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

Studies on Lignin and Related Compounds. LXV. Re-ethanolysis of Isolated Lignins[1]

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Recent reviews by Hibbert[2] have emphasized the importance in lignin chemistry of monomeric propylphenol derivatives, such as 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone,[3] 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione,[4] and 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone[5] and their corresponding 4-hydroxy-3,5-dimethoxyphenyl homologs[3,4,6] which have been isolated from the mixture of products obtained by treating wood meal with ethanolic hydrogen chloride. That these substances are true constituents of the more complex amorphous lignins is indicated by their method of isolation and by a study of the mechanism of the wood ethanolysis procedure[7] but proof of a direct relationship between monomeric and polymeric lignin products has hitherto been lacking.

Preliminary studies[7,8] have shown that re-treatment of isolated amorphous lignins with ethanolic hydrogen chloride brings about partial degradation to low molecular weight oils and a more thorough study of this effect has now been made in an effort to furnish the desired proof of a close chemical connection. A number of amorphous ethanol lignin fractions were treated and the reaction products examined by a method similar to that used in the wood ethanolysis reaction.[7,9]

Experimental Series I (Table I)

A composite sample of "mildly extracted" maple ethanol lignin, prepared by successive re-treatments (one and two hours periods) of maple wood meal with fresh portions of ethanolic hydrogen chloride,[7] was subjected to three successive re-treatments with ethanolic hydrogen chloride as outlined in Table I. After a total re-ethanolysis time of sixty-three hours a maximum conversion to 31% water-soluble distillable oils occurred, a value considerably higher than the 12% yield previously obtained[7] from a sixty-hour re-ethanolysis of total water-insoluble ethanol lignin prepared by the usual ethanolysis for forty-eight hours. It would therefore appear that the "mildly extracted" ethanol lignin, which is assumed to be more closely related to the protolignin in the wood, is depolymerized or cleaved to a much greater extent than is the ethanol lignin isolated by the usual, but more drastic, method.[9]

TABLE I

RE-ETHANOLYSIS OF A COMPOSITE SAMPLE OF MILDLY EXTRACTED MAPLE ETHANOL LIGNIN[a]

		Per cent. of original lignin recovered			
			Water-soluble distillable oils		
Treatment	Time, hr.	Ethanol lignin	Pet. ether insoluble[c]	Pet. ether soluble[c]	
1	3	78	6.4	6.6	
2[b]	12	54	2.3	12.1	
3[b]	48	50	2.0	1.6	
Total time	63				
Recovery		50 +	10.7 +	20.3	= 81.0%
			31.0%		

[a] Sample was prepared by a multiple extraction process, involving successive, one- and two-hour treatments of maple wood meal with ethanol and hydrogen chloride (2%). [b] Carried out on the ethanol lignin recovered from the previous treatments (1 and 2, respectively). [c] From previous work[10] it is known that petroleum ether solubility is associated with very low molecular weight products, in general, monomeric substances.

Experimental Series II and III (Diagram 1 and Tables II and III)

Additional re-ethanolysis experiments were carried out on the ether-insoluble (C)[11] and ether-soluble (B) portions of the total water-insoluble lignins from *both* maple and spruce woods and also on maple water-soluble, petroleum ether-insoluble ethanol lignins (F and F′).

These lignin solvent groups were isolated from a "standard"[10] water-insoluble ethanol lignin by the method outlined in the flow sheet, Diagram 1. In each case (Groups B, C, F and F′ (Diagram 1)), the lignin sample was subjected to a preliminary twelve-hour, "standard" ethanolysis treatment and the recovered water-insoluble lignin then re-treated in the same way for a further thirty-six hour period. The results of these experiments are given in Tables II (maple) and III (spruce).

These two successive re-ethanolysis treatments of the maple ether-insoluble lignins (C) (Diagram 1) resulted in a conversion of this material into a cold-ethanol insoluble lignin (E) (16.1%), and an ethanol-soluble lignin which

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[1] From a thesis submitted to the Graduate Faculty of McGill University by William B. Hewson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1942.

[2] (a) Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941); (b) Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942).

[3] (a) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509, 2204 (1939); (b) MacInnes, West, McCarthy and Hibbert, *ibid.*, **62**, 2803 (1940).

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

[5] West and Hibbert, *ibid.*, **65**, 1170 (1943).

[6] Hunter, Cramer and Hibbert, *ibid.*, **60**, 2815 (1938); Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939).

[7] Hewson, McCarthy and Hibbert, *ibid.*, **63**, 3041 (1941).

[8] West, Hawkins and Hibbert, *ibid.*, **63**, 3038 (1941).

[9] Brickman, Pyle, McCarthy and Hibbert, *ibid.*, **61**, 868 (1939).

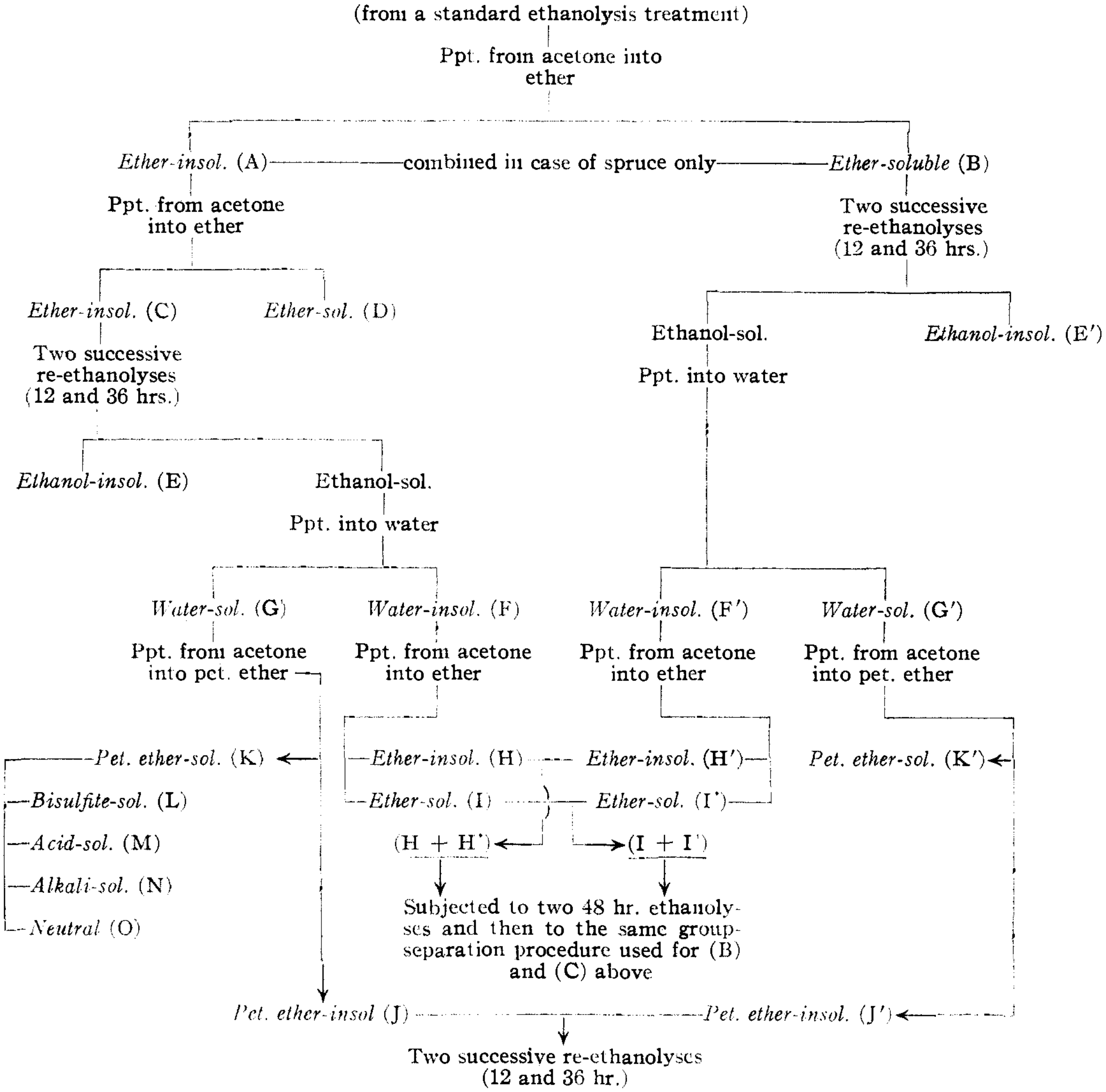
[10] Patterson, West, Lovell, Hawkins and Hibbert, *ibid.*, **63**, 2065 (1941).

[11] The capitalized letters refer in each case to the fractions isolated by the method portrayed in Diagram 1.

DIAGRAM 1

Total Water-insoluble Ethanol Lignin

(from a standard ethanolysis treatment)



was separated further into a water-soluble (G) (8.6%) and a water-insoluble (F) (58.7%) fraction. From (F) an ether-insoluble material (H) was obtained by precipitation from acetone solution into ether and this was then combined with the ether-insoluble lignin (H′) prepared from the ether-soluble maple lignin (B). The new fraction (H + H′) (Diagram 1) was then subjected to two successive 48-hour re-ethanolyses and yielded 11.6% of a cold ethanol-insoluble lignin and 2.0% of a water-soluble lignin (*cf.* (E) and (G) above).

From the water-insoluble lignins (F), obtained both from the maple ether-insoluble materials (C) and from (H + H′) on re-ethanolysis, ether-soluble fractions (I) were obtained in each case amounting to 16.9 and 19.5 per cent., respectively.

It has thus been demonstrated that, when a normal ether-insoluble lignin (C) is refluxed with ethanolic hydrogen chloride, both polymerization and depolymerization reactions take place as shown by the fact that the starting material, originally soluble in cold ethanol but insoluble in water, has given rise to both cold-ethanol-insoluble (E) and water-soluble (G) fractions. The latter (G) was separated into petroleum ether-soluble (K) and petroleum ether-insoluble (J) portions and the former (K) further separated, by the method previously described,[9] into bisulfite (L), acid (M), alkali (N) and neutral (O) fractions. 1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione and 1-(4-hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione were isolated from the bisulfite fraction (L)[4] and crystalline derivatives of 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and 2-ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone from the alkali fraction (N).[3a,12]

On the other hand, successive re-ethanolyses of the maple ether-soluble fractions (B) and of (I + I′) (Diagram 1) gave in these cases (maple) no cold-ethanol-insoluble

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(12) Hunter, Cramer and Hibbert, THIS JOURNAL, **61**, 516 (1939).

TABLE II

RE-ETHANOLYSIS OF MAPLE ETHANOL LIGNIN FRACTIONS

Re-ethanolysis lignin products[a]	Ethanol lignin fraction[a,b]				
	Ether-insoluble		Ether-soluble		Pet. ether-insoluble
	(C) g.	(H + H')[c,d] g.	(B) g.	(I + I')[c,e] g.	(J + J')[e] g.
Ethanol-insoluble (E)	16.1	11.6	0	0	0
Water-insoluble (F,F')	58.7	79.1	69.0	..	34.8
Water-soluble (G,G')	8.6	2.0	21.1	7.8	59.6
Ether-insoluble (H,H')	41.7	56.2	21.4	..	9.1
Ether-soluble (I,I')	16.9	19.5	48.5	..	25.6
Petroleum ether-insoluble (J,J')	3.5	..	11.4	5.0	43.5
Petroleum ether-soluble (K,K')	4.9	..	9.7	2.8	16.2
Bisulfite-soluble (L,L')	1.71	..	1.78	0.64	..
Bicarbonate soluble (M,M')	0.24	..	0.37	0.08	..
Alkali-soluble (N,N')	1.63	..	4.15	0.98	..
Neutral (O,O')	0.34	..	1.24	0.36	..

[a] Letters in parentheses refer to those on the flow sheet, (Diagram 1). [b] Data are given in percentage of original ethanol lignin fraction recovered as a re-ethanolysis lignin product. Successive twelve- and thirty-six-hour re-ethanolyses were used except as noted in (*d*). [c] These ethanolysis lignin fractions were obtained by combining the fractions designated by the letters. [d] Re-ethanolysis was for two forty-eight-hour periods. [e] Re-ethanolysis was for one forty-eight-hour period.

fraction (E') such as was obtained from the ether-insoluble materials ((C) and also (H + H')) but, as might be expected, the yields of water-soluble lignin (G') were much greater (21.1 and 7.8% as compared with 8.6 and 2.0%). The water-soluble fraction (G'), obtained by re-ethanolysis of the ether-soluble fraction (B), was divided into a petroleum ether-insoluble (J') and a petroleum ether-soluble (K') fraction. The latter (K'), when subjected to the same treatment as (K), yielded the same four monomolecular lignin building units. The water-insoluble lignin (F') was separated into an ether-insoluble fraction (H') (21.4% of the original ether-soluble lignin (B)) and an ether-soluble fraction (I'). The ether-soluble lignin (B) had also undergone changes involving both polymerization (typified by formation of ether-insoluble lignin) and depolymerization (typified by formation of water-soluble products) reactions, as a result of re-treatment with ethanolic hydrogen chloride. Here, however, in the case of the ether-*soluble* lignin, depolymerization has taken place to a greater extent than was the case with the more complex ether-*insoluble* maple ethanol lignin.

Examination of Table II shows that re-ethanolysis of the water-soluble petroleum ether-insoluble maple lignin (J + J') (Diagram 1) for successive periods of twelve and thirty-six hours also brings about both polymerization and depolymerization reactions, in that both water-insoluble (34.8%) and petroleum ether-soluble (16.2%) fractions are obtained.

The increasing yields of petroleum ether-soluble lignins obtained by re-ethanolysis of the increasingly soluble, ether-insoluble (C), ether-soluble (B) and petroleum ether-insoluble (J + J') fractions (4.9, 9.7 and 16.2%, respectively) indicate a decreasing complexity in these groups, the more soluble of which are thought to resemble more closely the protolignin in the wood, and the less soluble the more complex polymerization products.

The results obtained by the re-ethanolysis of *spruce* ethanol lignin fractions are summarized in Table III and illustrate the fact that also with this wood both polymerization and depolymerization changes are induced by the action of ethanolic hydrogen chloride. From spruce ether-insoluble lignin (C) (Diagram 1) a high yield of cold-ethanol-insoluble (E) material was obtained (30.4% for spruce as compared with 16.1% for maple)—a phenomenon which may be regarded as strictly in conformity with the greater difficulty of removing lignin from spruce wood. It seems probable that the ethanolysis of spruce wood meal is accompanied by rapid formation of an insoluble polymer which tends to occlude the remaining protolignin and thus hinder its extraction. The difference in behavior between spruce and maple lignins is apparently due to the freedom, in the former, of the nuclear position ortho to the phenol hydroxyl group.

TABLE III

SUCCESSIVE RE-ETHANOLYSES OF SPRUCE WOOD ETHANOL LIGNIN FRACTIONS FOR 12 AND 36 HOURS, RESPECTIVELY

Re-ethanolysis lignin product[a]	Ethanolysis lignin fraction,[a,b] g.	
	Ether-insoluble (C)	Ether-soluble (B + D)
Ethanol-insoluble (E,E')	30.4	1.0
Water-insoluble (F,F')	58.7	84.0
Water-soluble (G,G')	3.3	7.8
Ether-insoluble (H,H')	22.0	17.1
Ether-soluble (I,I')	36.8	59.5
Petroleum ether-insoluble (J')	..	2.4
Petroleum ether-soluble (K,K')	..	5.4
Bisulfite-soluble (L,L')	..	1.29
Bicarbonate-soluble (M,M')	..	0.08
Alkali-soluble (N,N')	..	2.54
Neutral (O,O')	..	0.65

[a,b] See footnotes (*a*) and (*b*) in Table II.

A comparison of the results given in Tables II and III also shows that the ether-insoluble and ether-soluble spruce lignins investigated yielded smaller water-soluble fractions (G, 3.3%, G', 2.8%) than did the maple (8.6% and 21.1%). This spruce ether-soluble lignin (B + D) (Diagram 1) is also converted in 1% yield into a cold-ethanol-insoluble material, this latter type of solvent-insoluble product not being obtained by re-ethanolysis of a *maple* ether-soluble lignin.

As in the case of maple lignin, the water-soluble spruce lignin (G′) could be separated into a petroleum ether-insoluble (J′) and a petroleum ether-soluble (K′) fraction and the latter separated further into a bisulfite (L′), an acid (M′), an alkali (N′) and a neutral (O′) fraction. From the bisulfite and alkali fractions 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione and 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, respectively, were isolated and identified by the usual methods.[3]

Thus re-ethanolysis of both spruce and maple ethanol lignin fractions yields the same products as isolated by use of the standard wood ethanolysis procedure and there would seem to be no doubt but that the extraction of lignin by the action of ethanolic hydrogen chloride involves the previously-discussed[7] concurrent polymerization-depolymerization changes. The amount of polymerization is evidently greater, and the depolymerization less, in spruce (a gymnosperm) than in maple (an angiosperm). The fact that 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione and 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone from spruce wood and these two derivatives together with their 4-hydroxy-3,5-dimethoxyphenyl homologs from maple wood are the only, as yet, isolable cleavage products of each ethanol lignin fraction indicates that they are either ***primary*** cleavage products or, as now seems more probable, stabilized end-products formed from much more reactive lignin progenitors or units. Hibbert has recently suggested certain chemical structures for the building units of lignin[2b] and favors a polymeric form of 1-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-propanone as best in accordance with the experimental facts, but points out that such structures cannot account for the formation of the 1,2-diketones.

A more satisfactory hypothesis would now seem to consist in the assumption, based on as yet unpublished work, that lignin is made up in greater part of units of the hydroxy- and dihydroxyconiferyl alcohol types united by oxygen linkages.[2b]

Acknowledgment.—The authors gratefully acknowledge the kind financial assistance accorded them by the Canadian Pulp and Paper Association.

Summary

1. Successive re-ethanolyses of ethanol lignins extracted from maple wood under very mild conditions, namely, short-period successive re-ethanolyses, bring about depolymerization to low molecular weight units to a much greater extent than does similar treatment of ethanol lignins isolated by the more drastic conditions hitherto employed by Hibbert and co-workers in ethanolysis extractions of lignin.

2. The results obtained by the re-ethanolysis of maple and spruce ethanol lignins support the theory that the action of ethanolic hydrogen chloride on wood involves both polymerization and depolymerization changes.

3. Depolymerization of isolated ethanol lignins by the action of ethanolic hydrogen chloride yields the same lignin building units as are obtained by use of the customary wood ethanolysis procedure, *viz.*, 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione; 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and, in addition, for hardwoods only, their 4-hydroxy-3,5-dimethoxyphenyl homologs.

4. A direct relationship between these simple propylphenol units and the more complex ethanol lignins is established by the isolation of the former from the latter by ethanolysis.

MONTREAL, CANADA RECEIVED FEBRUARY 23, 1943

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

Studies on Lignin and Related Compounds. LXVI. The Ethanolysis of Maple Wood

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In previous communications[1,2,3] descriptions were given of methods for the isolation of water-soluble ethanolysis products from spruce and maple woods. These "water-soluble oils" represented a mixture of distillable oils (essentially monomeric) and non-distillable resinous material. The presence of the resins was found to interfere with the fractionation of the oils and to facilitate their decomposition, due to their heat sensitivity, into non-distillable products.[4]

An account is now presented of an improved procedure whereby resin formation is minimized and the monomolecular water-soluble ethanolysis products isolated in a purer state. As a consequence, two new components have been isolated from the bisulfite fraction from maple.[5] In addition new components, representing approximately

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(1) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509 (1939).

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

(3) Brickman, Pyle, McCarthy and Hibbert, *ibid.*, **61**, 868 (1939).

(4) Levi and Hibbert, unpublished results.

(5) Kulka and Hibbert, THIS JOURNAL, **65**, 1189 (1943).