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 $\text{—O—CH}_2\text{—O—}$, methyl groups being absent. Upon cleavage of these latter types of polymers the side chains would become free to rearrange from the labile $\text{—CH}_2\text{—COCH}_2\text{OH}$ form to the more stable configurations isolated (I-IV). The actual presence of terminal carbinol groups, or end $\text{—CH}_2\text{—O—CH}_2\text{—}$ 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 $\text{RCH}_2\text{COCH}_2\text{OH}$ 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 $\text{R—CH}_2\text{COCH}_2\text{OH}$ 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 $\text{CH}_3\text{COCH}_2\text{—}$, $\text{CH}_3\text{CHOHCHOH—}$, $\text{CH}_3\text{CH}_2\text{O—}$, and $\text{CH}_3\text{CH=CH—}$. 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).

In the present investigation the chromic acid oxidation technique has been applied to lignin-type substances, wood ethanolysis products, extracted lignins and woods, in order to obtain further information concerning the structures of native and isolated lignins, and especially to determine the amount of terminal methyl groups present, if any, in the two latter.

TABLE I

OXIDATION OF LIGNIN BUILDING UNITS AND RELATED COMPOUNDS

(R) = (4-hydroxy-3-methoxyphenyl)

Expt.	Substance	Acetic acid % obtained	Acetic acid % of theory
1	Isoeugenol	30.9 28.6	84 78
2	Dehydrodiisoeugenol	31.7 30.9	86 84
3	1-(R)-propane	31.2	85
4	1-(R)-2-propanone	29.8 29.5	90 89
5	1-(3,4-Dimethoxyphenyl)-1-propanone	30.4	97
6	2-Hydroxy-1-(R)-1-propanone	28.4 25.6	93 84
7	2-Ethoxy-1-(R)-1-propanone	50.2 48.8	94 91
8	3-Ethoxy-1-(R)-1-propanone	23.1	87
9	1-(R)-1,2-propanedione	28.0 29.2	92 96
10	Semicarbazone of 2-ethoxy-1-(R)-1-propanone	39.6	93
11	Semicarbazone of 1-ethoxy-1-(R)-2-propanone	40.5	95
12	3-Hydroxy-1-(R)-1-propanone	0.7 0.4	.. ..
13	1-(R)-2,3-propanediol	0.7	..
14	Eugenol	0.6	..
15	Vanillin semicarbazone	0.5	..
16	Acetovanillone	33.2 32.9	92 91
17	2-(3,4-Dimethoxyphenyl)-2-propanol	11.1 13.6	36 44
18	Acetophenone[9]		10

As shown in Table I, oxidation with chromic acid of (4-hydroxy-3-methoxyphenyl)-propane derivatives containing a terminal methyl group (Expts. 1–9) yields, in agreement with the observations of Kuhn and l'Orsa,[9] at least 80% of the theoretical amount of acetic acid. The ethoxyl group is also oxidized practically quantitatively to acetic acid (Expts. 7, 8, 10 and 11). Where the terminal methyl group either is replaced by carbinol (Expts. 12 and 13) or is absent (Expts. 14 and 15) no acetic acid is obtained. The procedure is therefore suitable for the detection of terminal methyl groups in lignin-type compounds.

The effect of aromatic ring stability on yield of acetic acid is shown clearly in Expts. 16, 17 and 18 where, in each case, the methyl group is attached to a carbon atom in the position α to the ring. Where the ring is *stable* (Expt. 18), oxidation results in formation of aromatic carboxylic acids in good yield with accompanying oxidation of the methyl group to carbon dioxide and water. However, as the stability of the ring *decreases* (Expts. 16 and 17) oxidation is accompanied by ring opening permitting of cleavage and formation of acetic acid.

With the remaining products of Table I, the methyl group (where present) is part of the skeletal form $R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}$, the methyl group being attached to a carbon atom in the position β to the ring. Since the tendency to cleave is through the α position (carboxylic acid formation) the yield of acetic acid will be high even in the case of $R{-}CH_2{-}CH_2{-}CH_3$.

The acetic acid yield from similarly situated methyl groups appears to be the same irrespective of whether the structure be mono- or polymolecular. This is evidenced in the high yield of acetic acid from dehydrodiisoeugenol (Table I, Expt. 2), the yield in this case being enhanced by the labilizing effect of the phenolic hydroxyl group (that is, oxidation of dehydrodiisoeugenol parallels that of acetovanillone). On the other hand, it is to be expected that this same effect will be inhibited in a chain polymer of the dehydrodiisoeugenol type due to the phenolic ether linkages (with the exception of the methyl group attached to the terminal member) so that yields of 40–50% of theoretical are to be anticipated (*cf.* Table I, Expt. 17). On this basis a polymer of the Freudenberg type V should give at least 40–50% of the theoretical amount of acetic acid, or approximately twice the amount found by Freudenberg, and it is very likely that the acetic acid obtained in his experiment originated solely from methyl groups on terminal units.

When spruce and maple woods (previously extracted successively with benzene–alcohol and water) were oxidized (Table II, Expts. 4 and 5), the acetic acid obtained was that due solely to the ester acetyl groups. Thus native lignin in these woods contains only a small percentage (if any) of end methyl groups. Cellulose and holocelluloses (Expts. 1, 2 and 3) gave no acetic acid other than that from the acetyl groups present.

The yields of acetic acid from the lignin ethanolysis products from spruce and maple woods were determined in similar fashion (Table II, Expts. 6, 7, 8, 9, 10). The low molecular weight lignin water-soluble ethanolysis oils from these two woods yielded 7.3 and 10.8% acetic acid, respectively, in excess of that arising from the introduced ethoxyl groups (Table II, Expts. 7 and 10). By chemical fractionation of the same oils, methyl-containing $C_6{-}C_3$ units have been isolated in quantity sufficient to account for 68% of the acetic acid from the spruce ethanolysis

TABLE II

OXIDATION OF WOODS AND ISOLATED LIGNIN FRACTIONS

Expt.	Substance	Klason lignin, %	Ethoxyl, %	Methoxyl, %	% Acetic acid			
					Total obtained, %	From acetyl groups, %	From ethoxyl groups,[a] %	From lignin terminal methyl groups, %
1	Cellulose	0.0	..	..	0.05	0	0	..
2	Spruce holocellulose	0.0	..	..	2.2	2.4	0	..
3	Maple holocellulose	0.0	..	..	4.9	5.4	0	..
4	Spruce wood	27.9	..	..	2.4 2.3 2.2	2.6	0	..
5	Maple wood	21.0	..	..	6.4 5.5 5.3	5.6	0	..
6	Spruce water-insoluble ethanol lignin[b]	..	11.0	14.1	20.7 19.7	...	13.6	**6.6**
7	Spruce water-soluble ethanolysis oils[b]	..	20.7	8.6	32.7 33.3	...	25.7	**7.3**
8	Maple ether-insoluble ethanol lignin[b]	..	9.1	19.2	10.3 10.8	...	11.3	..
9	Maple ether-soluble ethanol lignin[b]	..	13.2	17.8	16.9 15.7 16.7	...	16.4	..
10	Maple water-soluble ethanolysis oils[b]	..	12.5	18.4	25.2 27.3	...	15.5	10.8

[a] 93% of theoretical (*cf.* Table I). [b] Fractions designated as in previous communication, Pt. LXVI, THIS JOURNAL, **65**, 1176 (1943).

TABLE III

YIELD OF ACETIC ACID DERIVED FROM MONOMOLECULAR COMPOUNDS ISOLATED FROM ETHANOLYSIS OILS

Substance	Percentage of total oil	Calcd. yield[a] of acetic acid, %	Calcd. yield[b] of acetic acid from end methyl groups, %
Spruce ethanolysis oils			
2-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone	14.7	7.3	3.6
1-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone	4.3	2.1	1.0
1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione	1.4	0.4	0.4
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	0.12	0.04	0.04
Total	20.5	9.8	5.0
Maple ethanolysis oils			
2-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone	11.8	5.9	2.9
2-Ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone	8.5	3.7	1.8
1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione 1-(4-Hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione	8.3	2.1	2.1
1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone	0.6	0.1	0.1
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	0.3	0.1	0.1
Total	29.5	11.9	7.0

[a] Calculated from the yields of acetic acid obtained upon oxidation of the pure compounds (Table I), *e. g.* 11.8 × 0.50 = 5.9. [b] The acetic acid (93% of theory) from ethoxyl groups has been deducted.

oils[4,5,6,7] (7.3 × 68/100 = 5.0) and 65% of that from the maple ethanolysis oils[11] (10.8 × 65/100 = 7.0) as shown in Table III. The acetic acid is therefore derived from these isolable units.

The oxidation of amorphous water-insoluble *spruce* and *maple* ethanol lignins varied markedly, in that the former gave a 6.6% yield of acetic acid, derived from terminal methyl groups (Table II, Expt. 6), while the acetic acid derived from the maple water-insoluble lignin fractions is entirely accounted for by ethoxyl groups present in these materials (Table II, Expts. 8 and 9), thus indicating a pronounced difference in structure between the two types. This was further emphasized by the fact that the water-soluble lignin ethanolysis oils from maple wood (Table II, Expt. 10) contained *all* of the constituents characterized by the presence of terminal methyl groups. Occasionally, due to variations in the ethanolysis reaction, cleavage of the native maple lignin polymers was not always complete and in one case a *water-insoluble* maple ethanol lignin fraction yielded, upon oxidation, 1.5% of acetic acid from terminal methyl groups.

Re-ethanolysis of an ether-soluble spruce lignin fraction resulted in only a slight decrease in the methyl groups in the *recovered* petroleum ether-insoluble lignin as shown by the decrease in yield of acetic acid from 6.1 to 5.4% (Table IV). However, the oily, petroleum ether-soluble lignin fraction isolated simultaneously (amounting to 31% of the total re-ethanolysis products) yielded 16.1% acetic acid from terminal methyl groups on oxidation (Table IV). The effect of the re-ethanolysis treatment of the *ether-soluble* spruce ethanol lignin was to increase the yield of acetic acid from end methyl groups from 6.1 to 8.4% (see footnote, Table IV).

This actual formation of methyl groups during ethanolysis of spruce wood lignin is in accord with Hibbert's oxyconiferyl alcohol theory of lignin structure.[2d,8]

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(11) Kulka, Fisher, Baker and Hibbert, THIS JOURNAL, **66**, 39 (1944).

TABLE IV

RE-ETHANOLYSIS OF ETHER-SOLUBLE SPRUCE ETHANOL LIGNIN

	Substance	Weight, g.	Acetic acid: Total obtained, %	From ethoxyl groups, %	From terminal methyl groups (by diff.), %	From terminal methyl groups, g.
I	Spruce ether-soluble ethanol lignin	9.7	22.8	16.7	6.1	0.59
II	Petroleum ether-*insoluble* fraction from re-ethanolysis of I	6.4	17.6	12.2	5.4	0.35 } 0.82[a]
III	Petroleum ether-*soluble* fraction from re-ethanolysis of I	2.9	29.2	13.0	16.1	0.47 }

[a] 0.82 g. acetic acid represents a combined yield of 8.4% based on the original weight (9.7 g.) of the ether-soluble spruce ethanol lignin.

Experimental

Preparation of Samples.—The wood samples were ground in a Wiley mill to 40-mesh, extracted forty-eight hours with 1:1 alcohol–benzene, twenty-four hours with alcohol, thoroughly washed with water, and dried under reduced pressure. The holocelluloses were prepared from the same wood samples by the procedure of Van Beckum and Ritter.[12] The ethanol lignin fractions were obtained by the standardized procedure used in these Laboratories.[13]

Oxidation.—The sample (0.2–0.5 g.) was placed in a 500-cc. flask fitted with dropping funnel, nitrogen inlet, and distillation outlet.[9] Twenty grams of chromium trioxide in 50 cc. of water was then introduced from the dropping funnel, and a slow stream of nitrogen (1 to 2 bubbles per second) passed through the reaction mixture. Heating in a wax-bath, maintained at 160°, was commenced and 25-cc. portions of water were added at half-hour intervals until all the acetic acid was removed (seven additions were generally sufficient). The distillate, which comprised a solution of acetic acid plus a small amount of acidity derived from chromic acid, was transferred to an Erlenmeyer flask, boiled to remove dissolved carbon dioxide, and titrated with 0.1 *N* sodium hydroxide.

In each analysis the "corrected value" for acetic acid in the distillate was determined as follows: Two cc. excess 0.1 *N* alkali was added to the titrated solution and the solution concentrated to 2 to 4 cc. The acetate in the solution was then determined by the method of Clark.[14] This latter value for acetic acid is recorded in the tables. Blank determinations showed an acidity equivalent to 0.2 cc. of 0.1 *N* sodium hydroxide due to chromic acid.

In the oxidation of wood and holocelluloses 1 to 2 g. samples were taken and oxidized with a solution of 50 g. of chromium trioxide in 70 cc. of water.

Re-ethanolysis of Spruce Ethanol Lignin.—Spruce ether-soluble ethanol lignin (9.7 g.) dissolved in 350 cc. of 2 % ethanolic hydrogen chloride was refluxed forty-eight hours in an atmosphere of carbon dioxide. The resulting solution was neutralized with the calculated amount of sodium bicarbonate, filtered and the filtrate concentrated under reduced pressure to 50 cc. This solution was then added in a fine stream to 1500 cc. of petroleum ether (b. p. 60–70°) with rapid stirring, and the amorphous precipitate removed by filtration, giving a brownish powder (6.4 g.). The petroleum ether filtrate was evaporated under reduced pressure, the residual oil dissolved in 25 cc. of benzene, and the benzene distilled to remove any adhering petroleum ether. The process was repeated and the residual oil brought to constant weight under reduced pressure at 70°, removal of the solvent being facilitated by bubbling carbon dioxide through the oil during this process. After a total evaporation time of twelve hours the material reached a constant weight of 3.9 g. The samples for analysis and oxidation were aliquots of this material. 71.2 mg. of this oil was dried thirty hours in an oven at 105°. The final weight was 52.6 mg.; the true yield of oil was, therefore, 2.9 g.

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Summary

1. Chromic acid oxidation of oxygenated side-chain phenylpropane derivatives related to lignin yielded 80 to 95% of the theoretical amount of acetic acid, thereby providing a method for the quantitative determination of $\overset{|}{\underset{|}{\text{—C}}}\text{—CH}_3$ groupings in such products.

2. Oxidation of spruce and maple woods showed that the native lignin present in each wood contains no appreciable quantity of end methyl groups.

3. A difference between extracted, amorphous spruce and maple ethanol lignins was observed, in that the former was found to contain an appreciable quantity of —C—CH_3 groupings (one for each four or five C_6—C_3 units) whereas the latter contained few or no such groups.

4. Re-ethanolysis of spruce ethanol lignin effected an increase in the proportion of terminal methyl groups.

5. Strong experimental support is thus found for the theory of Hibbert that native lignin is characterized by the absence of terminal methyl groups and that their presence in extracted lignins is the result of intramolecular changes undergone by very reactive side chains such as are present in oxyconiferyl alcohol.

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(12) Van Beckum and Ritter, *Paper Trade J.*, **104**, 257 (1937).

(13) Patterson, West, Lovell, Hawkins and Hibbert, THIS JOURNAL, **63**, 2065 (1941).

(14) Clark, *Ind. Eng. Chem., Anal. Ed.*, **8**, 487 (1936).