

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XLIII. The Absence of the Piperonyl Group in the Lignin Structure

BY M. J. HUNTER¹ AND HAROLD HIBBERT

Formaldehyde was first isolated from lignin materials by Freudenberg and Harder,² a discovery confirmed by Sarkar,³ the yields amounting to 0.5–2.0% calculated on the weight of (Klason) lignin present. Freudenberg⁴ as well as Sarkar³ regards the isolation of formaldehyde as direct proof of a piperonyl radical in the lignin complex and the former uses the formaldehyde values to calculate the size of the lignin building unit.⁴ Phillips and Goss⁵ have objected to this interpretation. Formaldehyde yields from various lignins were given recently⁶ and it was shown that these are dependent on the method of extraction of the lignin from the wood. The improbability of the existence of the dioxymethylene group in lignin as part of a piperonyl radical was indicated.

Recently, Freudenberg⁷ has found additional support for the presence of the piperonyl group in new experimental technique involving acridane formation by the action on lignin and related products of a mixture of aniline and concentrated hydrochloric acid at a high temperature and pressure. The use of such a drastic procedure with a highly sensitive complex such as lignin would seem open to serious objection as a criterion for distinguishing between formaldehyde formation from piperonyl groups and other sources, respectively.

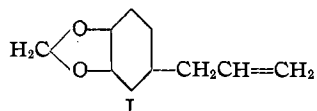
It was shown recently⁶ that the dioxymethylene group in the piperonyl radical, when subjected to various reagents and procedures used in lignin extraction, is decomposed to the extent of only 25%, so that if present in "protolignin" it also should be found to a correspondingly large extent in the extracted lignin. However, the wide variation in formaldehyde yields from various lignins^{6b}

may be considered as indirect evidence against the view of the piperonyl group as the formaldehyde precursor. The approximate relationship found in certain acetic acid lignins between the amounts of furfural and formaldehyde cleavage products indicated the possibility of both being formed simultaneously from certain hexoses, adsorbed by, or combined with, the extracted lignins. Hexoses⁶ gave traces of formaldehyde and furfural in most cases on treatment with mineral acids, but the yields were much too low to account for the amounts obtained from isolated lignins; also certain lignins which gave the highest amounts of formaldehyde yielded only traces of furfural.

The outstanding relationship noted⁶ was that extracted lignins when refluxed with 95% formic acid gave a very low yield of formaldehyde. The stability of the piperonyl group to formic acid and the action of the latter reagent on ethanol lignin, both with respect to removal of this group and to the suppression of the formaldehyde-yielding constituent, have now been investigated.

Piperonal on refluxing with formic acid (95%) for sixteen hours was decomposed to the extent of only 15%, while treatment of ethanol lignins removed 90–95% of the formaldehyde-producing component.

Klason⁸ regarded lignin as related to coniferyl alcohol, present as a glucoside in coniferin, the latter being found in the cambium sap of a wide variety of woods. Since safrole (I) is found in the cambium sap of the roots of the sassafras tree (*Sassafras sassafras*), the behavior of ethanol



sassafras lignin toward hot dilute acids was investigated. This lignin was prepared by the usual procedure⁹ and the yields of formaldehyde obtained from it and maple and spruce ethanol lignins are shown in Table I.

(8) Klason, *Arkiv. Kemi. Mineral. Geol.*, **3**, No. 5, 17 (1908).

(9) Cramer, Hunter and Hibbert, *THIS JOURNAL*, **61**, 509 (1939); Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939); Brickman, Pyle, McCarthy and Hibbert, *ibid.*, **61**, 568 (1939).

(1) From a thesis submitted to McGill University by Melvin J. Hunter in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, May, 1939.

(2) Freudenberg and Harder, *Ber.*, **60**, 581 (1927); Freudenberg and Sohns, *ibid.*, **66**, 282 (1933).

(3) Sarkar, *J. Indian Chem. Soc.*, **11**, 691 (1934).

(4) Freudenberg, "Tannin, Cellulose, Lignin," Verlag von Julius Springer, Berlin, 1933, p. 134.

(5) Phillips and Goss, *THIS JOURNAL*, **54**, 3374 (1932).

(6) (a) Hunter, Wright and Hibbert, *Ber.*, **71**, 734 (1938); (b) *ibid.*, Table 3.

(7) Freudenberg, Klinck, Flickinger and Sobek, *ibid.*, **72**, 217 (1939).

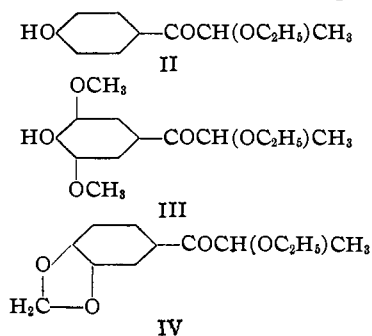
TABLE I
YIELDS OF FORMALDEHYDE FROM SASSAFRAS, MAPLE AND SPRUCE ETHANOL LIGNINS

Wood species	Method of isolation	Hrs.	Secondary treatment, refluxed with	Alkoxy content calcd. as methoxyl, %	Formaldehyde analyses			
					Sample, g.	Dimedone deriv., g.	Formaldehyde, %	
1	Maple	Ethanol-2% HCl	20	27.1	1.000	0.0490	0.50
2	Maple	Ethanol-0.3% HCl	100	28.4	1.000	.1229	1.26
3	Maple	Ethanol-0.3% HCl	100	95% formic acid for 16 hrs.	23.6	1.000	.0064	0.066
4	Sassafras	Ethanol-2.0% HCl	24	26.4	1.000	.0392	.40
5	Sassafras	Ethanol-2.0% HCl	24	95% formic acid for 16 hrs.	23.2	1.000	.0032	.033
6	Spruce	Ethanol-3.0% HCl	40	19.2	1.000	.0244	.25

The analyses show that boiling 95% formic acid removes the component responsible for formaldehyde formation from maple and sassafras ethanol lignins with equal ease, and, since the piperonyl group in various derivatives is decomposed to the extent of only 15% under identical conditions, the results provide conclusive evidence against the existence of the piperonyl group in lignin.

Also piperonal when refluxed for twenty-four hours with absolute ethanol containing 3% hydrogen chloride can be recovered in 90% yield, while, from the data given in Table I, it would appear that a large percentage of the original formaldehyde-producing constituent is removed, or transformed, even by the action of the (2%) ethanol-hydrochloric acid during the lignin extraction, since an extracted lignin prepared from maple wood meal by heating with ethanol, containing only 0.3% hydrogen chloride, for one hundred hours, showed a much higher formaldehyde content.

The water-soluble oils obtained in the ethanolysis of sassafras wood⁹ gave no formaldehyde on treatment with hot dilute acids by the customary procedure. If sassafras lignin contained a piperonyl group, this should be present as α -ethoxypropiopiperonylone (IV) in the neutral water-soluble ethanolysis fraction⁹ as an analog of the guaiacyl (II) and syringyl (III) compounds⁹ ob-



tained from the ethanolysis of spruce and maple woods, respectively, but not the slightest trace of formaldehyde could be obtained.

Regarding the origin of the formaldehyde from extracted lignins, Freudenberg¹⁰ has shown recently that cinnamyl alcohol when distilled with 28% sulfuric acid gives about 2% formaldehyde. He concludes¹⁰ that this configuration, if present in lignin, is not responsible for the formaldehyde formation since no acridane formation⁷ takes place with cinnamyl alcohol under conditions whereby it is formed both from lignins and piperonyl derivatives. The drastic conditions employed, namely, heating with aniline and concentrated hydrochloric acid under pressure at 270-290° for thirty-four hours, would seem to preclude application of this method to such a highly reactive substance as the lignin aggregate.

Whilst the more unstable methylals and cyclic acetals¹¹ would yield formaldehyde readily under the conditions employed, no evidence has been found, as yet, indicating the presence of such groupings in wood.

According to Kohler¹² vinyl phenyl ketone loses formaldehyde spontaneously at room temperature and the possible relation of this type of structure to that of α -hydroxypropiosyringone and α -hydroxypropiovanillone should not be overlooked.

The amount, if any, of piperonyl-containing constituent present in lignin would seem to be so small that it cannot be regarded as an essential part of the lignin structure, and the evidence obtained thus far appears to indicate that the formaldehyde (1-4%) is formed from an aromatic side-chain, possibly one existing as part of a complex present in lignin condensation polymers¹³ and similar to cinnamyl alcohol.

(10) Freudenberg, Engler, Flickinger, Sobek and Klinck, *Ber.*, **71**, 1810 (1938).

(11) Hibbert and Carter, *THIS JOURNAL*, **50**, 3120 (1928).

(12) Kohler, *Am. Chem. J.*, **42**, 380 (1909).

(13) Hibbert, *THIS JOURNAL*, **61**, 730 (Structure XXXVI) (1939).

Experimental

Determination of the Formaldehyde Liberated by the Action of Acids on Extracted Lignins and Related Substances.—This was carried out as described in the previous communication.⁶

Stability of Piperonal toward Boiling Formic Acid (95%).—Piperonal (2.000 g.) was refluxed with 95% formic acid (20 cc.) for sixteen hours following the method of Wright and Hibbert.¹⁴ After removing the formic acid under reduced pressure, the residue was dissolved in ether and the ether solution extracted with cold 1% sodium hydroxide solution. The ether extract was dried over anhydrous calcium chloride, concentrated, and the residue distilled under reduced pressure. The distillate (1.696 g., equivalent to 84.8%) crystallized at room temperature, m. p. 36–38°. A mixed melting point with the original product showed no depression.

Stability of Piperonal to Hot Ethanol Containing 3% Hydrogen Chloride.—Piperonal (2.000 g.) was refluxed for twenty-four hours with absolute ethanol containing 3% hydrogen chloride. These conditions were somewhat more drastic than those used for the ethanolysis of maple and sassafras woods. The ethanol was removed under reduced pressure, the residue dissolved in ether, and the piperonal isolated as above: weight of recovered piperonal, 1.827 g. (91.3%).

Behavior of Lignins toward Boiling Formic Acid (95%).—The various ethanol lignins (3.0 g.) were each refluxed with 95% formic acid (30 cc.) for sixteen hours. The solution was then poured with stirring into 300 cc. of distilled water and the precipitated lignins washed free from acid. The precipitates were vacuum dried over calcium chloride at room temperature and then over phosphorus pentoxide at 56° (14 mm.). The products were analyzed for methoxyl and the formaldehyde yield determined. The results are shown in Table I.

Preparation of Sassafras Ethanol Lignin.—Sassafras woodmeal (450 g.) previously extracted with (i) alcohol-

benzene, (ii) benzene and (iii) water, after drying was refluxed for twenty-four hours with 3 liters of absolute ethanol containing 2% hydrogen chloride, as previously described.⁹ This gave 52.0 g. of sassafras ethanol lignin and 36.3 g. of crude ether soluble oils, as compared with 44.6 g. of lignin and 36.7 g. of crude oils from a similar run with maple wood. From the sassafras crude oils there was obtained a neutral fraction of 2.2 g. Distillation of this latter with 28% sulfuric acid gave no formaldehyde.

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Summary

The absence of the piperonyl group in the structure of lignin is indicated by (a) the inability of workers in this field to isolate from an extracted lignin a piperonyl-containing derivative; (b) the pronounced instability toward formic acid of the formaldehyde-producing constituent in lignin as compared with the very much greater stability of the piperonyl radical present in known compounds; (c) the liberation of formaldehyde from such derivatives as cinnamyl alcohol, and the probability of the presence of this type of grouping in extracted lignins; (d) the behavior of ethanol sassafras lignin and the water-soluble ethanolysis products from sassafras wood toward hot dilute acids, whereby yields of formaldehyde similar in amount to those found with other woods are obtained from the former, and none from the latter.

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(14) Wright and Hibbert, *THIS JOURNAL*, **59**, 125 (1937).

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Studies on Lignin and Related Compounds. XLIV. The Ethanolysis of Maple Wood; Separation and Identification of the Water-Soluble Aldehyde Constituents¹

BY JAMES J. PYLE, LEO BRICKMAN AND HAROLD HIBBERT

In two recent communications² of this series, a description was given of the isolation, in considerable amount, of water-soluble aromatic constituents formed in the ethanolysis of spruce and maple woods. The crude oils were shown to consist of a phenolic, aldehydic, acidic and neutral

(1) From a thesis submitted to the Faculty of Graduate Studies and Research, McGill University, by James J. Pyle in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1939.

(2) (a) Cramer, Hunter and Hibbert, *THIS JOURNAL*, **61**, 509 (1939); (b) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

fraction. In a later paper,³ a revised method for their isolation was given by which much improved yields were obtained. The phenol fraction from spruce wood^{2a} has been shown to consist in large part of α -ethoxypropiovanillone and that from maple wood^{2b} of a mixture, in approximately equal amounts, of this and α -ethoxypropiosyringone.

In the present communication an account is given of the separation and identification of the

(3) Brickman, Pyle, McCarthy and Hibbert, *ibid.*, **61**, 888 (1939).