favor C—C cleavage more than would the open system. The other product of such a reaction would be a 2,4-dialkyl guaiacol, and if we are able to isolate a compound of this type (XIII), our evidence will be complete.

A β,β'-carbon-carbon linkage between lignin monomeric units (XIV) has also been proposed.[15] It is supported by the isolation of a guaiacyl and, more especially, syringyl methane (XV) derivative, because again, competitive hydrogenolysis induces some carbon-carbon bond cleavage. The relatively high molar ratio observed for the syringyl methane compound, and the fact that it cannot form a phenyl coumaran system increase the probability that this structure appears in lignin.



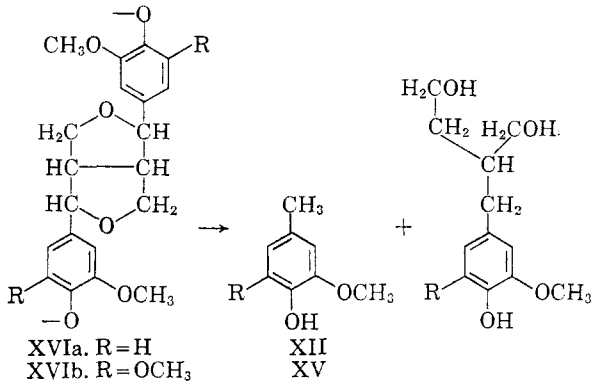
XIV



XV

The syringylresinol (XVIb) and pinoresinol (XVIa) type structures[16] may also be cleaved under these conditions to give relatively small amounts of methyl guaiacyl or syringyl products. No satisfactory explanation for the derivation of the ethyl homologs can be given at the present time.

Despite variations in the lignins, in the conditions of hydrogenation, and in the nature of the products, it appears that a consistent percentage of the lignin (20% in this study, 30% in the researches of Harris[2] and Hibbert[3]) is converted to a resinous material which does not distill *in vacuo*. Earlier investigators proposed that this polymeric substance is derived from a portion of the lignin in which the "building stones" are connected by C—C bonds rather than by C—O—C bonds. The fact that our yields of this resin are slightly lower supports the contention that hydrogenation and hydrogenolysis are competitive reactions; if less reduction occurs initially, then more cleavage results. Thus, even though the lignin monomeric units are joined by some C—C linkages, it may be possible, under the proper conditions, to cleave them by hydrogenation and hydrogenolysis.



XVIa. R = H
XVIb. R = OCH_3

XII

XV

EXPERIMENTAL

I. *Preparation and hydrogenation of the milled-wood lignins.* Milled-wood lignins of oak and birch were prepared in yields of 40% according to the described procedure,[7] with the exception that the wood was not subjected to premilling. The elementary analyses, ultraviolet and infrared spectra of these lignins were reported earlier.[1a]

Lignin (6–7 g.) was dissolved in 250 ml. of anhydrous dioxane, and an equal weight of copper "chromite" was added. The mixture was placed in a hydrogenation bomb and subjected to an initial hydrogen pressure of 100 atm. at originally 240–260° for 48 hr. The bomb temperature varied ± 2.5°. The catalyst was removed by centrifugation, and the supernatant was filtered to remove any suspended material. The resulting liquid was dark brown in color. Dioxane and all material boiling below 100° were removed by distillation. The brown viscous residue was distilled *in vacuo* through a 10-cm. Vigreux column, and in the case of the birch lignin, four fractions were collected over the range 30–140°/1 mm. The mixture from the oak lignin distilled in two fractions at 60–120°/1 mm. These products exhibited typical phenolic characteristics.[1a]

II. *Vapor phase chromatography of the hydrogenation products.* The several fractions of distillate were subjected to gas-liquid chromatographic analysis in an Aerograph 110-C instrument equipped with a 130 disc integrator attachment. It was found that the guaiacyl derivatives (with the exception of dihydroconiferyl alcohol) were best separated on a 5-ft. column of 15% diethylene glycol succinate on 60/80 mesh firebrick at 168°. Helium was used as the carrier gas at a flow rate of 77 ml./min. Syringyl derivatives were fractionated at an optimum temperature of 192° on the same column with a 72 ml./min. flow rate. Dihydrosinapyl alcohol was fractionated on a 5-ft. silicone rubber on firebrick column at 177° and at a flow rate of 76 ml. of helium/min.

For dihydroconiferyl alcohol, a 5-ft. 15% Carbowax 20M on 60/80 mesh firebrick column was substituted for the diethylene glycol succinate, as the latter cannot be heated above 225°, and the dihydroconiferyl alcohol required a column temperature of at least 239°. Only the last fraction of distillate contained this compound, and due to the high viscosity of this fraction, it was injected into the column in a chloroform solution. The flow rate employed for the isola-

(15) H. Erdtman, *Svensk Papperstidn.*, **44**, 243 (1941).
(16) H. Erdtman, *Svensk Papperstidn.*, **43**, 255 (1940).

tion of dihydroconiferyl alcohol was 63 ml. of helium/min. The other guaiacyl and syringyl derivatives were also separable on the Carbowax column, but the diethylene glycol succinate provided superior fractionation.

Retention times were determined, and the various compounds were collected as they emanated from the column in special receivers immersed in a Dry Ice bath. After several collections, sufficient material was obtained for the determination of infrared spectra. The individual compounds were washed out of the receivers with chloroform, and their solutions were added dropwise to a sodium chloride window. Upon evaporation of the chloroform, the compound remained as a smear on the crystal. Hereupon, another window was added, the crystals were mounted, and the spectrum was taken on a Perkin-Elmer model 21 double beam recording infrared spectrophotometer. The spectra were then compared with those of model compounds. Because of the volatility of the stationary phase, the infrared spectrum of the compound invariably contained peaks attributable to diethylene glycol succinate. To compensate for this, the model compounds were passed through the column and collected in the same fashion as were the hydrogenation products. The spectra were found to be identical except in cases where the hydrogenation product was present in very low concentration, and several runs were necessary to collect sufficient material for a spectrum. (Here, the bands of the stationary phase were very intense.) For the purchased chemicals, this technique also served to provide a purified sample for spectral comparison. Determinations of the concentrations of the various constituents were made using a disc integrator attached to the 1-mv. recorder.

III. *Preparation of model compounds.* 4-Methyl guaiacol was purchased from Distillation Products Industries, Rochester, N. Y.

4-Ethyl guaiacol. (a) *4-Vinyl guaiacol.*[17] To 5 g. of ferulic acid dissolved in 10 g. of quinoline, 1 g. of copper bronze was added, and the mixture heated to 240° in a metal bath. After the evolution of carbon dioxide had ceased, the residue was cooled, dissolved in ether and washed first with dilute sodium carbonate solution. The ether solution was then extracted with aqueous sodium hydroxide; the latter was acidified, back extracted with ether, washed and dried over anhydrous sodium sulfate. The 4-vinyl guaiacol distilled at approximately 100°/1 mm. in 10% yield.

(*b*) *4-Ethyl guaiacol.* 4-Vinyl guaiacol (0.4 g.) was dissolved in 20 ml. of absolute ethanol, treated with 0.5 g. of 5% palladium-charcoal, and the mixture subjected to low pressure hydrogenation at room temperature. After filtering the catalyst, the ethanol was removed and 0.35 g. of 4-ethyl guaiacol distilled at 60°/1 mm.; yield; 89%. A 3,5-dinitrobenzoate of the phenol melted at 127° (corr.), lit. m.p. 121.5°.[18]

4-Ethyl guaiacol-3,5-dinitrobenzoate.

Anal. Calcd. for $C_{16}H_{14}O_7N_2$: N, 8.48. Found: N, 8.12.

4-n-Propyl guaiacol (dihydroeugenol).[19] Fifty grams of eugenol in 200 ml. of ethanol was treated with 0.5 g. of 10% palladium-charcoal and hydrogenated to dihydroeugenol at room temperature and an initial hydrogen pressure of 48 p.s.i. On removal of the catalyst and solvent, a clear oil was obtained which distilled *in vacuo* at 97°/1 mm.

Anal. Calcd. for $C_{10}H_{14}O_2$: OCH_3 18.67. Found: 18.40.

The 3,5-dinitrobenzoate melted at 118–119.5°, lit. m.p. 116.2°.

Anal. Calcd. for $C_{17}H_{16}O_7N_2$: N, 7.75. Found: N, 7.69.

4-Methyl syringol. To 3 g. of syringaldehyde in 200 ml. of acetic acid, 1.5 g. of 5% palladium-charcoal was added and the mixture hydrogenated at room temperature for 17 hr. at an initial hydrogen pressure of 45 p.s.i. After the water and acid were removed, the residue distilled at 109°/1 mm. in almost quantitative yields. After standing a short time, the oil crystallized; m.p. 40.5–41.5° (corr.), lit. m.p. 41°.[21]

Anal. Calcd. for $C_9H_{12}O_3$: OCH_3, 36.90. Found: OCH_3, 35.30.

A benzoate was prepared, m.p. 125–126° (corr.), lit. m.p. 118°.[22]

Anal. Calcd. for $C_{16}H_{16}O_4$: OCH_3, 22.79. Found: OCH_3 22.22.

4-Ethyl syringol. (a) *1-Acetyl syringol.*[23] Fifty grams of syringol was dissolved in 50 ml. of anhydrous benzene and 33 g. of pyridine and placed in a 500-ml. three-neck flask attached with a reflux condenser, mechanical stirrer, and dropping funnel. With vigorous stirring, 30 g. of acetyl chloride was added dropwise, the mixture heated at 60° for 2 hr., cooled and filtered. On drying, 52.5 g. of a crystalline solid was obtained, m.p. 53.5° (corr.), lit. m.p. 53.5°[24]; yield: 81%.

(*b*) *Acetosyringone.*[23] 1-Acetyl syringol (52.5 g.) was dissolved in 350 ml. of nitrobenzene in a three-neck flask provided with a reflux condenser and stirrer. With vigorous stirring, 71 g. of anhydrous aluminum chloride was added slowly, maintaining the temperature of the solution between 0° and 5°. The mixture was stirred for 2 hr. at 0° and then allowed to stand for 22 hr. at room temperature. On addition of the product to 2.5 kg. of ice and 250 ml. of concd. hydrochloric acid, an unfilterable suspension was obtained. This suspension was neutralized and extracted with a large excess of ether. The ether extracts were then back-extracted with dilute aqueous sodium hydroxide to isolate the salt of the phenol. This was then acidified, extracted with benzene and, after removal of the solvent, distilled *in vacuo* at 80°/1 mm. The yellow crystalline product was recrystallized from ether, giving 2.6 g. of material melting at 117–120° (corr.), lit. m.p. 121–122°,[23] yield: 5%.

(*c*) *4-Ethyl syringol.* Acetosyringone (2.6 g.) in 40 ml. of methanol was treated with 0.25 ml. of concd. hydrochloric acid, 0.1 g. of palladium chloride, and 1 g. of charcoal. This mixture was subjected to an initial hydrogen pressure of 42 p.s.i. at room temperature. Upon filtering the catalyst, the solution was neutralized, the solvent removed, the residue reacidified, and then extracted with ether 2.0 g. of 4-ethyl syringol distilled at 109°/1 mm.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 64.74, H, 7.72.

The *p*-nitrobenzoate melted at 151–152° (corr.), lit. m.p. 151–152°.[23]

Anal. Calcd. for $C_{17}H_{17}O_6N$: C, 61.62; H, 5.17. Found: C, 61.68; H, 5.11.

4-n-Propyl syringol. (a) *1-Allyl syringol.*[25] In a three-neck flask equipped with stirrer and reflux condenser, 77 g. of syringol was dissolved in 200 ml. of anhydrous acetone, and 60.5 g. of allyl bromide added. To this solution, 90 g. of anhydrous potassium carbonate was added and the resulting mixture refluxed for 10 hr. The acetone was distilled, and the residue treated with 50 ml. of water, extracted with ether and washed twice with dilute aqueous sodium hydroxide. After additional washings with water, the ether solution was dried over anhyd. calcium chloride, and then distilled *in vacuo* at 105°/1 mm., yield: 88%.

(b) *4-Allyl syringol.*[25] 1-Allyl syringol (82.8 g.) was refluxed at 240°/100–145 mm. for 1 hr. and then distilled at 123–125°/2 mm.; yield: 54%.

(c) *4-n-Propyl syringol.*[19] The 4-allyl syringol (44.4 g.) was dissolved in 180 ml. of absolute ethanol and treated with 1 g. of 5% palladium-charcoal. The mixture was hydrogenated at

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room temperature at an initial hydrogen pressure of 47 p.s.i. On removal of the catalyst and alcohol, the 4-propyl syringol was distilled *in vacuo* at 145–148°/4 mm. in 93% yield.

Anal. Calcd. for $C_{11}H_{16}O_3$: OCH_3, 31.62. Found: OCH_3, 31.28.

An acetate of the syringol wasp repared, m.p. 87–88° (corr.), lit. m.p. 87–88°.[26]

Anal. Calcd. for $C_{13}H_{18}O_4$: OCH_3, 26.05. Found: OCH_3, 25.90.

Dihydroconiferyl alcohol. (a) *Dihydroferulic acid.* Fifteen grams of ferulic acid, dissolved in 200 ml. of methanol, was mixed with 1 g. of 5% palladium-charcoal and subjected at room temperature to an initial hydrogen pressure of 44 p.s.i. After hydrogenation, the catalyst was filtered and the methanol evaporated, leaving white crystals of dihydroferulic acid, m.p., 91–93°, lit. m.p. 90–91°.[27]

(b) *Ethyl dihydroferulate.* The ethyl ester of dihydroferulic acid was prepared[26] in 74% yield. It distilled at 150–157°/1 mm.

(c) *Dihydroconiferyl alcohol.* In a three neck flask equipped with a ground-glass stirrer, reflux condenser (with drying tube) and a dropping funnel, 5 g. of lithium aluminum hydride was dissolved in 500 ml. of absolute ether by prolonged vigorous stirring. Ethyl dihydroferulate (13.1 g.) dissolved in 400 ml. of absolute ether was added over a period of 2 hr. The mixture was refluxed for 1 hr. and then treated with 50 ml. of cold water–cautiously at first. A cold solution of 20 ml. of concd. sulfuric acid in 200 ml. of water was then carefully added, and after separation, the aqueous layer extracted with additional ether. The combined ether extracts were washed with water, dried over anhydrous sodium sulfate, and then distilled *in vacuo* at 168–170°/1 mm. A cloudy white material was obtained in 50% yield. On refrigeration for several days it became crystalline, m. p. 63–65°, lit. m.p. 65–70°.[28]

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Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C 66.34, H, 7.91.

The bis-*p*-nitrobenzoate melted at 120.5–122° (corr.); lit. m.p. 121–122°.[29]

Anal. Calcd. for $C_{24}H_{20}O_9N_2$: C, 60.00; H, 4.20. Found: C, 60.21; H, 4.38.

Dihydrosinapyl alcohol. (a) *Sinapic acid.* Sinapic acid was prepared in 63% yield from syringealdehyde,[25] m.p. 190–192°. corr.); lit. m.p. 191–192°.[30]

(b) *Dihydrosinapic acid.* Dihydrosinapic acid was prepared from sinapic acid by the same method used for dihydroferulic acid, m.p. 101.5–103° (corr.); lit. m.p. 102–103°.[19]

(c) *Ethyl dihydrosinapate.* The ethyl ester of dihydrosinapic acid was prepared[26] in 84% yield. It distilled at 195–200°/1 mm.

(d) *Dihydrosinapyl alcohol.* Dihydrosinapyl alcohol was prepared in the same manner as dihydroconiferyl alcohol, m.p. 75–76.5° (corr.); lit. m.p. 75.5–76.5°.[26]

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60, OCH_3, 29.24. Found: C, 62.21; H, 7.69; OCH_3, 29.40.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO.]

Synthesis and Some Novel Reactions of α,α-Dichloroperfluoroalkyl Esters

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Photochlorination of α,α-dihydroperfluoroalkyl perfluoroalkanoates at 100–140° gave 90% of the corresponding α,α-dichloro ester distillable *in vacuo*. Thermal or catalytic cracking of the α,α-dichloro ester gave two perfluoro acid chlorides (same or different) in high yield. Reaction of the α,α-dichloro ester with water, amines, or alcohols gave an equivalent of the two corresponding acids, amides, or esters. The α,α-dichloro ester is, in effect, a dimeric acid chloride. Pyrolysis of α,α-dichloroperfluoroalkyl trichloroacetates gave trichloroacetyl chloride and a perfluoroalkanoyl chloride, while bis(α,α-dichloroperfluoroalkyl)carbonates were cleaved in two steps to phosgene and two moles of the perfluoro acid chloride. These reactions provide a convenient route to ω-chloroperfluoroalkanoic acids and their carboxyl-linked derivatives.

Photochlorination of α.α,ω-trihydroperfluoroalkanols (*A*) [$H(CF_2CF_2)_nCH_2OH$, n = 1,2,3, *etc.*] at 20–80° gave hemiacetals of the corresponding aldehydes,[1] and increasing amounts of α,α,ω-trihydroperfluoroalkyl ω'-hydroperfluoroalkanoates (*B*) as the conversion of alcohol to hemiacetal was raised.[1,2] From *B* a 90% yield of α,α,ω-trichloroperfluoroalkyl

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(2) Chlorine substitution occurred when chlorination was continued at 20° until no further reaction occurred, but a complicated mixture of products was obtained.