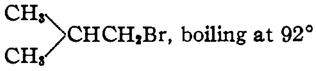
72–92°. The monobromides were then hydrolyzed three times, each time with a fresh quantity of water, for two hours on a steam-bath. The combined water layers were salted out by means of potassium carbonate, resulting in a layer of pure tertiary butyl alcohol of b. p. 83°. The unhydrolyzed product was a pure monobromide



$(CH_3)_2CHCH_2Br$, boiling at 92°

From the butene obtained by dehydration of 37 g. of isobutyl alcohol, 60.5 g. of monobromides was formed, resulting after hydrolysis in 15 g. of unhydrolyzable primary monobromide [Br determination: calcd. for C_4H_9Br: Br, 58.39. Found: Br, 58.01] and 22.1 g. of tertiary butyl alcohol.

The authors acknowledge the grant of the Fellowship to one of us (P. Yoder) by the Universal Oil Products Company, Chicago.

Summary

1. The butene mixtures obtained by the catalytic dehydration of butyl alcohols by phosphoric acid catalysts were analyzed by low temperature distillation in a Podbielniak column.

2. It was found that both 1- and 2-butenes were obtained by the dehydration of normal and secondary butyl alcohols, but that pure isobutene resulted from the dehydration of isobutyl alcohol.

3. The results of King and Mitchell were found to be incorrect due to the inaccuracy of the dibromide method of identifying the butenes.

EVANSTON, ILL. RECEIVED SEPTEMBER 13, 1934

[244TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Chemistry of Lignin. IX. Lignin from Barley Straw

BY MAX PHILLIPS AND M. J. GOSS

Although the literature on lignin is now rather extensive, comparatively few papers have been published dealing with the chemistry of lignin from annual plants. Most investigators have studied the chemistry of lignin from wood, particularly spruce wood. The present paper is one of a series to be published from this Bureau dealing with the chemistry of lignin from cereal straws.

Among the older investigations may be mentioned those of Cross and Bevan[1] on the lignin from jute. Beckmann, Liesche and Lehmann[2] reported on a lignin fraction isolated from winter rye straw. Powell and Whittaker[3] isolated the lignin from flax shoves by the alkali method, and found that its composition agreed with the formula $C_{45}H_{48}O_{16}$. Several papers[4] dealing with the chemistry of lignin from corncobs and from oat hulls have been published from this Bureau.

The two lignin fractions described in this paper were isolated from barley straw by extracting it successively and exhaustively, first with an alcoholic sodium hydroxide solution at room temperature, and then by refluxing with 4% aqueous sodium hydroxide solution. The composition of the first lignin fraction agreed with the formula $C_{40}H_{48}O_{15}$. On the basis of a compound having a molecular weight represented by this formula, four methoxyl groups and five hydroxyl groups definitely were shown to be present. Three of the five hydroxyl groups could be methylated with diazomethane, thus indicating that these are more acidic, possibly phenolic or enolic in character. The other two hydroxyl groups could be methylated only after repeated treatment with dimethyl sulfate and 40% potassium hydroxide solution.

The analytical results on the residual lignin fraction isolated by means of aqueous sodium hydroxide solution are more in agreement with that represented by the formula $C_{40}H_{42}O_{16}$. In this lignin fraction four hydroxyl and four methoxyl groups were shown to be present.

By means of a method previously described,[4d] the alkoxyl groups in both lignin fractions were shown to be methoxyls. The presence of other alkoxyl groups, such as, for example, ethoxyl groups, was definitely excluded.

When either of the two lignin fractions was distilled with 12% hydrochloric acid, a small quantity of formaldehyde was obtained in the distillate. Freudenberg and Harder[5] distilled

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(1) Cross and Bevan, "Cellulose," Longmans, Green and Co., London, 2d ed., 1895, p. 137; Vol. III, 1912, p. 104.

(2) Beckmann, Liesche and Lehmann, *Z. angew. Chem.*, **34**, 285 (1921).

(3) Powell and Whittaker, *J. Chem. Soc.*, **125**, 357 (1924).

(4) (a) Phillips, THIS JOURNAL, **49**, 2037 (1927); (b) **50**, 1986 (1928); (c) **51**, 2420 (1929); (d) **52**, 793 (1930); (e) **53**, 768 (1931); (f) *Science*, **73**, 368 (1931); (g) Phillips and Goss, THIS JOURNAL, **54**, 1518 (1932); (h) **54**, 3374 (1932); (i) *Ind. Eng. Chem.*, **24**, 1436 (1932); (j) THIS JOURNAL, **55**, 3466 (1933).

(5) Freudenberg and Harder, *Ber.*, **60**, 581 (1927).

lignin from wood with 12% hydrochloric acid and identified formaldehyde as one of the hydrolytic products. In a subsequent paper, Freudenberg, Harder and Markert[6] advanced the hypothesis that the formaldehyde arises from a methylene dioxide group (—O—CH$_2$—O—) present in the lignin molecule, as compounds having the methylene dioxide group are known to yield formaldehyde when they are distilled with hydrochloric acid. However, this interpretation of the reaction involved has been questioned by some investigators.[7] The isolation of a small quantity of a rather non-specific fission product, such as formaldehyde, from a highly polymerized substance, such as lignin, cannot be accepted as definite proof of the presence of a methylene dioxide group in lignin. In the absence of other evidence, the presence of this group in lignin must be regarded with some uncertainty.

Experimental

One kilogram of ground barley straw (909 g. of moisture-free material) which had been extracted with 1:2 alcohol–benzene solution was treated with 10 liters of a 2% alcoholic sodium hydroxide solution (made by dissolving 200 g. of sodium hydroxide in 4 liters of water and adding sufficient 95% ethanol to make a volume of 10 liters) and allowed to stand at room temperature for twenty-four hours. The reaction mixture was agitated manually from time to time. At the end of the twenty-four-hour period, the liquid was poured off and neutralized with hydrochloric acid, and the alcohol was distilled off under reduced pressure. The aqueous residue was acidified with hydrochloric acid, and the precipitated lignin was filtered off. This process of extraction with alcoholic sodium hydroxide solution was repeated until no more lignin was extracted. Five such extractions were required, and 4 liters of alcoholic sodium hydroxide solution were used for each extraction. The lignin fractions thus obtained were combined and washed with distilled water until the wash water no longer gave a test for the chlorine ion. The crude lignin thus obtained, after being dried in a desiccator over sulfuric acid, amounted to 62 g. (6.2% yield calculated on the weight of straw taken). This was treated with one liter of an acetone–alcohol solution (2 volumes of acetone to 1 volume of 95% ethanol), the lignin solution was filtered, and the alcohol and acetone were removed by distillation under reduced pressure. The lignin thus obtained was washed with water and dried at 56° over sulfuric acid in the vacuum Abderhalden drier. The yield of this purified lignin amounted to 47 g. (4.7% calculated on the weight of straw taken or 5.1% yield calculated on the weight of dry straw). The lignin was obtained as a light tan amorphous powder. A carbon and hydrogen determination made upon the lignin gave the following results: *Anal.* Found: C, 62.50, 62.62; H, 6.08, 6.15.

The lignin when boiled with 12% hydrochloric acid solution gave no coloration with aniline acetate paper, showing that the lignin preparation was free from furfural-yielding substances. It was also free from carbohydrates in general.

A methoxyl determination made according to the Kirpal and Bühn modification of the Zeisel method gave the following results: *Anal.* Found: OCH$_3$, 16.38, 16.34; C:OCH$_3$ = 9.88:1.

This ratio of percentage of total carbon to the percentage of carbon present in the form of methoxyl indicates the number of carbon atoms present in each unit containing one methoxyl group. From the data given above it is evident that for every unit of ten carbons there is one methoxyl group. This is in agreement with Freudenberg's[8] conception of the structure of spruce lignin. He postulates that the building unit of lignin consists of a benzene nucleus which contains three substituents, one of which is a methoxyl group and the other two, an hydroxyl group and a three-carbon side chain, respectively. An aromatic compound having such substituents, namely, 1-*n*-propyl-3-methoxy-4-hydroxybenzene, was obtained as a degradation product of corncob lignin.[4f,4g]

In order to prove definitely the nature of the alkoxyl group in this lignin fraction, a sample of the material was distilled with hydriodic acid, as in the Zeisel method, and the alkyl iodide absorbed in dimethylaniline, as recommended by Willstätter and Utzinger.[9] The crystalline trimethylphenylammonium iodide was identified by its melting point and mixed melting point.

The above-mentioned results prove fairly conclusively that the methoxyl group is present in this lignin fraction. In order to prove definitely that no alkoxyl groups other than methoxyl are present in this lignin fraction, the method described by one of us in a previous communication[4d] was used. This method consists essentially in making a methoxyl determination by the Zeisel method (where the alkyl iodide is absorbed in an alcoholic silver nitrate solution) and by the method of Kirpal and Bühn (where the alkyl iodide is absorbed in pyridine). If the percentages of alkoxyl (calculated as methoxyl) found by both methods agree within the experimental error of analytical methods employed, it is reasonably certain that only the methoxyl group is present. *Anal.* Found: (Zeisel method) OCH$_3$, 16.38, 16.56; (Kirpal and Bühn method), 16.38, 16.34.

The foregoing data agree with a compound having the empirical formula C$_{40}$H$_{48}$O$_{15}$, 768; C, 62.50, H, 6.25. Assuming the presence of four methoxyl groups in a compound of such molecular weight, the calculated percentage is 16.06. Found: 16.36.

Acetylation.—The lignin was acetylated by the method described in a previous investigation.[4a] The acetyl derivative was dried at 56° in the Abderhalden drier over phosphorus pentoxide.

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(6) Freudenberg, Harder and Markert, *Ber.*, **61**, 1760 (1928).

(7) Fuchs and Horn, *ibid.*, **62**, 2647 (1929); Phillips and Goss, THIS JOURNAL, **54**, 3374 (1932).

(8) Freudenberg, *Sitzb., Heidelber. Akad. Wiss., Math. Naturw. Klasse*, Abhandlung 19 (1928); Freudenberg, Zocher and Dürr, *Ber.*, **62**, 1814 (1929); Freudenberg, Sohns, Dürr and Niemann, *Cellulosechem.*, **12**, 263 (1931); Freudenberg, *Papier-Fabr.*, **30**, 189 (1932); *J. Chem. Educ.*, **9**, 1171 (1932); Freudenberg and Sohns, *Ber.*, **66**, 262 (1933).

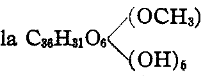
(9) Willstätter and Utzinger, *Ann.*, **382**, 148 (1911).

Anal.[10] Calcd. for $C_{36}H_{31}O_{11}(OCH_3)_4(COCH_3)_5$: CH_3CO, 21.9. Found: CH_3CO, 20.74, 20.70.

A methoxyl determination made on the acetylated lignin gave the following results.

Anal. Calcd. for $C_{36}H_{31}O_{11}(OCH_3)_4(COCH_3)_5$: OCH_3, 12.67. Found: OCH_3, 13.17, 13.21.

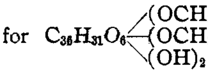
This lignin fraction may therefore be represented by the dissected formula



$$C_{36}H_{31}O_6\begin{cases}(OCH_3)_4\\(OH)_5\end{cases}$$

Methylation with Diazomethane.—Four grams of lignin was added to an ether solution containing approximately 2 grams of diazomethane, and the reaction mixture was allowed to remain at room temperature for three days, with occasional shaking. The methylated lignin was filtered off and air dried, and finally dried in the Abderhalden drier at 56° over phosphorus pentoxide; yield, 4.0 g. Light-tan amorphous powder.

Anal. Calcd. for



$$C_{36}H_{31}O_6\begin{cases}(OCH_3)_4\\(OCH_3)_3\\(OH)_2\end{cases}$$

: OCH_3, 26.79. Found: OCH_3, 26.49, 26.34.

It would appear from these data that three of the five hydroxyls in this lignin fraction are quite different from the other two, that is, they are more acidic, possibly phenolic or enolic in character. The other two hydroxyl groups are in all probability alcoholic in nature.

Methylation with Dimethyl Sulfate.—Five grams of lignin was dissolved in a solution containing 10 g. of sodium hydroxide in 100 cc. of water, and 24 cc. of dimethyl sulfate was added drop by drop, and the reaction mixture was stirred mechanically. After all the dimethyl sulfate had been added, the reaction mixture was heated on the steam-bath for thirty minutes. The methylated product which separated out was filtered off and washed with water until free of alkali. A methoxyl determination on the material which had been dried over phosphorus pentoxide gave these results: *Anal.* Found: OCH_3, 29.38, 29.06.

The product was remethylated with dimethyl sulfate and 40% sodium hydroxide solution under conditions similar to those described above. The methylation was repeated four times until finally a product was obtained in which all the hydroxyl groups originally present in the lignin were methylated.

Anal. Calcd. for $C_{36}H_{31}O_6(OCH_3)_4(OCH_3)_5$: OCH_3, 33.29. Found: OCH_3, 33.66, 33.29.

Distillation with 12% Hydrochloric Acid.—Two grams of lignin was distilled with 12% hydrochloric acid according to the same procedure used in the determination of pentosans by the A. O. A. C. method. The distillate gave a positive reaction for aldehydes with Schiff's reagent. However, when a saturated solution of barbituric acid in 12% hydrochloric acid was added to the distillate, as suggested by Freudenberg and Harder,[5] and the solution allowed to remain in the refrigerator for three days, no precipitate was obtained. The distillate from a second experiment, carried out similarly to the one above, was neutralized with sodium carbonate, then cohobated and the first 50 cc. of distillate was retained. This was treated with an alcoholic solution of dimethylcyclohexanedione, as suggested by Weinberger.[11] A crystalline precipitate was obtained, which was recrystallized from dilute alcohol, m. p. 191–192°, mixed m. p. 191–192°. The presence of formaldehyde was therefore definitely established.

Chlorination of Lignin.—The chlorination of this lignin fraction was carried out as described in a previous communication.[4a] A yellowish-brown product was obtained.

Anal. Calcd. for $C_{36}H_{24}O_{11}Cl_{12}(OCH_3)_4$: Cl, 36.01; OCH_3, 10.4. Found: Cl, 36.72, 36.68; OCH_3, 8.82, 8.87.

It will be observed that there was a loss of methoxyl brought about by the chlorination process. A similar observation was made by Friedrich and Pelikan[12] in connection with the bromination of spruce wood lignin.

Isolation of the Residual Lignin.—The residual straw (933 g.), which had been extracted exhaustively with alcoholic sodium hydroxide solution, was treated with a sufficient 4% aqueous sodium hydroxide solution to cover it completely and heated under a reflux condenser at 100° for four hours. The reaction mixture was filtered and the lignin precipitated by the addition of concentrated hydrochloric acid to the filtrate. The residual straw was again treated with a 4% sodium hydroxide solution, and the operation was repeated until the alkaline extract when acidulated with hydrochloric acid no longer gave a precipitate of lignin. The cellulosic residue obtained amounted to 544 g. It still contained 4.8% of lignin as determined by the fuming hydrochloric acid method. The lignin obtained from the several extractions was combined and purified by dissolving it in 500 cc. of 2% aqueous sodium hydroxide solution and adding to it one liter of 95% ethanol. The precipitate was filtered off, the filtrate was acidified with hydrochloric acid, and the alcohol was removed by distillation. The lignin obtained was washed with water until the wash water gave no test for chloride with silver nitrate solution and dried at 56° over sulfuric acid *in vacuo;* yield, 10 g. An amorphous brown substance was obtained.

Anal. Found: C, 61.93, 61.82; H, 5.36, 5.36.

Methoxyl.—The alkoxyl groups present in this lignin fraction were definitely shown to be methoxyls. The method previously referred to for the identification of the alkoxyl groups was used.

Anal. Found: OCH_3 (Kirpal and Bühn method), 15.61, 15.61; OCH_3 (Zeisel method), 15.52. $C:OCH_3$ = 10.2:1.

From the analytical data given above the formula $C_{40}H_{42}O_{16}$ or $C_{36}H_{30}O_{12}(OCH_3)_4$ was assigned for this lignin fraction. The percentage composition of a compound of this formula is: C, 61.68; H, 5.43, OCH_3, 15.92.

Acetyl Derivative.—This was prepared by the method previously referred to. The percentage of acetyl was determined by the same method used for the analysis of the acetyl derivative of the first lignin fraction.

Anal. Calcd. for $C_{36}H_{26}O_8(OCH_3)_4(OCOCH_3)_4$: CH_3CO, 18.18. Found: CH_3CO, 17.9, 18.0.

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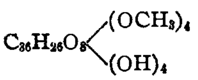
[10] The percentage of acetyl was determined by the improved method described by one of us, *Ind. Eng. Chem., Anal. Ed.*, **6**, 321 (1934).

[11] Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).

[12] Friedrich and Pelikan, *Biochem. Z.*, **239**, 461 (1931).

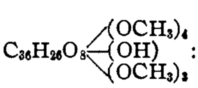
The dissected formula for this lignin fraction is therefore



$C_{36}H_{26}O_8{<}\begin{matrix}(OCH_3)_4\\(OH)_4\end{matrix}$

Methylation with Diazomethane.—One-half gram of lignin was added to an ether solution containing 0.6 g. of diazomethane and allowed to remain at room temperature for three days. The methylated lignin was filtered off, air-dried and finally dried under reduced pressure at 56°.

Anal. Calcd. for

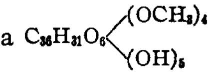


$C_{36}H_{26}O_8\begin{matrix}(OCH_3)_4\\(OH)\\(OCH_3)_3\end{matrix}$: OCH_3, 26.46. Found: OCH_3, 26.59, 26.64.

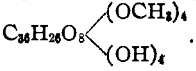
Distillation with 12% Hydrochloric Acid.—The distillation of the lignin with the subsequent cohobation of the distillate was carried out as previously described. Formaldehyde was identified in the distillate by the dimethylcyclohexanedione method of Weinberger.

Summary

1. Two lignin fractions were isolated from barley straw by extracting it successively and exhaustively, first with a 2% alcoholic sodium hydroxide solution at room temperature and then by refluxing with 4% aqueous sodium hydroxide solution. All the data agree with the dissected formula



$C_{36}H_{31}O_6{<}\begin{matrix}(OCH_3)_4\\(OH)_5\end{matrix}$ for the first lignin fraction. Of the five hydroxyl groups only three could be methylated with diazomethane, thus indicating that in all probability these three hydroxyl groups are more acidic, possibly phenolic, or enolic in character. The other two hydroxyl groups could be methylated only after repeated treatment with dimethyl sulfate and 40% potassium hydroxide solution. The results obtained in connection with the second lignin fraction agree with the dissected formula



$C_{36}H_{26}O_8{<}\begin{matrix}(OCH_3)_4\\(OH)_4\end{matrix}$. Three of the hydroxyl groups could be methylated with diazomethane.

2. The alkoxyl groups present in both lignin fractions were proved definitely to be methoxyls.

3. Both lignin fractions when distilled with 12% hydrochloric acid afforded some formaldehyde. The identification of formaldehyde in the distillate is discussed from the standpoint of the probable presence of a methylene dioxide group in the lignin molecule.

WASHINGTON, D. C.

RECEIVED SEPTEMBER 15, 1934

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Synthesis of 1-Methylcyclopropanecarbonitrile from Diazomethane and Alpha-Methylacrylonitrile[1]

BY DANIEL GOTKIS AND JOHN B. CLOKE

As a part of a program on the study of certain cyclic ketimines and related compounds, it has been necessary to synthesize suitable alkyl and aryl substituted cyclopropanecarbonitriles. A previous paper by Knowles and Cloke[2] has described the preparation of 1-phenylcyclopropanecarbonitrile, $\underline{CH_2CH_2C}(C_6H_5)CN$ (I), and a related compound, which can be obtained quite readily by the condensation of phenylacetonitrile with a suitable alkylene halide by the use of sodium amide.

The synthesis of the 1-methylcyclopropanecarbonitrile, $\underline{CH_2CH_2C}(CH_3)CN$ (II), on the other hand, has presented greater difficulty. Thus, several attempts to prepare the compound (II) by the condensation of ethylene halides with propionitrile in accordance with the method for the synthesis of (I) gave no definite results. Likewise, attempts to obtain (II) by the direct methylation of cyclopropyl cyanide, $\underline{CH_2CH_2CH}CN$ (III), have also been of no avail as yet. In addition, considerable effort has been expended in endeavors to prepare the compound (II) from α-methyl-γ-halogenobutyronitriles by the same procedure that leads to the formation of (III), but to date the synthesis of the necessary amount of the pure butyronitriles has been the source of trouble. When this work is completed, it will be discussed elsewhere.

The final successful synthesis of (II) was suggested by the well-known tendency of diazomethane to add to various ethylenic compounds to give pyrazolines, which generally decompose, when suitably heated, to give cyclopropane de-

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[1] This paper is an abstract of a part of a thesis presented by Daniel Gotkis to the Rensselaer Polytechnic Institute in June, 1934, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).