

in the latter only the corresponding guaiacyl components are present.

3. It is suggested that in hard woods the lignin building unit may be a mixed dimer, derived, for example, from one mole each of α -hydroxy-

propiovanillone and α -hydroxypropiosyringone.

4. A method for the synthesis of α -hydroxypropiosyringone (possibly a building unit of hard wood lignins) is described.

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Studies on Lignin and Related Compounds. XLII. The Isolation of a Bisulfite Soluble "Extracted Lignin"

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The fact that "extracted lignins," isolated for example by the use of acids and of organic solvents in presence of a catalyst (hydrochloric acid, etc.), are insoluble on heating with bisulfite solution points to their having undergone deep-seated changes in structure during their isolation, since "protolignin" as present in the wood is readily bisulfite soluble.

In a recent investigation² it was shown that an acetylated oak lignin isolated by the acetylation procedure developed by Suida and Titsch³ (use of a mixture of acetic anhydride, glacial acetic acid and a small amount of concentrated sulfuric acid) gave, on deacetylation, and for the first time, an extracted lignin completely soluble in hot bisulfite solution at 110°. As shown in another communication⁴ the oak lignin sulfonic acid thus formed, on heating with alkali, gave a mixture of vanillin and syringaldehyde in approximately equal amounts.

Under the same conditions of acetylation, the reactive sugar, fructose,⁵ and its dehydration product, hydroxymethylfurfural,⁶ yield crystalline acetates and no appreciable amounts of acetylated lignin-like materials.

These results thus serve to indicate that lignin is not formed during isolation from carbohydrate material as postulated by Hilpert.⁷

This method of lignin isolation, through acetylation, evidently gives a relatively unchanged,

and only slightly polymerized, form of "protolignin." This recently has been confirmed by the partial reconversion of an acetylated lignin, isolated in this manner, to simple lignin building units by treatment with hydrogen chloride and ethanol.⁸

More recently it has been shown that after deacetylation the recovered oak lignin can also be depolymerized in the same manner.⁹

Experimental

Extraction with Alkali.—The procedure followed was that used by Suida and Titsch.³ Alcohol-benzene and hot water extracted red oak meal (600 g.) was stirred for forty-eight hours at room temperature with 12 liters of 5% sodium hydroxide solution. The wood meal was then removed by filtration, washed with water at 60°, and the extraction repeated in an identical manner three times to ensure complete removal of soluble hemicelluloses. An atmosphere of nitrogen was maintained during the alkali treatments. The extracted wood meal was finally washed with distilled water, 1% acetic acid, water and methyl alcohol, in the order named, and dried (50° at 15 mm.). The pale yellow residual wood meal represented about 80% of the original wood.

Anal. Found: methoxyl, 6.8; lignin, 31.0; cellulose, 66.6; pentosan, 13.3.

Acetylation of the Extracted Wood Meal and Isolation of Acetylated Oak Lignin.—The dried, alkali-extracted oak wood meal (50 g.) was acetylated with a mixture of acetic anhydride (450 g.), glacial acetic acid (250 g.), and concentrated sulfuric acid (3.5 g.), the reaction being carried out in a bronze Werner-Pfleiderer mixer provided with a water cooling system. The temperature was allowed to rise gradually from 15 to 30°, as follows: two and one-half hours at 15°, one-half hour at 15–20°, two hours at 20–25°, and two hours at 25–30°. The highly viscous, dark brown solution was allowed to stand overnight in an atmosphere of nitrogen without stirring. It was then poured into 2 liters of a vigorously stirred 20% sodium acetate solution. The resulting solid, acetylated product

(8) Peniston, McCarthy and Hibbert, *THIS JOURNAL*, **61**, 530 (1939).

(9) Peniston, McCarthy and Hibbert, unpublished results.

(1) From the thesis of William H. Steeves submitted to McGill University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, May, 1936. (Previous paper, *THIS JOURNAL*, **59**, 1768 (1937).)

(2) Steeves, Ph.D. Thesis, McGill University, 1936; Hibbert and Steeves, *THIS JOURNAL*, **59**, 1768 (1937).

(3) Suida, Hermann and Titsch, *Monatsh.*, **54**, 700 (1929).

(4) Hawkins, Wright and Hibbert, *THIS JOURNAL*, **59**, 2447 (1937).

(5) Hudson and Brauns, *ibid.*, **37**, 1233 (1915).

(6) Blanksma, *Chem.-Zig.*, **2**, 1220 (1909).

(7) Hilpert and Hellwege, *Cellulosechemie*, **17**, 25 (1936).

was collected in a cotton sack and washed for forty-eight hours with running water and dried; yield approximately 80 g.

The dried acetylated wood meal was then mixed with a liter of chloroform, stirred for two hours, and allowed to stand for twelve hours at room temperature. The viscous solution was then filtered through finely powdered, anhydrous sodium sulfate, leaving an insoluble residue amounting to about 10 g. The clear chloroform solution was concentrated under reduced pressure and the residual solvent allowed to evaporate in air at room temperature. The resulting hard, glassy solid was crushed, pulverized, and extracted with acetone for five days in a Soxhlet apparatus. The acetone extract was concentrated to 200 cc., filtered, and poured into two liters of water. The acetylated lignin product was collected on a filter, washed with water, and dried; yield 27 g.

Purification of the Fully Acetylated Crude Oak Lignin.

—The dry, acetylated product (10 g.) was dissolved in acetone (50 cc.), filtered, and precipitated by pouring in a fine stream into anhydrous ether (500 cc.). A very light-colored precipitate was obtained which was collected on a filter, washed with ether, then with petroleum ether, and dried.

Anal. Found: OCH_3 , 11.0; COCH_3 , 35.4; Klason lignin, 75.2.

The acetylated oak lignin was fractionated further by precipitating from dioxane solution into anhydrous ether. After three such precipitations, the methoxyl content remained unchanged (11.1%). Apparently, either the non-ligneous materials present are chemically bound to the acetylated lignin or the acetylated carbohydrates have solubility characteristics very similar to those of the acetylated lignin. The purified product contained about 10% pentosan which could be completely removed by deacetylation of the material with dilute alkali.

Deacetylation and Isolation of Native Oak Lignin.

Thirty grams of crude acetylated oak lignin (OCH_3 , 11.1%) was dissolved in 1 liter of acetone, and 1 liter of 20% sodium hydroxide was slowly added with stirring. The mixture was allowed to stand for twenty-four hours at room temperature, the acetone removed under reduced pressure, and water added to maintain the volume at 2 liters. After two weeks' standing, the mixture was filtered to remove the alkali insoluble material (about 5 g.). After washing with water and drying, this was found to contain 4.1% methoxyl. The alkaline filtrate was acidified with 5% sulfuric acid and the resulting buff-colored precipitate collected, washed free from sulfate and dried; yield 15 g. The product was purified by dissolving in 50 cc. of dioxane and precipitating into anhydrous ether. The precipitate was collected in a centrifuge, washed with ether followed by petroleum ether, and dried. Found: OCH_3 , 20.8.

The alkali insoluble material apparently is composed of methoxyl-containing substances still chemically bound to polysaccharides. It was found to be insoluble in all common organic solvents.

The alkali soluble, deacetylated native oak lignin, after purification by precipitation from dioxane solution into ether, could be fractionated into a chloroform soluble and a chloroform insoluble fraction. Chloroform soluble

fraction: OCH_3 , 23.4. Chloroform insoluble fraction: OCH_3 , 20.6; C, 64.0; H, 6.2.

On methylation with diazomethane in dioxane solution both of the above fractions gave, after three treatments, products having the same constant methoxyl value of 26.6%.

Acetylation of the Native Oak Lignin.—Ten grams of the unfractionated native oak lignin (OCH_3 , 20.6%) was acetylated at room temperature with a mixture of 50 cc. of acetic anhydride and 100 cc. of pyridine. After standing for twelve hours, the solution was poured into a liter of ice water and the precipitate removed by filtration, washed, dried, and reprecipitated from acetone into ether. Found: OCH_3 , 18.2. Ten grams of the acetylated product was reacylated by dissolving in a mixture of acetic anhydride (100 g.), glacial acetic acid (50.0 g.) and concentrated sulfuric acid (0.7 g.). The mixture was held at 20–25° for twenty-four hours and then poured into a liter of 20% sodium acetate. The product was filtered, washed, dried, and purified by precipitation from acetone into ether followed by a reprecipitation from dioxane into ether. Found: C, 62.3; H, 5.9; OCH_3 , 16.8; COCH_3 , 22.9.

Solubility of Native Oak Lignin in Bisulfite Solution.—A sample of the chloroform soluble fraction of native oak lignin (OCH_3 , 23.4%) was heated in a sealed tube with a bisulfite solution containing 6.0% "total" and 1.4% "combined" sulfur dioxide. Solution was complete on heating for twelve hours at 110°.

Preparation of 5-Acetoxyethylfurfurylidene Diacetate.—The method of Blanksma⁶ was used. A higher yield (75%) was obtained by adding the sulfuric acid to the acetic anhydride and keeping the temperature below 0°. This mixture was added slowly to the hydroxymethylfurfural. The acetate was isolated in the manner outlined by Blanksma; m. p. 73°.

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Summary

1. A description is given of a simple method for the isolation of a lignin from oak wood which retains the reactive character of "protolignin," namely, solubility in hot bisulfite solution.

2. Under the same conditions of acetylation used in the isolation of the above "native oak lignin," fructose and hydroxymethylfurfural yield crystalline acetylated products with practically no formation of material resembling lignin. This is considered an argument against Hilpert's theory⁷ of lignin formation as a change arising during the extraction process from the action of the extractant on a sensitive carbohydrate.

3. It has been found possible to reacylate "native oak lignin" to give a product soluble in acetone or dioxane and containing 22.9% acetyl.