[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LXXXIV. The High Pressure Hydrogenation of Maple Wood: Hydrol Lignin[1]

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In the investigation of the structure of lignin, the techniques of oxidation[5,6] and ethanolysis have been extensively employed. Oxidation of spruce and maple woodmeal gave yields of aldehydes of 25 and 46%, respectively, based on the lignin originally present, but as these compounds are only lignin degradation products, they give no clue to the structure of the side-chains existing in the original lignin unit. On the other hand, while the yields of identifiable lignin products isolated from the ethanolysis procedure are low, they possess a marked significance with respect to the structure of lignin inasmuch as they evidently represent stabilized end-products of the more reactive, true lignin progenitors.[7]

Previous to this investigation, the products of high pressure catalytic hydrogenation of wood and lignin have been isolated mainly in the form of propylcyclohexane derivatives.[8a,b,c,9] This paper describes a method for isolating lignin from wood under hydrogenation conditions in a form believed to be essentially unchanged from that in the wood. In addition, several new products of lignin degradation have been isolated and identified.

This method consists in hydrogenating maple woodmeal over Raney nickel catalyst[10] in a neutral solution of ethanol–water (1:1) under mild conditions (165–170° for four hours) and separating the lignin from the cellulose degradation products by extraction with chloroform. In this way 75–85% of the original lignin is removed from the wood under such conditions that little or no condensation should occur. This new lignin product has been named "hydrol" lignin.

Preliminary investigations show that hydrol lignin contains phenol and methoxyl groups, but no carbonyl groups or ethylenic linkages. It is not degraded when subjected to ethanolysis, and thus appears to be more stable than lignin isolated by ethanolysis.[11] Hydrogenation of hydrol lignin at 205° results in only partial saturation, as indicated by the high yield of phenolic material in the reaction mixture. Since most aromatic derivatives are completely reduced under the conditions of this hydrogenation, this result is considered unusual.

Hydrogenation of hydrol lignin over Raney nickel and copper chromium oxide at 225° yielded a water-soluble fraction containing 4-ethylcyclohexanol to the extent of 9.7% of the original weight of lignin. This product probably resulted from the hydrogenation of 3-(4-hydroxycyclohexyl)-1-propanol, as does ethylcyclohexane from 3-cyclohexyl-1-propanol in 80% yield.[12] No identifiable products were isolated from the water-insoluble portion.

At 250°, hydrogenation of hydrol lignin over copper chromium oxide produced 4-*n*-propylcyclohexanol (I), 3-cyclohexyl-1-propanol (II), and 3-(4-hydroxycyclohexyl)-1-propanol (III), in yields of 3.1, 3.4, and 5.5%, respectively, based on the original Klason lignin. These products have been isolated in previous investigations[8,9] and thus indicate a marked similarity of behavior between hydrol lignin, other isolated lignins and protolignin.

Hydrol lignin was solvent-fractionated by precipitation into 30–50° petroleum ether, yielding 10–15% of a soluble fraction. This product was distilled through a 28-plate column,[13] but the variations in refractive indices and methoxyl contents of the distillate indicated preliminary separation was necessary. Accordingly, a separation into acid-soluble, alkali-soluble and neutral portions was made, and the large, alkali-soluble portion was fractionally distilled. The following products were thereby isolated: 3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol, (IV), 3-(4-hydroxy-3-methoxyphenyl)-1-propanol, (V) and 3-(4-hydroxy-3,5-dimethoxyphenyl)-propane (VI) in yields of 1.4, 0.84 and 0.83%, respectively, based on the original lignin.

An additional quantity of IV amounting to 7.4% of the lignin, was obtained by precipitating the petroleum ether-insoluble hydrol lignin into diethyl ether, and fractionally distilling the alkali-soluble portion of the ether-soluble lignin.

Synthesis of IV (not previously reported), was carried out by the following series of reactions

$$\text{Maple wood} \xrightarrow[\text{Nitrobenzene}]{\text{NaOH}} \text{RCHO} \xrightarrow{CH_2(COOH)_2}$$

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(5) Freudenberg, Lautsch and Engler, *Ber.*, **73**, 167 (1940).

(6) Creighton, McCarthy and Hibbert, THIS JOURNAL, **63**, 312 (1941).

(7) Hibbert, *Ann. Rev. Biochem.*, **12**, 183 (1942).

(8) (a) Harris, D'Ianni and Adkins, THIS JOURNAL, **60**, 1467 (1938); (b) Adkins, Frank and Bloom, *ibid.*, **63**, 549 (1941); (c) Harris, Salmon and Sherrard, *Ind. Eng. Chem.*, **32**, 440 (1940).

(9) Cooke, McCarthy and Hibbert, *ibid.*, **63**, 3052, 3056 (1941).

(10) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

(11) West, Hawkins and Hibbert, *ibid.*, **63**, 3038 (1941).

(12) Adkins, "Reactions of Hydrogen." University of Wisconsin Press, Madison, Wisconsin, 1937.

(13) Cooke and Bower, *Ind. Eng. Chem. Anal. Ed.*, **15**, 290 (1943).

$$\mathrm{RCH{=}CHCOOH}^{(13a)} \xrightarrow{\mathrm{H_2}} \mathrm{RCH_2CH_2COOH} \xrightarrow{\mathrm{EtOH,\ H_2SO_4}} \mathrm{RCH_2CH_2COOEt} \xrightarrow{\mathrm{Na,\ EtOH}} \underset{\mathrm{(IV)}}{\mathrm{RCH_2CH_2CH_2OH}}$$

(R = 4-hydroxy-3,5-dimethoxyphenyl)

The isolation of the previously known saturated compounds, I, II, III, by the hydrogenation of hydrol lignin indicated the similar behavior of this material, wood, and isolated lignins when subjected to the same conditions of hydrogenation. The structure of these isolated products pointed to their derivation from propylphenol derivatives containing terminal oxygen atoms on the side chains, probably in the form of ether or acetal linkages.

Isolation of the aromatic derivatives (IV, V and VI) provides valuable support for the above theory, since 92% of these products contain terminal carbinol groups on the side chain. Furthermore, the methoxyl groups are left intact, thus permitting the isolation of guaiacyl (4-hydroxy-3-methoxyphenyl) and syringyl (4-hydroxy-3,5-dimethoxyphenyl) derivatives as wood hydrogenation–hydrogenolysis products for the first time.

Moreover, the difference in yields between the guaiacyl- and syringyl- containing propylphenol derivatives points to a marked difference in the mode of linkage by which these are united to similar units in protolignin, and supports the theory that in the former we are concerned largely with —C—C— linkages, and in the latter with —C—O—C— linkages between propylphenol units.

Experimental

Preparation of Hydrol Lignin.—Maple woodmeal (22 g. 20.3% Klason lignin, 6.1% OCH_3 and 4–6% water) was mixed with 1:1 ethanol:water (220 cc.) and moist Raney nickel catalyst (16.5 g.) and hydrogenated for four hours at 165–170° with an initial hydrogen pressure of 3000 lb./sq. in. The pulp yield was 65% of the dry wood and the lignin removal was 75–85%, based on the original lignin in the wood. The pulp was filtered from the reaction medium, the solution concentrated to incipient precipitation, and then extracted three times with an equal volume of chloroform. The chloroform solution was dried and concentrated to a clear, red-brown viscous oil containing 24–25% OCH_3 and representing 70–80% of the lignin in the wood. Hydrol lignin prepared in this way was used in all further experiments.

Hydrogenation of Hydrol Lignin. I. At 250°.—Hydrol lignin (7 g.) was hydrogenated in dioxane (150 cc.) for five hours at 250° over copper–chromium oxide catalyst[12] (10 g.) with an initial hydrogen pressure of 3000 lb./sq. in. The catalyst was removed by centrifugation, and the dioxane and lower boiling compounds by distillation. The residual colorless oil was dissolved in ether (20 cc.) and the solution extracted five times with 10-cc. portions of water. The extracted ether solution contained 3.1 g. water-insoluble oils, while the water extract contained 1.4 g.

(a) **Isolation and Identification of 4-*n*-Propylcyclohexanol and 3-Cyclohexyl-1-propanol.**—The water-insoluble oils (3.1 g.) were fractionated through a Podbielniak column[15] at 0.1 mm. pressure and bath temperatures up to 250° to yield two identifiable fractions, 4-*n*-propylcyclohexanol (n^{25}D 1.4640–1.4648) and 3-cyclohexyl-1-propanol (n^{25}D 1.4650–1.4679), identified as their phenylurethans, m. p. 126–127° and 84–85°, respectively. Yields were 0.4 and 0.43 g., respectively.

(b) **Isolation and Identification of 3-(4-Hydroxycyclohexyl)-1-propanol.**—The water-soluble oils (1.4 g.) were fractionated in a semi-micro column[13] to give 0.7 g. of a semi-crystalline fraction n^{53}D 1.4768–1.4786 identified as 3-(4-hydroxycyclohexyl)-1-propanol by oxidation to β-(4-ketocyclohexyl)-propionic acid and preparation of the semicarbazone.[9]

II. **At 225°.**—Hydrol lignin (10.9 g.) was hydrogenated in dioxane (180 cc.) for seven and one-half hours at 225° over Raney nickel (10 g.) and copper–chromium oxide (8 g.) with an initial hydrogen pressure of 3100 lb./sq. in. The products were separated into water-soluble (0.5 g.) and -insoluble (3.9 g.) fractions as described above, and the latter fractionally distilled through a 28-plate column.[13] From the products a fraction with n^{25}D 1.4600–1.4615 was isolated and identified as 4-ethylcyclohexanol by a mixed melting point of the phenylurethan with an authentic sample. Melting point of urethan 113.5–114.5°; yield 1.25 g.

The water-soluble portion (0.5 g.) was not identified.

Fractionation of Hydrol Lignin.—(1) Hydrol lignin (9.5 g.) was dissolved in chloroform (100 cc.) and precipitated by pouring into two liters of 30–50° petroleum ether with stirring. The oily precipitate was allowed to separate, the clear supernatant liquor was decanted, and the residual solvent removed by evaporation, leaving the petroleum ether-soluble fraction as a viscous oil (1.0 g.). The petroleum ether-insoluble material (8.4 g.) was further fractionated by dissolving in chloroform (80 cc.) and extracting four times with 20 cc. of saturated sodium bicarbonate solution. The extracts were combined, neutralized with 10% sulfuric acid and back-extracted with four 20-cc. portions of chloroform, which were then combined, dried over sodium sulfate and the solvent removed; yield of acid fraction 0.6 g. A similar treatment of the residual chloroform solution with 5% sodium hydroxide solution yielded an alkali-soluble fraction of 6.4 g. and left a neutral fraction of 0.8 g. in the residual chloroform solution.

(2) A quantity (17.4 g.) of the petroleum ether-insoluble hydrol lignin obtained according to the above procedure was dissolved in chloroform (100 cc.) and precipitated into 1 liter of diethyl ether. A light buff-colored amorphous precipitate (6.4 g.) was removed by filtration, and evaporation of the filtrate left a reddish oil, 11 g. (42% of Klason lignin). An aliquot (9.6 g.) of this oil was separated into acid (0.95 g.), alkali-soluble (6.6 g.), and neutral fractions (0.7 g.) by the procedure described above in I.

Isolation and Identification of 3-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanol, IV.—The alkali-soluble fraction (6.4 g.) of petroleum ether-soluble hydrol lignin (from 108 g. of Klason lignin) was fractionated through a 28-plate column[13] (270–290° bath temp. at 0.25 mm. pressure) and yielded a white, crystalline product, m. p. 75.5–76.5° after recrystallization from benzene. A mixed m. p. with a synthetic sample described below showed no depression; yield 1.5 g. (1.4% of lignin).

The alkali-soluble portion (6.6 g.) of the petroleum ether-insoluble, diethyl ether-soluble hydrol lignin was fractionated in the same column to yield an additional quantity of the same crystalline product; yield 1.72 g. (7.4% of the Klason lignin).

Isolation and Identification of 3-(4-Hydroxy-3-methoxyphenyl)-1-propanol (V).—Fractions (1.35 g., n^{50}D 1.5200–1.5380) obtained in the fractionation of the alkali-soluble portion of petroleum ether-soluble hydrol lignin described in the previous section were combined and refractionated in a smaller column,[13] (bath temp. 170° at 0.2 mm. pressure) to yield a clear, colorless oil, n^{50}D 1.5360–1.5380, identified as 3-(4-hydroxy-3-methoxyphenyl)-1-propanol

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(13a) Sinapic acid melted at 178-183° (reported 191-192°[14]) and could not be further purified by recrystallization.

[14] Graebe and Martz, *Ber.*, **36**, 1031 (1903).

[15] Podbielniak, *Ind. Eng. Chem. Anal. Ed.*, **3**, 177 (1931); **5**, 119 (1933).

by a mixed melting point of the bis-*p*-nitrobenzoate with that of the synthetic derivative; yield was 0.9 g. (0.84% of Klason lignin).

Isolation and Identification of 3-(4-Hydroxy-3,5-dimethoxyphenyl)-propane (VI).—Fractions (1.45 g., n^{50}_{D} 1.5000–1.5150), also obtained from the fractionation of alkali-soluble, petroleum ether-soluble hydrol lignin, were combined and refractionated to yield a clear, colorless oil identified as 3-(4-hydroxy-3,5-dimethoxyphenyl)-propane by a mixed m. p. of the acetate with that of the synthetic product; yield was 0.89 g. (0.83% of Klason lignin).

Synthesis of Products Isolated from Hydrol Lignin. I. 3-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanol (IV) Syringaldehyde.—A mixture of vanillin and syringaldehyde was prepared by the oxidation of maple woodmeal, using the method of Creighton.[16] The syringaldehyde was separated from the vanillin by the method of Hunter and Hibbert.[17] A total of 400 g. of maple woodmeal was treated to yield 18 g. of syringaldehyde, m. p. 110–112°.

β-(4-Hydroxy-3,5-dimethoxyphenyl)-acrylic Acid (Sinapic Acid).[18]—A mixture of syringaldehyde (11.1 g.), malonic acid (14.5 g.), pyridine (33 cc.) and piperidine (0.7 cc.) was heated together at 80–85° for four hours, cooled, and dilute hydrochloric acid added (125 cc.). The product crystallized out immediately in fine, pale-yellow needles; m. p., 178–183°; yield was 8.2 g. (60%).

β-(4-Hydroxy-3,5-dimethoxyphenyl)-propionic Acid (Hydrosinapic Acid).—Sinapic acid (7.2 g.), ethanol (155 cc.), water (50 cc.) and Raney nickel catalyst (3 g.) were hydrogenated at an initial hydrogen pressure of 2200 lb./sq in. The charge was heated to 110–115° in fifteen minutes, then allowed to cool for one hour with agitation. Removal of the solvent left a grey-white solid which was recrystallized from water and then from ether–petroleum ether, m. p. 102–103°, yield 6.7 g. (92%). The product crystallized in white needles, readily soluble in ethanol and ether.

Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.4; H, 6.25; OCH_3, 27.5. Found: C, 58.4; H, 6.4; OCH_3, 27.6.

Ethyl Hydrosinapate.—Hydrosinapic acid (5.2 g.) was esterified by the method of Nomura and Hotta.[19] A clear, colorless oil was obtained, b. p. 178–179° (1 mm.), n^{25}_{D} 1.5250; yield was 5.4 g. (93%).

Anal. Calcd. for $C_{13}H_{18}O_5$: C, 61.4; H, 7.14; OR, 36.6. Found: C, 61.5; H, 7.2; OR, 36.6.

3-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanol, IV.—To sodium (0.96 g.), in small pieces, was added rapidly with stirring a solution of the ester (1.76 g.) in absolute ethanol (10.6 g.). The mixture was refluxed for four hours, 15 cc. of water added and the refluxing continued for one hour. The ethanol was then removed, the residual solution neutralized with 10% sulfuric acid and extracted with four 10-cc. portions of ether. The latter were combined, extracted with five 5-cc. portions of sodium bicarbonate solution, dried and evaporated to dryness. The residue was recrystallized from ether–petroleum ether, from which, on cooling, fine white needles separated, m. p. 75.5–76.5°; yield was 15–20%. No further change in melting point was found on repeated recrystallization.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.2; H, 7.61; OCH_3, 29.3. Found: C, 62.3; H, 7.8; OCH_3, 29.1.

II. **3-(4-Hydroxy-3-methoxyphenyl)-1-propanol, V.**—This was synthesized by the same method as used above, save that vanillin was used as a starting material. The alcohol was a colorless, slightly cloudy oil, b. p. 197° (15 mm.), n^{25}_{D} 1.5545.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.95; H, 7.7; OCH_3, 17.05. Found: C, 65.95; H, 7.95; OCH_3, 17.0.

The **bis-*p*-nitrobenzoate** was prepared by the method of Kawai and Sugiyama,[20] m. p. 119.5–120.5°, yield 30%.

III. **Acetate of 3-(4-Hydroxy-3,5-dimethoxyphenyl)-propane.**—A sample (0.112 g.) of 3-(4-hydroxy-3,5-dimethoxyphenyl)-propane[17] (b. p. 123–126° (0.1 mm.), n^{25}_{D} 1.5285), glacial acetic acid (0.1 cc.) and acetyl chloride (0.065 cc.) were refluxed for one hour and then poured over ice (2 cc.), whereupon a brown oil separated. The oil and aqueous mixture was extracted with ether, the ether solution dried over sodium sulfate and the solvent removed, leaving a white crystalline solid. Recrystallization from ethanol yielded 0.09 g. of a pure product, m. p. 87–88°.

IV. **4-Ethylcyclohexanol.**—Acetovanillone (5 g.), dioxane (60 cc.) and copper–chromium oxide catalyst (3 g.) were hydrogenated for 1.3 hr. at 273–278° at an initial hydrogen pressure of 2930 lb./sq. in. The residual oil was distilled to yield 2.7 g. of a clear colorless oil (b. p. 83–84° (10 mm.), n^{25}_{D} 1.4607) identified as the phenylurethan, m. p. 114–115°.[21]

Summary

1. A new method has been developed for the extraction of lignin from maple wood by a hydrogenation–hydrogenolysis procedure. A separation of this extracted lignin from carbohydrate material has been achieved, and the purified product has been designated as "hydrol" lignin.

2. Hydrogenation studies of hydrol lignin have indicated a marked similarity of behavior to other isolated lignins and to wood under the same conditions of hydrogenation.

3. From hydrol lignin three new propylphenol derivatives have been isolated, *viz.*, 3-(4-hydroxy-3,5-dimethoxyphenyl) -1- propanol, 3-(4-hydroxy-3-methoxyphenyl)-1-propanol and 3-(4-hydroxy-3,5-dimethoxyphenyl)-propane in yields of 8.8, 0.84 and 0.83%, respectively, based on the original Klason lignin. The structural significance of these derivatives to the lignin nucleus rests on the fact that they are the first propylphenol derivatives, isolated from wood or lignin by hydrogenation, in which a terminal —CH_2OH group is present in the side chain.

4. The synthesis and properties of a new compound, 3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol, are reported.

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[16] Creighton, McCarthy and Hibbert, THIS JOURNAL, **63**, 3049 (1941).

[17] Hunter and Hibbert, *ibid.*, **61**, 2190 (1939).

[18] Brand and Westerburg, *Arch. Pharm.*, **269**, 326 (1931).

[19] Nomura and Hotta, *Sci. Repts. Tohoku Imp. Univ.*, *1st ser.*, **17**, 693 (1928).

[20] Kawai and Sugiyama, *Ber.*, **72B**, 367 (1939).

[21] Adkins, Frank and Bloom, THIS JOURNAL, **63**, 549 (1941).