

bromide +  $\text{PBr}_3$  (in ether)  $\longrightarrow$  addition compound  $\longrightarrow$  thiophenol (on hydrolysis).

MINNEAPOLIS, MINNESOTA

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## THE HYDROLYSIS OF LIGNIN WITH 12% HYDROCHLORIC ACID

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Hägglund and Björkman<sup>1</sup> and later Hägglund and Rosenqvist<sup>2</sup> distilled lignin (isolated by the fuming hydrochloric acid method) with 12% hydrochloric acid and obtained a distillate which gave a precipitate with phloroglucinol, barbituric acid and with thiobarbituric acid. The substance present in the distillate was not definitely identified, but was shown to be neither furfural, methylfurfural nor hydroxymethylfurfural.

Freudenberg and Harder<sup>3</sup> distilled lignin (isolated from wood by a method similar to that used by Urban<sup>4</sup>) with 12% hydrochloric acid and identified the volatile hydrolytic product as formaldehyde. In a subsequent paper, Freudenberg, Harder and Markert<sup>5</sup> advanced the hypothesis that the formaldehyde arises from a methylene dioxide group ( $-\text{O}-\text{CH}_2-\text{O}-$ ) present in the lignin molecule, as compounds containing 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 Fuchs and Horn.<sup>6</sup> They distilled with hydrochloric acid lignin, acetylated lignin and two oxidized acetylated lignin preparations and found that lignin itself gave a greater yield of formaldehyde-barbituric acid condensation product than the other three modified lignin preparations.

The present investigation was undertaken for the purpose of determining (1) whether lignin isolated from materials other than wood gives formaldehyde when distilled with 12% hydrochloric acid, and (2) whether the method employed for the isolation of the lignin has any effect on the formaldehyde-yielding component presumably present in lignin.

### Experimental

The lignin used in these experiments was isolated from three different sources by the following different methods. The lignin was isolated from corn cobs by the alco-

<sup>1</sup> Hägglund and Björkman, *Biochem. Z.*, **147**, 74 (1924).

<sup>2</sup> Hägglund and Rosenqvist, *ibid.*, **179**, 376 (1926).

<sup>3</sup> Freudenberg and Harder, *Ber.*, **60**, 581 (1927).

<sup>4</sup> Urban, *Cellulosechem.*, **7**, 73 (1926).

<sup>5</sup> Freudenberg, Harder and Markert, *Ber.*, **61**, 1760 (1928).

<sup>6</sup> Fuchs and Horn, *Ber.*, **62**, 2647 (1929).

holic<sup>7</sup> and aqueous sodium hydroxide<sup>8</sup> methods, by the fuming hydrochloric acid method of Willstätter and Zechmeister<sup>9</sup> and by Urban's method<sup>4</sup> as modified by Freudenberg and Harder.<sup>10</sup> The lignin from oat hulls was isolated by the alcoholic and aqueous sodium hydroxide methods,<sup>11</sup> by the method of Willstätter and Zechmeister<sup>9</sup> and by Freudenberg and Harder's modification<sup>10</sup> of Urban's method. The lignin from spruce wood was prepared by the aqueous sodium hydroxide method and according to the procedure of Freudenberg and Harder.<sup>10</sup>

**Distillation of the Lignin with 12% Hydrochloric Acid.**—The distillation of the lignin with the 12% hydrochloric acid was carried out exactly as in the determination of pentosans by Tollens' method, as described in the official book of methods of the Association of Official Agricultural Chemists.<sup>12</sup> In all experiments, three grams of lignin was used for each distillation. The distillate was made up with water to a volume of 500 cc. in a volumetric flask. A portion of this solution was tested immediately for formaldehyde by the Schryver<sup>13</sup> modification of the Rimini<sup>14</sup> test. This test is specific for formaldehyde. Furfural, which might be expected to be present in some of the distillates, gives no reaction with the reagents employed in the formaldehyde test when the dilution reaches 1:100,000. When the concentration of the furfural is approximately 1:1000, or greater, an apricot-yellow color is formed which on addition of concentrated hydrochloric acid turns green and rapidly disappears. Formaldehyde, on the other hand, gives a fuchsin-like color which is quite permanent.

TABLE I  
HYDROLYSIS OF LIGNIN WITH 12% HYDROCHLORIC ACID

Source of lignin	Method for isolation of lignin	Formaldehyde in distillate Calcd. on wt. of lignin used, %	Furfural (Qualitative test with aniline acetate paper) <sup>a</sup>
Corn cobs	Alcoholic sodium hydroxide	—	—
Corn cobs	Aqueous sodium hydroxide	—	—
Corn cobs	Willstätter and Zechmeister	—	+
Corn cobs	Urban's, modified by Freudenberg and Harder	—	Trace
Oat hulls	Alcoholic sodium hydroxide	—	—
Oat hulls	Aqueous sodium hydroxide	—	—
Oat hulls	Willstätter and Zechmeister	Trace	+
Oat hulls	Urban's, modified by Freudenberg and Harder	+	0.61
Spruce wood	Aqueous sodium hydroxide	—	+
Spruce wood	Urban's, modified by Freudenberg and Harder	+	0.79

<sup>a</sup> —, Test was negative; +, test was positive.

<sup>7</sup> Phillips, *THIS JOURNAL*, **49**, 2037 (1927).

<sup>8</sup> Phillips, *ibid.*, **51**, 2421 (1929).

<sup>9</sup> Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

<sup>10</sup> Ref. 3, page 583.

<sup>11</sup> Phillips, *THIS JOURNAL*, **52**, 793 (1930).

<sup>12</sup> "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Association of Official Agricultural Chemists, Washington, D. C., 1925.

<sup>13</sup> Schryver, *Proc. Roy. Soc. (London)*, **82B**, 226 (1910).

<sup>14</sup> Rimini, *Bull. Soc. Chim. France*, [3] **20**, 896 (1898).

The formaldehyde in the distillates was determined quantitatively by the iodine titration method.<sup>15</sup> The results obtained are given in Table I.

It will be observed from Table I that formaldehyde was obtained in appreciable quantity in the distillates from only two of the eight lignin preparations, namely, in that of the lignin from oat hulls prepared by the Freudenberg and Harder modification of Urban's method, and in the distillate of the lignin from spruce wood prepared by the same method. In the distillates from all the other lignin preparations, except one, no formaldehyde could be detected. In the distillate of the lignin from oat hulls prepared by the method of Willstätter and Zechmeister, the test for formaldehyde was so slight that it can be characterized only as a "trace." The percentage formaldehyde obtained from the lignin of spruce wood is in substantial agreement with that recorded by Freudenberg and Harder.<sup>16</sup>

It would appear from the data that the source of the lignin and the method employed for its isolation from the lignified plant materials are two factors which determine whether formaldehyde is obtained as an hydrolytic degradation product from lignin. Thus, lignin from oat hulls prepared by Freudenberg and Harder's modification of Urban's method, when hydrolyzed with 12% hydrochloric acid, yielded a quantity of formaldehyde equivalent to 0.61% of the weight of the lignin, whereas lignin isolated from corn cobs by the same method gave absolutely no test for formaldehyde when similarly hydrolyzed. On the other hand, the hydrolysate of the lignin from oat hulls prepared by the alcoholic sodium hydroxide method gave no test for formaldehyde and that from the lignin isolated from the same source by the method of Willstätter and Zechmeister contained only a trace of formaldehyde. The hydrolysate from the last-mentioned lignin preparation, however, gave a positive test for furfural so that in this case the minute quantity of formaldehyde may have originated from some carbohydrate impurity.

If we were to accept the explanation of Freudenberg, Harder and Markert<sup>5</sup> that the formaldehyde arises from a methylene dioxide group present in the lignin molecule, the conclusion would have to be drawn that this group is present only in lignin isolated from certain plant materials. Furthermore, it is rather difficult to conceive how such a mild treatment as that employed in the isolation of lignin by the alcoholic sodium hydroxide method could bring about the removal of such a comparatively stable group as the methylene dioxide group. In this connection, attention is called to the fact that no formaldehyde was found in the distillate from the lignin fraction isolated from oat hulls by the alcoholic sodium hydroxide method, whereas in the distillate from the lignin isolated from the same source by Freudenberg and Harder's modification of Urban's method (where a solution comprising concentrated hydrochloric acid and sirupy phosphoric acid is employed for the removal of the cellulose and other carbohydrates) formaldehyde was obtained to the extent of 0.61% of the weight of the lignin. It would seem therefore, questionable whether the formaldehyde that is obtained in the hydrolysis of certain lignin preparations can be considered as a fission product of a methylene dioxide group.

### Summary

Lignin isolated from corn cobs, oat hulls and spruce wood by the method of Willstätter and Zechmeister, by the alcoholic and aqueous sodium hydroxide methods and by Freudenberg's modification of Urban's method, was distilled with 12% hydrochloric acid. Formaldehyde was obtained in appreciable quantity only in the distillate from the lignin isolated from oat

<sup>15</sup> Smith, *THIS JOURNAL*, **25**, 1028 (1903).

<sup>16</sup> Ref. 3, page 585.

hulls by the Freudenberg and Harder modification of Urban's method, and in the distillate of the lignin from spruce wood prepared by the same method. The result so far as the lignin from spruce wood is concerned is in agreement with that recorded by Freudenberg and Harder.

The results obtained are discussed from the standpoint of the probable presence of the methylene dioxide group in the lignin molecule.

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## ROTENONE. XXIII. THE STRUCTURE OF ROTENONONE

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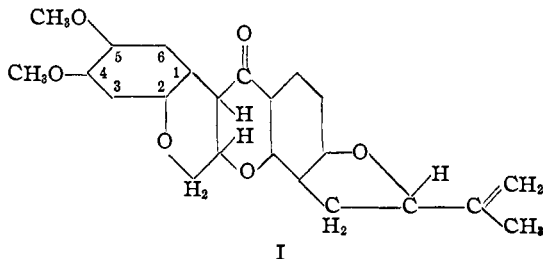
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Rotenonone is obtained from rotenone by chromic acid oxidation, or by the action of nitrous acid. Butenandt assumed the compound to be a 1,2-diketone of formula  $C_{23}H_{20}O_7$  arising from the oxidation of a methylene group adjacent to the carbonyl group present in rotenone. It is converted by the action of strong alkali, with the addition of one mole of water, into an acid of the supposed formula  $C_{23}H_{22}O_8$ , a reaction which was interpreted by Butenandt as a benzylic acid rearrangement.<sup>1</sup>

In a previous article<sup>2</sup> we have shown that the analogs of rotenonone are obtained not only from dihydrorotenone, isorotenone and rotenonic acid, but even more readily from the corresponding dehydro derivatives and that all derivatives of the rotenonone type belong to the dehydro series. Therefore rotenonone should be represented by the formula  $C_{23}H_{18}O_7$ , rotenonic acid by  $C_{23}H_{20}O_8$ , and corresponding formulas should be applied to the other derivatives. These formulas in fact correspond more closely to the analytical figures obtained for the respective compounds.

After the complete formula for rotenone (I) had been established,<sup>3</sup>



it became evident that the formula for rotenonone proposed by Butenandt was untenable.

<sup>1</sup> Butenandt, *Ann.*, **464**, 253 (1929).

<sup>2</sup> LaForge and Smith, *THIS JOURNAL*, **52**, 1091 (1930).

<sup>3</sup> LaForge and Haller, *ibid.*, **54**, 810 (1932).