dinitrophenylhydrazones was determined by a modified Dumas procedure using an apparatus of semi-micro proportions. The suggestions of Pregl for micro analysis by the Dumas method were followed closely. Resort was not made, however, to his empirical method for correcting the volume of nitrogen obtained as it is probably not applicable to the larger type of apparatus used by us. It was found that our procedure could be closely standardized as to the time and the amount of carbon dioxide used in an analysis and that by a blank on the apparatus it was possible to determine a correction factor for the small amount of residual gas in the carbon dioxide. This was subsequently applied to all of the analyses.

Summary

The 2,4-dinitrophenylhydrazones of ten normal alkyl and three isoalkyl esters of levulinic acid have been prepared and their melting points determined. Experimental data are offered in explanation of conflicting reports in the literature on the melting point of the corresponding levulinic acid derivative.

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Chemistry of Lignin. VIII. The Oxidation of Alkali Lignin

BY MAX PHILLIPS AND M. J. GOSS

Oxidation, probably the most common method used for the degradation of an organic compound for the purpose of ascertaining its structure, has thus far afforded no interesting results on the structure of lignin. The products of oxidation have been, with one or two exceptions, simple organic acids. A review of the literature on this subject up to 1926 is given by Fuchs.[1] Some of the more recent articles are those of Rassow and Zickmann,[2] Schaarschmidt, Nowak and Zetzsche,[3] and Horn.[4] Fischer, Schrader and Freiedrich[5] subjected lignin to what these investigators designate as "pressure oxidation," and obtained, in addition to some simple aliphatic acids, small quantities of aromatic acids. However, in view of the rather drastic method of oxidation employed by Fischer and co-workers, it seems doubtful whether their results can be interpreted as definitely indicating that an aromatic nucleus is present in the lignin molecule.

The present paper concerns itself with the oxidation of alkali lignin isolated from corn cobs. It has been found that this lignin when subjected to oxidation affords chiefly oxalic acid. However, when the lignin is first

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[1] Walter Fuchs, "Die Chemie des Lignins," Julius Springer, Berlin, 1926.

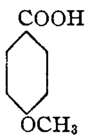
[2] Rassow and Zickmann, *J. prakt. Chem.*, [2] **123**, 216 (1929).

[3] Schaarschmidt, Nowak and Zetzsche, *Z. angew. Chem.*, **42**, 618 (1929).

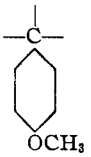
[4] Horn. *Brennstoffchem.*, **10**, 364 (1929).

[5] Fischer, Schrader and Friedrich, *Gesamm. Abhand. Kenn. Kohle*, **6**, 1 (1923).

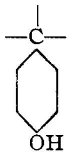
methylated and then subjected to oxidation with either dilute nitric acid or ozone, anisic acid (I) is obtained. The question then presented itself as to whether the methoxyl group in the anisic acid obtained in the oxidation of methylated lignin is one which was originally in the lignin molecule or had been introduced by the methylation process; in other words, whether the nucleus (II) or (III) is present in lignin. This question was definitely answered in favor of (III), for when lignin is ethylated and then oxidized, *p*-ethoxybenzoic acid (IV) is the product isolated.



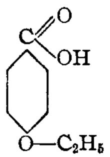
I
Anisic acid



II



III



IV
p-Ethoxybenzoic acid

When methylated lignin is treated with 5 *N* nitric acid there is obtained, in addition to the anisic acid, an orange-colored amorphous product containing 5.25% nitrogen, of which 29.1% is in the form of the nitro group. The ease of nitration of the methylated lignin even with the comparatively dilute nitric acid, together with the fact that the C:H ratio of the nitration product of methylated lignin is nearly 1:1, indicates the presence of an aromatic nucleus in the alkali lignin from corn cobs. The nitration product of methylated lignin when oxidized with hydrogen peroxide or with potassium permanganate in acetone solution, yields small quantities of anisic acid.

Experimental

The alkali lignin used in the experiments recorded in this paper was isolated from corn cobs by the method described in a previous communication.[6]

Methylation of the Lignin.—Twenty-five grams of lignin was added to 500 g. of 10% sodium hydroxide solution, and the product was heated to 60° under a reflux condenser. The resulting solution was stirred mechanically while 160 g. of dimethyl sulfate was added slowly from a dropping funnel. After all the dimethyl sulfate had been added, the stirring and heating were continued for one-half hour. The reaction product was removed by filtration and the methylation process repeated. After the second methylation, the reaction product was filtered and washed with distilled water until free from sulfates. The product was dried over sulfuric acid in the Abderhalden drier, *in vacuo*, at 56°, yield, 25.0 g.

Anal. Found: OCH_3, 27.20, 27.13.

Oxidation of Methylated Lignin with Nitric Acid.—A mixture of 25 g. of methylated lignin and 250 cc. of 5 *N* nitric acid was heated on the steam-bath for one-half hour, whereupon a copious evolution of oxides of nitrogen took place. The product was cooled, filtered, and the orange, amorphous residue (A) washed until free from acid and dried at 56° in an Abderhalden drier over sulfuric acid; yield, 16 g.

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(6) Phillips, THIS JOURNAL, **51**, 2421 (1929).

Anal. of (A) Found: C, 53.69, 53.62, 53.61; H, 4.64, 4.52, 4.50; N,[7] 5.23, 5.27; NO_2,[8] 5.13, 4.96; OCH_3, 17.45, 17.43; NO_3,[9] 10.29.

The acid filtrate from (A) was repeatedly extracted with ether, the ether solution dried over anhydrous sodium sulfate, and the ether removed. The residue, on standing, deposited some crystals, which were recrystallized from hot water. Needle-like crystals were obtained, m. p. 184°, mixed with pure anisic acid, m. p. 184° (corr.). The optical properties of the crystals were also found to be identical with those of anisic acid.[10]

The acid filtrate from (A), which had been extracted with ether, was evaporated to dryness on the steam-bath and the crystalline residue redissolved in hot water, decolorized with Norit, and concentrated. On standing, crystals separated. The *p*-toluide of this product was prepared according to the method of Mulliken,[11] m. p. 275°, mixed with pure oxal-*p*-toluide, m. p. 275° (corr.). The crystalline product obtained was therefore oxalic acid.

Ethylation of Lignin and Subsequent Oxidation of the Ethylated Product with Nitric Acid.—Ten grams of lignin was dissolved in 200 g. of 10% sodium hydroxide solution, and the solution was heated to 60° under a reflux condenser. To this 80 g. of diethyl sulfate was added, drop by drop, while the reaction mixture was stirred mechanically. The stirring was continued for two hours after all the diethyl sulfate had been added. The reaction product was filtered, washed with water until free from sulfates, and then air-dried; yield, 11 g. Its alkoxyl content was determined upon a portion dried at 56° *in vacuo* over phosphorus pentoxide in the Abderhalden drier. (The alkyl iodides were absorbed in an alcoholic solution of silver nitrate.)

Anal. Calcd. as OCH_3: 25.69, 25.50. Methoxyl content of original lignin: 13.85, 13.88. Therefore, OC_2H_5, 17.02.

Oxidation of Ethylated Lignin.—Ten grams of the ethylated lignin was oxidized with 5 *N* nitric acid by the method previously described for oxidation of methylated lignin. The insoluble amorphous product (B) was filtered off, washed free from acid, and dried at 56° in an Abderhalden drier over sulfuric acid.

Anal. of (B) Found: C, 55.10, 55.34; H, 4.81, 4.97; N, 5.37, 5.23; NO_2, 5.07, 5.21; OCH_3,[12] 16.20, 16.27; NO_3, 9.85.

The filtrate from (B) was exhaustively extracted with ether, the ether removed and the crystalline residue when recrystallized from dilute ethanol yielded colorless needles; m. p. 201°, mixed m. p. with pure *p*-ethoxybenzoic acid, 201° (corr.). The optical properties of the crystals were also found to be identical with those of *p*-ethoxybenzoic acid.

Oxidation of the Nitration Product of Methylated Lignin with Hydrogen Peroxide.—A solution of 3 g. of (A) in 150 cc. of dilute ammonia was heated to boiling on the water-bath, and 50 cc. of 30% hydrogen peroxide ("Superoxol") was added in small portions. Considerable foaming took place. After filtration the filtrate was acidified with dilute sulfuric acid. An amorphous precipitate (C) was obtained (1.0 g.), which consisted largely of unoxidized starting material.

The acid filtrate from (C) was distilled in a current of steam but the distillate

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[7] The A. O. A. C. total nitrogen method was used. Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 1930, p. 21. Association of Official Agricultural Chemists, Washington, D. C.

[8] This was determined by the method of English, *Ind. Eng. Chem.*, **12**, 994 (1920).

[9] Silberrad, Phillips and Merriman, *Z. angew. Chem.*, **19**, 1601 (1906).

[10] All identifications of compounds by optical methods were made by Mr. G. L. Keenan of the Microanalytical Laboratory of the Food and Drug Administration of this Department.

[11] S. P. Mulliken, "A Method for the Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1905, Vol. I, p. 84.

[12] The total silver iodide obtained was calculated as $—OCH_3$.

afforded nothing of interest. The ether extract of the residual solution yielded some anisic acid which was identified by the melting point, mixed melting point, and optical properties.

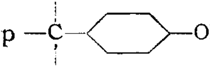
Oxidation of Nitration Product of Methylated Lignin with Potassium Permanganate.—Three grams of the material was dissolved in 200 cc. of acetone (freed from reducing substances), and 8 g. of powdered potassium permanganate was added in small portions, while the reaction mixture was mechanically stirred. When all the potassium permanganate had been reduced, the reaction mixture was filtered and the manganese dioxide washed with acetone. The acetone filtrate was distilled on the steam-bath, and only a small amount of gummy material was obtained.

The manganese dioxide obtained in the oxidation above was extracted with boiling absolute alcohol and the alcoholic extract distilled on the steam-bath. A gummy residue was obtained, which on standing deposited some crystals which were recrystallized from hot water and were identified as anisic acid by the melting point, mixed melting point, and optical properties.

Ozonation of Methylated Lignin.—A solution of 10 g. of the material in 100 cc. of glacial acetic acid was treated for twenty-five hours with a current of dry ozonized oxygen (containing approximately 6% ozone by volume). At the end of this period the solution changed from dark brown to yellow. The small quantity of amorphous material that separated was removed, and the filtrate was distilled under reduced pressure at a temperature not exceeding 30°. The residual sirup was poured into 200 cc. of cold water and a small quantity of an amorphous lemon-yellow precipitate (D) was obtained. Nothing definite could be isolated from this precipitate. The filtrate from (D) was extracted with ether, the extract was dried over anhydrous sodium sulfate, and the ether removed. A gummy residue was obtained which on standing deposited some crystals. After repeated crystallization from hot water, they were finally obtained as colorless needles and were identified as anisic acid by the melting point, mixed melting point and optical properties.

Ozonation of Alkali Lignin.—Two grams of lignin was added to 20 cc. of glacial acetic acid, and a current of ozonized oxygen was passed through until the dark-colored solution (containing some of the lignin in suspension) cleared. The reaction product was treated according to the procedure previously described for methylated lignin. The residue obtained after removing the glacial acetic acid by distillation under reduced pressure, when allowed to stand for several days, deposited some crystals. These were filtered off and recrystallized from glacial acetic acid, and identified as oxalic acid. (The *p*-toluide was prepared according to the directions given by Mulliken,[11] m. p. 275°, mixed with pure oxal-*p*-toluide, m. p. 275° (corr.).)

Summary

1. Alkali lignin from corn cobs was methylated and then oxidized with ozone and dilute nitric acid. Anisic acid was identified as one of the oxidation products. When the lignin was ethylated and subsequently oxidized, *p*-ethoxybenzoic acid was obtained, thus indicating that the group  $-\overset{|}{\underset{|}{C}}-C_6H_4-OH$ is present in alkali lignin from corn cobs.

2. When the methylated lignin is treated with dilute nitric acid, there is obtained, in addition to the anisic acid, an orange-colored amorphous product containing 5.25% of nitrogen, of which 29.1% is present in the form of the nitro group. The ease of nitration, together with the fact that the C:H ratio of the nitration product of methylated lignin is

very nearly 1:1, tends to indicate the presence of an aromatic nucleus in alkali lignin from corn cobs.

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The Nitration of *o*-Dichlorobenzene

BY JOHN R. RUHOFF[1]

When *o*-dichlorobenzene is nitrated, theoretically two mononitro isomers may be formed, namely, 2,3-dichloronitrobenzene and 3,4-dichloronitrobenzene. This reaction has been the subject of several investigations. Beilstein and Kurbatow[2] obtained from *o*-dichlorobenzene upon treatment with fuming nitric acid a "half liquid mixture," the solid portion of which melted at 43° after crystallization from alcohol and consisted of 3,4-dichloronitrobenzene. Holleman[3] obtained by the same method a mixture of a solid and a liquid; the solid melted at 43° after several recrystallizations from alcohol. Kipriyanov and Mikhaĭlenko[4] state that *o*-dichlorobenzene forms on nitration a mixture of 2,3- and 3,4-dichloronitrobenzenes, that one part solidifies on standing, and that both the solid and liquid fractions consist for the most part of 3,4-dichloronitrobenzene. McMaster and Magill[5] nitrated *o*-dichlorobenzene with a mixture of sulfuric and nitric acids and obtained a mixture of a liquid and a solid which they believed to be two forms of 3,4-dichloronitrobenzene, both of which changed spontaneously at 22° to an equilibrium mixture containing about half solid and half liquid.

The purpose of the present work was to investigate the "liquid form" obtained by the nitration of *o*-dichlorobenzene, and to determine, if possible, whether two isomers actually were present.

o-Dichlorobenzene[6] was purified by fractionation through a six-foot column. The portion boiling from 179.9 to 180.6° was nitrated according to the method of McMaster and Magill.[5] From 845 g. of *o*-dichlorobenzene 750 g. of a brown oil was obtained which boiled from 189.2 to 189.4° at 100 mm. The product was perfectly clear and homogeneous at 40°; it became cloudy at 35° and solidified to a mass of hard crystals at 15°. A portion of this material was partially frozen, and the resulting slush filtered. By repeating this process several times, 165 g. of a liquid and 200 g. of a solid were obtained having the characteristics given in Table I.

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[1] Kewaunee Manufacturing Company Fellow in Chemistry.

[2] Beilstein and Kurbatow, *Ann.*, **176**, 41 (1875).

[3] Holleman, *Rec. trav. chim.*, **23**, 357 (1904).

[4] Kipriyanov and Mikhaĭlenko, *Ukrainskiĭ Khem. Zhur.*, **5** Tech. pt., 225–39 (1930); *C. A.*, **25**, 5033 (1931).

[5] McMaster and Magill, THIS JOURNAL, **50**, 3038 (1928).

[6] Generously furnished by the du Pont Company.