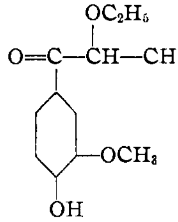
[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LXXVII. Re-investigation of the Ethanolysis Products of Maple Wood

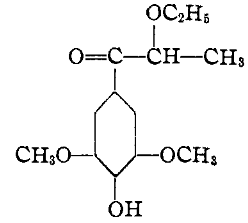
BY MARSHALL KULKA, HERBERT E. FISHER, SAMUEL B. BAKER AND HAROLD HIBBERT

Treatment of maple wood with a 2% solution of hydrogen chloride in ethanol yields around 25–30% of the lignin as a mixture of water-soluble, largely monomeric, propylphenol derivatives (termed ethanolysis oils) which are separable into bisulfite-soluble, alkali-soluble and neutral fractions.[1] The alkali-soluble fraction[2] consists of α-ethoxypropiovanillone [2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone] (I) and α-ethoxypropiosyringone [2-ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone] (II). The amount of these two compounds isolated (approximately 5% based on the Klason lignin present in the original wood) constituted only about a third of the total alkali-soluble fraction of the ethanolysis oils.



I

2-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone



II

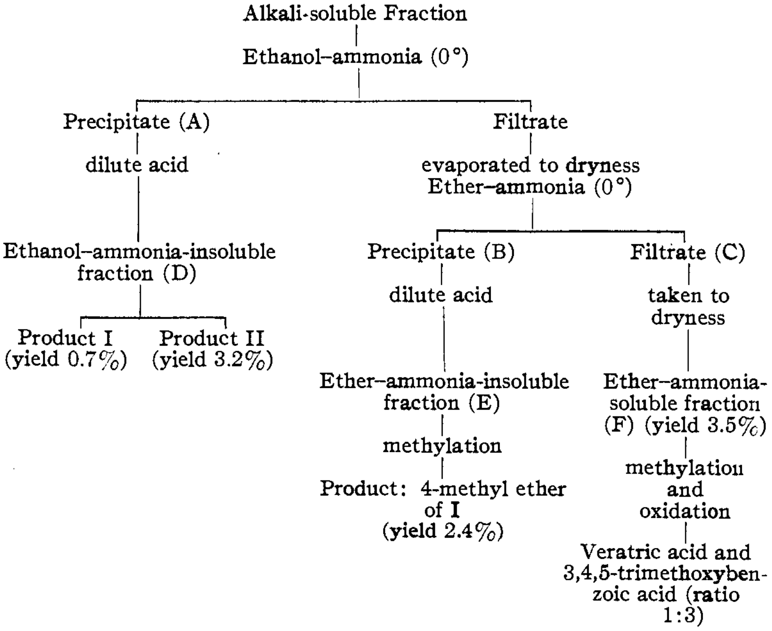
2-Ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone

The purpose of this re-investigation was to separate the components more completely and to identify the unknown components. While (I) and (II) have been isolated in increased yield (3.1 and 3.2%, respectively, based on the Klason lignin present in the original maple wood), due to the complexity of the remaining material no other components could be identified. The improved technique adopted provides a method applicable to a wide variety of plant products and is outlined in Chart I. Fraction D on rectification gave 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (I) and 2-ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone (II) in yields of 0.7 and 3.2%, respectively.[3] The latter (II), previously isolated as a liquid, was now obtained as a light-colored crystalline compound. Since fraction E decomposes on distillation it was methylated with diazomethane, then fractionally distilled and heterogeneous fractions refractionated in a smaller column. The "crystalline fractions" isolated were identified as the methyl ether of (I) and represented 2.4% based on the Klason lignin present in the original wood.

An investigation of the ether-ammonia-soluble fraction (F) (methoxyl value 15.1%; ethoxyl value 22.8%) showed that only about one-half was precipitable as the 2,4-dinitrophenylhydrazone. This had an indefinite melting point and could not be purified by recrystallization; no other crystalline derivative could be isolated. The product (F) was not readily distillable at low pressures (0.001 mm.) but treatment with diazomethane gave a distillable methylated product from which, however, no pure products could be prepared. Attempts to effect a fractionation of (F) into homogeneous carbonyl- and non-carbonyl-containing fractions by oximation[4] followed by extraction with 10%

CHART I

SEPARATION OF COMPONENTS OF THE ALKALI-SOLUBLE FRACTION OF MAPLE WOOD ETHANOLYSIS OILS (YIELDS ARE BASED ON KLASON LIGNIN)



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[1] West, MacGregor, Evans, Levi and Hibbert, THIS JOURNAL, 65, 1176 (1943).

[2] Hunter, Cramer and Hibbert, *ibid.*, 61, 516 (1939).

[3] All yields are based on the amount of Klason lignin present in the original wood.

[4] Bryant and Smith, THIS JOURNAL, 57, 57 (1935).

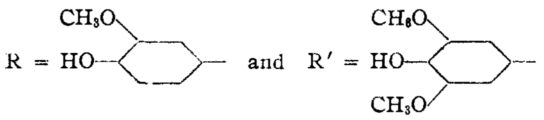
sodium hydroxide were unsuccessful. However, potassium permanganate oxidation of the methylated product (F) proved its aromatic nature and that its components contain the 3,4-dimethoxyphenyl- and 3,4,5-trimethoxyphenyl- nuclei.

The compounds isolated from the ethanolysis products to date and their yields are summarized in Table I.

TABLE I

COMPONENTS OF THE WATER-SOLUBLE ETHANOLYSIS OILS OF MAPLE WOOD

	Compound isolated	Wt. from 1000 g. of maple wood, g.	% based on Klason lignin
1.	R—CO—CH(OEt)—CH_3 (I)	6.2	3.1
2.	R′—CO—CH(OEt)—CH_3 (II)	6.4	3.2
3.	R—CO—CO—CH_3[5]	1.3	0.6
4.	R′—CO—CO—CH_3[5]	3.8	1.9
5.	R—CHO[6]	0.2	0.1
6.	R′—CHO[6]	1.3	0.6
7.	R—CH_2—CO—CH_3[6]	0.1	0.05
8.	R′—CH_2—CO—CH_3[6]	0.4	0.2
	Total identified products		9.75
9.	Unidentified but containing R and R′ nuclei	7.0	3.5
		Total	13.25



Experimental

Separation of the Components of the Alkali-soluble Fraction of Maple Wood (Chart I).—The alkali-soluble ethanolysis oils (31.6 g.) were dissolved in cold absolute ethanol (0°, 450 cc.) and the solution saturated with dry ammonia gas. The cream-colored ammonium salt (A) (10.9 g.) was filtered, washed with a solution of dry ammonia in absolute ethanol and dried *in vacuo*. The solvent was removed from the combined filtrate and washings under reduced pressure at room temperature, the residual oil dissolved in cold anhydrous ether (0°, 250 cc.) and the solution saturated with ammonia at 0°. The ammonium salt (B) was filtered, washed with a solution of anhydrous ammonia in ether and dried *in vacuo*. The ammonium salts (A) and (B) were each dissolved separately in water, the solutions acidified and extracted with benzene. Removal of the solvents yielded three oily fractions, the ethanol-ammonia-insoluble fraction (D) (10.1 g.), the ether-ammonia-insoluble fraction (E) (13.0 g.) and the ether-ammonia-soluble fraction (F) (7.0 g.).

Investigation of the Ethanol-Ammonia-insoluble Fraction (D).—The oil (10.1 g.) was fractionally distilled in the Cooke-Bower column[7] at a pressure of 0.25 mm. Eight fractions were obtained of which the first three (bath temperature range, 161–172°, column temperature range, 100–105°) were light-colored oils and the last five (bath temperature range, 178–193°, column temperature range, 107–112°) were crystalline solids. Each of the crystalline fractions was recrystallized from a mixture of ether and petroleum ether, and from dilute ethanol, m. p. 73–74°; *p*-nitrobenzoyl ester, m. p. 143.5–144.5°; no depression in melting point when mixed with the *p*-nitrobenzoyl ester of 2-ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone (II). The first three oily fractions were each again fractionally distilled from a smaller fractionating column (five plates), the resulting fractions methylated with diazomethane and the methylated products recrystallized from petroleum ether, m. p. 80–81°; no depression in melting point when mixed with the methyl ether of 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (I). The amounts of each of the components found present in the ethanol-ammonia-insoluble fraction (D) were (I), 1.30 g.; (II), 6.35 g.; unidentified, 0.95 g.

Investigation of the Ether-Ammonia-insoluble Fraction (E).—The oil (E) (13.0 g.) was methylated with diazomethane and to insure complete reaction the non-methylated material was extracted with 5% sodium hydroxide and remethylated. The total methylated product was distilled and yielded two fractions, the first at bath temperature 150–200° (0.05 mm.) (8.6 g.) and the second at bath temperature 200–260° (0.025 mm.) (1.1 g.). The second fraction, a resinous oil, was not investigated further. The first fraction solidified on scratching the container and was recrystallized from a mixture of ether and petroleum ether; white crystals (2.5 g., m. p. 80–81°); no depression in melting point when mixed with pure methyl ether of (I). The filtrate from the recrystallization was evaporated to dryness and the residual oil (6.1 g.) was fractionally distilled (0.25 mm.) in the Cooke-Bower column.[7] Of the seven fractions collected, the second, third and fourth (bath temperature range, 168–180°, column temperature range, 90–92°) solidified and were shown (by mixed melting point) to be the methyl ether of (I) (2.4 g.). The very small first fraction, a colorless oil, was not investigated further. The last fraction, also not investigated, was a high-boiling resinous material probably dimeric or polymeric in type. The fifth and sixth fractions were combined and refractionated in a smaller column. The resulting fractions were of uniform composition ($n^{25}D$ 1.5200; alkoxyl (calcd. as methoxyl), 44.3%), but the 2,4-dinitrophenylhydrazone could not be purified by recrystallization and no other crystalline derivative could be isolated. The amounts of the components of the ether-ammonia-insoluble fraction (E) present were: (I), 4.9 g. (isolated as the pure methyl ether); unidentified, 3.8 g.; the remainder decomposed during fractionation.

Investigation of the Ether-Ammonia-soluble Fraction (F)

(a) **Fractional Distillation.**—The ether-ammonia-soluble fraction (F) (7.0 g.) was methylated completely with diazomethane and the methylated product (6.86 g.) distilled at 160–250° bath temperature (0.25 mm.); yield of light-colored distillate, 4.95 g. or 71%. This distillate (F′) was fractionally distilled (0.25 mm.) in the Cooke-Bower column.[7] The refractive indices of the fractions (F″, F‴, F⁗, etc.) thus obtained varied from 1.5200 to 1.5098 to 1.5312 at 25° and the alkoxyl values from 36.0 to 45.8%. Refractionation of several of these fractions in a smaller column failed to yield products of uniform composition.

(b) **Permanganate Oxidation.**—Portions (0.3 g.) of the different fractions F′, F″, F‴, etc., obtained in the above separation (a) were oxidized at 90–100° by slow addition of a 3% solution of potassium permanganate (50 cc.). The lower-boiling fractions yielded veratric acid (identified by mixed melting point) and the higher-boiling fractions yielded 3,4,5-trimethoxybenzoic acid (similarly identified) in yields of 20–25% by weight. The ratio of lower-boiling to higher-boiling material was approximately 1 to 3.

Acknowledgments.—The authors acknowledge their indebtedness to Canadian Industries Limited for a Fellowship (M. K.), to the National Research Council of Canada for a Studentship (H. E. F.) and to the Canadian Pulp and Paper Association for a Scholarship (S. B. B.).

Summary

1. The alkali-soluble fraction of the water-soluble lignin ethanolysis oils of maple wood has been re-investigated and the yields of its

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[5] Kulka, Hawkins and Hibbert, THIS JOURNAL, **63**, 2371 (1941).

[6] Kulka and Hibbert, *ibid.*, **65**, 1180 (1943).

[7] Bower and Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

known components, 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and 2-ethoxy-1-(4-hydroxy - 3,5 - dimethoxyphenyl) - 1 - propanone have been increased to 3.1% and 3.2%, respectively, based on the Klason lignin present in the original wood.

2. 2-Ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl-1-propanone previously reported as being a liquid was isolated in pure form and found to be a well-defined crystalline solid.

3. The material left after removal of the two known components from the alkali-soluble fraction of the ethanolysis oils was found to be a complex mixture, inseparable by fractional distillation, the methylated product containing the 3,4-dimethoxyphenyl- and 3,4,5-trimethoxyphenyl- nuclei in the ratio of 1 to 3.

4. A summary of the work on ethanolysis of maple wood shows that the yield of *pure* compounds isolated was 9.8% of the Klason lignin present in the original wood. In view of the experimental difficulties involved in their separation and isolation this percentage represents a very conservative figure, the *actual* value undoubtedly being appreciably higher.

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

Studies on Lignin and Related Compounds. LXXVIII. Chromic Acid Oxidation of Lignin-type Substances, Wood Ethanolysis Products and Wood[1]

BY W. S. MACGREGOR, T. H. EVANS AND HAROLD HIBBERT

The importance in lignin chemistry of propylphenol (C_6—C—C—C) units related to coniferyl alcohol is evident from recent reviews on the subject.[2] This is exemplified in the isolation of a considerable amount of wood lignin as hydroxylated propylcyclohexane derivatives from the hydrogenation products of wood;[3] in the isolation from spruce wood ethanolysis products of 2 - ethoxy - 1 - (4 - hydroxy - 3 - methoxyphenyl)-1 - propanone[4] (I), 1 - (4 - hydroxy - 3 - methoxyphenyl)-1,2-propanedione[5] (II), 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone[6] (III), 1-(4-hydroxy-3-methoxyphenyl)-2-propanone[7] (IV) and, in addition to these, the 4-hydroxy-3,5-dimethoxyphenyl analogs of I, II and IV from maple wood.

Theories concerning the mode of linkage of the propylphenol building-units in native lignin[2,8] are represented on the one hand by the Freudenberg[2a,8] postulate of spruce lignin as a mixture of polymers of the dehydrodiisoeugenol type and, on the other, by Hibbert's theory[2d,8] of native lignins as a series of polymers of dehydrodi-(oxyconiferyl alcohol) [dehydrodi-(β,γ-dioxyisoeugenol)] and dehydrodi-(oxysyringyl alcohol). Freudenberg's polymers are characterized by the presence of terminal methyl groups in the propyl side chains, while in Hibbert's the terminal groups are either primary alcohol groups or ether linkages —O—CH_2—O—, methyl groups being absent. Upon cleavage of these latter types of polymers the side chains would become free to rearrange from the labile —CH_2—$COCH_2OH$ form to the more stable configurations isolated (I-IV). The actual presence of terminal carbinol groups, or end —CH_2—O—CH_2— linkages in native lignin, is proven by the isolation of 1-(4-hydroxycyclohexyl)-3-propanol[3a,3b] and of 1-cyclohexyl-3-propanol[3c] upon hydrogenation of wood. Further, the ease with which the postulated rearrangements of RCH_2COCH_2OH to units I-IV (the latter characterized by the presence of terminal methyl groups)[8] are known to occur also forms supporting evidence for the views of Hibbert[2d,8] that these latter represent stabilized end-products formed from the more reactive R—CH_2COCH_2OH type.

By oxidizing organic substances containing methyl groups with hot, concentrated, aqueous chromic acid and simultaneous steam distillation of the acetic acid formed, Kuhn and l'Orsa[9] were able to account for the total carbon in many compounds as carbon dioxide, or as acetic acid, the yield of the latter being above 85% of theoretical for many structures containing methyl groups, such as CH_3COCH_2—, $CH_3CHOHCH$-OH—, CH_3CH_2O—, and $CH_3CH{=}CH$—. Freudenberg[10] oxidized spruce "cuproxam lignin" by the same method and obtained a 6% yield of acetic acid. This low yield, amounting to only twenty per cent. of that theoretically obtainable from his structural lignin polymer,[2a,8] was regarded by him as due to the inadequacy of the experimental technique employed.

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[1] This paper represents part of a thesis submitted to the Faculty of Graduate Studies and Research, McGill University, by Warren S. MacGregor, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1943.

[2] (a) Freudenberg, *Ann. Rev. Biochem.*, **8**, 88 (1939); (b) Erdtman, *Svensk. Papperstidn.*, **44**, 243 (1941); (c) Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941); (d) Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942); (e) *Chem. Soc. London, Ann. Reports*, **39**, 142 (1943).

[3] (a) Harris, D'Ianni and Adkins, THIS JOURNAL, **60**, 1467 (1938); (b) Godard, McCarthy and Hibbert, *ibid.*, **63**, 3061 (1941); (c) Bower, Cooke and Hibbert, *ibid.*, **65**, 1192 (1943).

[4] Cramer, Hunter and Hibbert, *ibid.*, **61**, 509 (1939).

[5] Kulka, Hawkins and Hibbert, *ibid.*, **63**, 2371 (1941).

[6] West, MacInnes and Hibbert, *ibid.*, **65**, 1187 (1943).

[7] Kulka and Hibbert, *ibid.*, **65**, 1185 (1943).

[8] Eastham, Fisher, Kulka and Hibbert, *ibid.*, **66**, 26 (1944).

[9] Kuhn and l'Orsa, *Z. angew. Chem.*, **44**, 847 (1931).

[10] Freudenberg, *Ber.*, **66**, 262 (1933).