and their wave lengths measured. The results show a progressive shift of the bands toward lower frequencies as methyl and ethyl groups are added. There is also a shift due to the position of the methyl group in the xylenes.

With a cell 80 cm. in length, benzene shows an absorption band at 7134 Å.

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[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, No. 132]

THE CHEMISTRY OF LIGNIN. I. LIGNIN FROM CORN COBS

BY MAX PHILLIPS

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In spite of the extensive literature on lignin the chemistry of this product remains obscure.[1] Nothing definite is known about its constitution, although various formulas have been proposed, among which may be mentioned that of Cross and Bevan[2] for lignin ("lignone") from jute, and those of Green,[3] Klason[4] and Schrauth.[5] Most of these formulas have little definite chemical evidence in their support. That of Schrauth is admittedly speculative, although this investigator has endeavored, with some success, to correlate the conflicting data on lignin found scattered in the literature. The difficulty in deducing a constitutional formula for lignin is primarily due to the fact that as yet no method has been developed for the isolation of lignin in the pure state, nor is there any method known by which its purity may be gaged. The usual criteria of purity cannot, of course, be applied. The problem as to whether lignin is a homogeneous substance or a mixture of closely related chemical substances, therefore, remains unsolved. This has been further complicated by the fact that various investigators have obtained their lignin from different sources and by different methods. It has been obtained from (1) sulfite or soda and sulfate liquors resulting from the preparation of paper pulp from wood, (2) wood treated with 64–72% of sulfuric acid, (3) wood or similar lignin-containing plant material treated with saturated

[1] An extensive review of the literature is found in a recent monograph by Walter Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, **1926**. Hawley and Wise, in their monograph on "The Chemistry of Wood," The Chemical Catalog Co., New York, **1926**, give a critical review of our present knowledge of the chemistry of lignin, particularly that obtained from wood. An excellent résumé of the literature is given in a paper by Zhereboff [*Paper Trade J.*, **86**, No. 27, 47 (1925)].

[2] Cross and Bevan, "Cellulose," Longmans, Green and Co., London, 2nd ed., **1895**, p. 137; Vol. III, **1912**, p. 104.

[3] Green, *Z. Farben Textilchemie*, **3**, 97 (1904).

[4] Klason, *Ber.*, **56**, 300 (1923).

[5] Schrauth, *Z. angew. Chem.*, **36**, 149 (1923).

hydrochloric acid (so-called Willstätter lignin),[6] (4) lignin-containing substance digested with 10% of sodium hydroxide solution at 130° (Powell and Whittaker),[7] or with 1.5% of aqueous or 2% of alcoholic sodium hydroxide solution at room temperature (Beckmann, Liesche and Lehmann).[8]

The lignin fraction described in this paper was prepared by the alcoholic sodium hydroxide method of Beckmann, Liesche and Lehmann, as this treatment was considered least likely to bring about any drastic changes in its composition. It would hardly be expected that the lignin obtained by the hydrochloric or sulfuric acid methods, or from the sulfite or soda and sulfate liquors, would be identical with that which occurs in the plant substance. That these drastic treatments do bring about marked changes in the composition of the lignin has been pointed out by a number of investigators.[5,9] On the other hand, the lignin obtained from flax shoves by the method of Powell and Whittaker and from winter rye straw by that of Beckmann, Liesche and Lehmann appears to have been a fairly homogeneous substance. The results obtained in this investigation agree closely with those of Beckmann, Liesche and Lehmann and of Powell and Whittaker. Recognizing that in the absence of any criteria of purity all data must be interpreted with considerable caution, the results obtained, nevertheless, warrant the conclusion that the lignin fraction from corn cobs is a fairly homogeneous substance or a mixture of closely related isomers. The fact that the results on lignin from corn cobs agree fairly closely with those of Powell and Whittaker, who used a somewhat different method for obtaining the lignin from flax shoves, is certainly noteworthy. All the data obtained agree fairly closely with the formula $C_{40}H_{46}O_{16}$ for lignin from corn cobs. (The formula given by Beckmann, Liesche and Lehmann for lignin from winter rye straw is $C_{40}H_{44}O_{15}$, and that of Powell and Whittaker for lignin from flax shoves, $C_{45}H_{48}O_{16}$.) It contains three methoxyl groups and at least four hydroxyl groups. No carboxyl groups are present. The acidity is due to phenolic hydroxyl groups.

There has been a great deal of discussion[10] on the question of whether pentosans or furfural-yielding bodies may be considered as part of the structural arrangement of the lignin molecule or as an impurity associated with lignin. The lignin fraction obtained from corn cobs, even after prolonged distillation with 12% hydrochloric acid, gave no test for furfural

[6] Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

[7] (a) Powell and Whittaker, *J. Chem. Soc.*, **125**, 357 (1924); (b) **127**, 132 (1925).

[8] Beckmann, Liesche and Lehmann, *Z. angew. Chem.*, **34**, 285 (1921).

[9] Schwalbe, "Die Chemie der Cellulose," Gebrüder Borntraeger, Berlin, **1911**, p. 421. Hönig and Spitzer, *Monatsh.*, **39**, 1 (1918). Lange, *Z. physiol. Chem.* **14**, 15, 217 (1890). Rinman, *Papier Ztg.*, **35**, 221 (1910).

[10] Hägglund, *Ber.*, **56**, 1866 (1923). Heuser, *Cellulosechemie*, **4**, 77 (1923). Hägglund and Malm, *ibid.*, **4**, 73, 85 (1923).

in the distillate. The absence of pentosans or furfural-yielding bodies in the lignin fraction from corn cobs must then be assumed.

Experimental Part

Isolation of Lignin.—One thousand g. of corn cobs, cut in small pieces, was treated with 4 liters of 2% alcoholic sodium hydroxide solution (made by dissolving 80 g. of sodium hydroxide in 1600 cc. of water and making this up to a volume of 4 liters with 95% ethanol) and allowed to stand at room temperature for three days. The yellow alcoholic solution was decanted off, the cobs were pressed out, and the liquid was added to the solution obtained by decantation. This was filtered, neutralized with hydrochloric acid and concentrated by distilling on the water-bath under reduced pressure. Hydrochloric acid was added to the concentrated liquid, whereupon the lignin separated as a light yellow gum. This was filtered off, washed free from acid, and dried at 80° under reduced pressure. The yield was 3.49% of the weight of cobs taken. The lignin was a light yellow, amorphous powder. It reduced Fehling's solution. A portion of the lignin obtained as described above was redissolved in cold, dil. sodium hydroxide solution and then reprecipitated with hydrochloric acid. A carbon and hydrogen determination made on this fraction and upon the original batch showed no material change in composition. Two typical analyses are given below:

Anal. Subs., 0.2070, 0.2065; CO_2, 0.4637, 0.4638; H_2O, 0.1095, 0.1080. Found: C, 61.08, 61.24; H, 5.91, 5.85.

A molecular-weight determination made upon the substance by the boiling-point method, using glacial acetic acid as the solvent, gave the following results.

Mol. Wt. Subs., 0.3787, 0.3633, 0.3445; solvent, W, 24.1160, 24.2970, 24.3570; Δt, 0.065, 0.060, 0.060. Found: M, 753, 777, 735; mean, 755.

From a consideration of all the data, the formula $C_{40}H_{46}O_{16}$ has been assigned as the most probable one for this lignin fraction from corn cobs. The molecular weight and the percentage composition calculated for a compound of this formula are: M, 782.5; C, 61.36; H, 5.92; O, 32.72.

A methoxyl determination made on the lignin using the Zeisl and Fanto[11] method gave the following results.

Methoxyl. Subs., 0.3000, 0.3000, 0.3000, 0.3000; AgI, 0.2766, 0.2800, 0.2712, 0.2705. Calcd. for $C_{37}H_{37}O_{13}(OCH_3)_3$: CH_3O, 11.9. Found: 12.1, 12.3, 11.9, 11.9.

A 2g. sample of the lignin was distilled with 12% hydrochloric acid, following the A. O. A. C. method[12] for the determination of pentosans. The distillate gave a negative test for furfural with aniline acetate test paper and no precipitate with the phloroglucinol reagent.

Acetylation of Lignin.—The acetylation of the lignin was carried out, following the method of Powell and Whittaker.[7a] Ten g. of lignin was treated with 20 cc. of acetic anhydride, a few drops of concd. sulfuric acid were added, and the mixture was heated on the steam-bath for one hour. After cooling, it was poured into ice water, and the precipitate filtered off, and washed with cold water until the washings were free from acid. The product was dried over sulfuric acid in a vacuum desiccator. It was obtained as a brown, amorphous powder, insoluble in cold, dil. alkali, indicating that the

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[11] Houben, "Die Methoden der Organischen Chemie," Vol. III, Georg Thieme, Leipzig, **1923**, p. 144.

[12] "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Association of Official Agricultural Chemists, Washington, D. C., **1925**.

acidity of the lignin is due to phenolic hydroxyl groups. The acetyl determination was made following the method of Perkin.[13]

Acetyl. Subs., 1.0000, 1.0000, required 8.06 cc., 8.08 cc. of 0.5N KOH. Subs., 0.3000, 0.3000; AgI, 0.2377, 0.2370. Calcd. for $C_{37}H_{33}O_{13}(CO.CH_3)_4(OCH_3)_3$: CH_3CO, 18.1; CH_3O, 9.8. Found: $CH_3.CO$, 17.3, 17.4; CH_3O, 10.4.

Chlorination of Lignin.—The directions given by Powell and Whittaker[7a] for the chlorination of lignin were followed. Ten g. of lignin was suspended in 80 cc. of carbon tetrachloride, and a slow stream of dry chlorine gas was passed in until no more hydrogen chloride was given off from the reaction mixture. The product was filtered off and dissolved in concentrated acetone solution (two volumes of acetone and one volume of water). The chlorolignin was precipitated by pouring the solution into dil. hydrochloric acid. It was filtered off, washed free from acid and dried over sulfuric acid in a vacuum desiccator.

Anal. Subs., 0.3072, 0.2214, 0.2235; AgCl, 0.3985, 0.2880, 0.2903. Calcd. for $C_{40}H_{36}O_{16}Cl_{10}$: Cl, 31.45. Found: Cl, 32.09, 32.17, 32.13.

Summary

The results of a chemical study of a lignin fraction from corn cobs indicate that the lignin is a fairly homogeneous substance or a mixture of closely related isomers. All the results agree closely with the formula $C_{40}H_{46}O_{16}$ for lignin from this source. The presence of four hydroxyl groups capable of being acetylated and of three methoxyl groups has been shown.

The results obtained on lignin from corn cobs are in close agreement with those obtained by Beckmann, Liesche and Lehmann on lignin from winter rye straw and with the results of Powell and Whittaker on lignin from flax shoves.

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ALICYCLIC DERIVATIVES OF RESORCINOL

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The search for a superior substance which will exert a bactericidal activity against the organisms of the urinary tract has led recently to the discovery of n-hexyl-resorcinol by Dohme, Cox and Miller.[2] Although this substance has proved disappointing in its clinical results as compared with expectations drawn from preliminary work,[3] nevertheless it presents an interesting field of bactericidal compounds.

The original investigators prepared various types of alkyl resorcinols,

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[13] Perkin, *Proc. Chem. Soc.*, **20**, 171 (1904).

[1] This communication is an abstract of a portion of a thesis submitted by Ralph H. Talbot in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Dohme, Cox and Miller, THIS JOURNAL, **48**, 1688 (1926).

[3] Leonard, *J. Am. Med. Assoc.*, **83**, 2005 (1924).