periment gave the corresponding ethyl ether; yield 10%; m. p. 50–51° (no mixed melting point depression).

(C) Action of Sodium Carbonate in Dioxane–Water Solution.—β-Acetoxypropioveratrone (1.2 g.) was dissolved in aqueous dioxane (1:1) (100 cc.) containing sodium carbonate (2 g.). After standing at room temperature for fourteen hours, the mixture was neutralized with dilute acetic acid and then extracted with benzene. On evaporation of the benzene a crystalline residue resulted; yield, 0.60 g. (60%). Alternate recrystallizations from ether and then from methanol gave a pure, crystalline product which corresponded in its analyses to the ethylene oxide (V); m. p. 93–94°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.4; H, 5.77; OCH_3, 29.8; mol. wt., 208. Found: C, 62.9; H, 5.80; OCH_3, 29.7; mol. wt., 225 (Rast).

This product formed a crystalline 2,4-dinitrophenylhydrazone; m. p. 182–183°.

Anal. Calcd. for $C_{17}H_{16}O_7N_4$: C, 52.2; H, 4.12; OCH_3, 15.9. Found: C, 52.1; H, 4.56; OCH_3, 15.7.

Acknowledgment.—The authors wish to thank the Canada Pulp and Paper Association for their kind financial assistance rendered in the form of a scholarship granted to one of them (K. A. W.).

Summary

1. β-Hydroxypropioveratrone has been synthesized and its properties studied, especially under conditions of ethanolysis.

2. Under the conditions customarily employed in wood ethanolysis, this product undergoes quantitative conversion into β-ethoxypropioveratrone.

3. Its acetyl derivative, β-acetoxypropioveratrone, is converted to β-alkyl ethers by the action of cold alcoholic potassium hydroxide.

4. The bearing of these results on the structure of lignin is discussed.

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

Studies on Lignin and Related Compounds. LVI. Stability of Lignin Building Units and Ethanol Lignin Fractions toward Ethanolic Hydrogen Chloride

BY KENNETH A. WEST, W. LINCOLN HAWKINS AND HAROLD HIBBERT

Two types of product have been obtained by the ethanolysis of spruce and maple woods. The first group includes monomeric propyl phenol "lignin building units"[1]; two of these monomers, α-hydroxypropiovanillone and -syringone, have been assumed to undergo etherification during ethanolysis with formation of the ethoxy derivative actually isolated from the reaction product. The second group consists of various amorphous lignin fractions separable by solvent fractionation methods.[2]

A study of these fractions has shown their pronounced tendency to polymerize under the influence of heat[3] but no evidence of depolymerization in these cases was reported. A previous attempt using an acetylated oak lignin fraction[4] gave a 36% yield of oils on ethanolysis. In order to determine the relationship existing between the amorphous lignin fractions[2] and the monomeric C_6–C_3 compounds, samples of each of the lignin fractions were subjected to ethanolysis conditions. The present paper is concerned with the results of this investigation.

The prolonged action of 2% ethanolic hydrogen chloride on the C_6–C_3 building units isolated by ethanolysis of various woods under the same conditions as used in all previous ethanolyses has been investigated in order to determine the stability of these products as well as their tendencies toward polymerization. The modified technique for separating the lignin "distillable oils," described in a recent communication,[2] has been followed in the isolation of the various products.

The fact that vanilloyl and syringoyl methyl ketones obtained from the bisulfite-soluble fraction of the ethanolysis oils are readily synthesized by mild oxidation from α-hydroxypropiovanillone and its syringyl analog, respectively, suggests the possibility that these diketones may have been formed in this manner during ethanolysis (in spite of efforts to maintain an oxygen-free atmosphere). However, both α-hydroxypropiovanillone and α-hydroxypropiosyringone were found to be readily convertible into their corresponding α-ethoxyethers without any evidence of oxidation to diketones. Thus the latter are primary prod-

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(1) For a comprehensive review, see Hibbert, "Status of the Lignin Problem," *Paper Trade J.*, **113**, no. 4, 35 (1941).

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

(3) Lovell and Hibbert, unpublished results.

(4) Peniston, McCarthy and Hibbert, THIS JOURNAL, **61**, 530 (1939).

TABLE I

REACTION OF LIGNIN BUILDING UNITS AND THEIR DERIVATIVES WITH 2% ETHANOLIC HYDROGEN CHLORIDE

	Lignin building unit	Concn., %	Percentage yield of Polymer	Percentage yield of Monomer	Monomer identified as
(1)	α-Hydroxypropiovanillone	0.2	4	90	α-Ethoxypropioveratrone
		.6	13	83	α-Ethoxypropioveratrone
		1.0	20, 18[a]	71, 76[a]	α-Ethoxypropioveratrone
		4.0	33	60	α-Ethoxypropioveratrone
(2)	Vanilloyl methyl ketone	0.2	4	91	Vanilloyl methyl ketone
		.6	9	88	Vanilloyl methyl ketone
		1.0	13	83	Vanilloyl methyl ketone
		4.0	30	65	Vanilloyl methyl ketone
(3)	α-Acetoxypropiovanillone	4.0	20	74	....
(4)	Mixture of (1) and (2)	0.2(1), 0.1(2)	4	90	....
(5)	α-Hydroxypropiosyringone	1.0	43	55[a]	*p*-Nitrobenzoate of α-ethoxypropiosyringone
(6)	Syringoyl methyl ketone	1.0	26	73[a]	Syringoyl methyl ketone
(7)	α-Acetoxypropiosyringone	1.0	76	20[a]	*p*-Nitrobenzoate of α-ethoxypropiosyringone
(8)	Mixture of (5) and (6)	0.5(5,6)	20	80[a]	Syringoyl methyl ketone

[a] These values were obtained by the modified procedure described in the experimental section.

ucts of ethanolysis and the propyl side chains of isolated lignin building units contain the configurations —$COCHOHCH_3$ and —$COCOCH_3$. This does not exclude, however, the possibility that other configurations of the propyl side chain also may play an important role in lignin structure although such derivatives have not, as yet, been isolated and identified. Hydrogenation data[5] indicate the existence of such and some aspects of this problem have been discussed in the preceding communication.[6] The composite results of the various reactions taking place with ethanolic hydrogen chloride are summarized in Table I.

Various concentrations of α-hydroxypropiovanillone and vanilloyl methyl ketone were subjected to treatment with 2% ethanolic hydrogen chloride. Although both derivatives are relatively stable in dilute solution their stability decreases sharply at higher concentrations. It is evident that the tendency toward polymerization is least with a concentration of 0.2% of either substance, that is, a value corresponding to that based on ethanolysis yields obtained under the usual conditions of ethanolysis extraction.

While α-hydroxypropiovanillone is converted, under ethanolysis conditions, into α-ethoxypropiovanillone (identified as α-ethoxypropioveratrone) the vanilloyl methyl ketone is recovered unchanged and similar results have been obtained with the corresponding syringyl derivatives. With both series, the diketones have been found to be more stable than the α-hydroxy derivatives. In general the syringyl derivatives are less stable than their guaiacyl analogs and show a more pronounced tendency to polymerize.

Action of ethanol–hydrochloric acid on mixtures of the α-hydroxy derivatives with their corresponding diketones did not increase the tendency toward formation of polymerized products. Thus with a mixture of α-hydroxypropiosyringone and syringoyl methyl ketone, the diketone component was recovered unchanged, in almost quantitative yield, indicating no tendency toward interaction or interconversion during the ethanolysis of maple wood.

In the guaiacyl series, α-acetoxypropiovanillone is found to be considerably more stable than the corresponding α-hydroxy derivative under ethanolysis conditions, which is in agreement with an earlier observation that reconversion to monomers proceeds readily in the case of an acetylated lignin.[4] With the corresponding syringyl derivatives, α-acetoxy- and α-hydroxypropiosyringone, the reverse is true, and, at the present time, no explanation for this anomaly can be offered. Both α-acetoxy derivatives are converted to the corresponding α-ethyl ethers under ethanolysis conditions.

This work was extended to include three of the fractions obtained from maple ethanol lignin[2]: namely, a water-soluble, an ether-soluble and an ether-insoluble product, these being characterized by an increase in the degree of polymerization, and the results indicate a correlation between degree of polymerization and reconversion to monomeric (petroleum ether–acetone soluble) products, the

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(5) Harris, D'Ianni and Adkins, THIS JOURNAL, **60**, 1467 (1938); Godard, McCarthy and Hibbert, *ibid.*, **63**, 3061 (1941); Cooke, McCarthy and Hibbert, *ibid.*, **63**, 3052 (1941).

(6) West, Hawkins and Hibbert, *ibid.*, **63**, 3035 (1941).

less highly polymerized fractions undergoing reconversion to a greater extent. These results are summarized in Table II.

TABLE II

REACTION OF MAPLE ETHANOL LIGNIN FRACTIONS WITH 2% ETHANOLIC HYDROGEN CHLORIDE

Fraction of maple ethanol lignin	Concn., %	Percentage yield of		Viscosity of lignin fraction	
		amorphous lignin	low-boiling oils	before treatment	after treatment
I Water-soluble	0.5	72	30	389	538
II Ether-soluble	.5	75	22	469	541
III Ether-insoluble	.5	87	12	600	...

Due to the limited amounts of lignin fractions available for this work, no attempt was made to isolate and identify specific products. However, the procedure used to isolate the low-boiling "distillable oils" is identical with that described for the isolation of ethanolysis oils by the modified ethanolysis technique as adapted to fractionation of lignin.[2] The crude oils recovered in this way were shown to be volatile to the extent of 87%. Simultaneously with reconversion into distillable products, the amorphous lignins isolated were found to be more highly polymerized, as shown by viscosity determinations, than the original materials. It would seem from these results that more complex polymerization–condensation polymers are actually formed, during the ethanolysis of wood, either from monomers initially present, or from low molecular weight polymers.

Experimental

Ethanolysis of Lignin Building Units.—The ethanolysis of α-hydroxypropiovanillone is given in detail as an example of the procedure used throughout this work. In certain cases, where large amounts of the particular lignin building units were not available, stability determinations were carried out using only 0.15 g. of material. Such small scale runs, however, gave results comparable to those obtained when larger quantities were employed.

α-Hydroxypropiovanillone (1.00 g.) was refluxed with 2% ethanolic hydrogen chloride (500 cc.) in an atmosphere of carbon dioxide for forty-eight hours in an all-glass apparatus. The reaction mixture was cooled, neutralized with sodium ethoxide, the solvent removed under reduced pressure and the residue taken up in chloroform (5 cc.). The chloroform solution was filtered to remove inorganic salts and the amorphous lignin-like product precipitated by pouring the filtrate, in a fine stream, into 30–50° petroleum ether (5 cc.). It was removed by centrifugation and the supernatant liquor taken to dryness. The residual reddish oil was dissolved in chloroform and again precipitated into 30–50° petroleum ether. A small amount of amorphous precipitate was removed as above and combined with that obtained previously; yield, 4%, based on weight of starting material.

On removal of the solvent from the petroleum ether–chloroform solution left after the second precipitation, a golden-colored oil remained which on methylation with diazomethane gave a white, crystalline product; m. p. 81–82°; mixed melting point with authentic α-ethoxypropioveratrone showed no depression; recovery 90%, based on α-hydroxypropiovanillone.

A modified procedure in which the neutralized reaction mixture was concentrated, filtered, and then precipitated directly into 30–50° petroleum ether gave values, both for the percentage recovery of α-hydroxypropiovanillone and for yield of amorphous product, agreeing closely with the first procedure.

Ethanolysis of Maple Ethanol Lignin Fractions.—Each of the maple ethanol lignin fractions was treated as follows. The **water-soluble** fraction (1.00 g.) was refluxed with 2% ethanolic hydrogen chloride (200 cc.) in an atmosphere of carbon dioxide for forty-eight hours in an all-glass apparatus. The reaction mixture was cooled, neutralized with sodium ethoxide and the solvent removed under reduced pressure in an inert atmosphere at a temperature below 25°. The residual amorphous product was dissolved in acetone (10 cc.) and the inorganic salts removed. Precipitation of the filtrate into 30–50° petroleum ether yielded an amorphous lignin. This was removed by centrifugation and reprecipitated from acetone into petroleum ether; yield, 0.720 g. or 72% recovery.

The petroleum ether–chloroform liquors from both precipitations were combined and the solvents removed leaving a reddish oil; yield, 0.304 g. or approximately 30% conversion to petroleum ether–soluble oils.

Acknowledgment.—The authors wish to thank the Canadian Pulp and Paper Association for their kind financial assistance, rendered in the form of a scholarship granted to one of them (K. A. W.).

Summary

1. α-Hydroxypropiovanillone and α-hydroxypropiosyringone are converted into their corresponding α-ethoxy ethers by the action of 2% ethanolic hydrogen chloride. Under the same conditions vanilloyl and syringoyl methyl ketone are recovered unchanged.

2. α-Hydroxypropiovanillone and vanilloyl methyl ketone are increasingly unstable to 2% ethanolic hydrogen chloride with increase in their concentrations.

3. Vanilloyl and syringoyl methyl ketones are more stable toward ethanolic hydrogen chloride than are α-hydroxypropiovanillone and -syringone and are not formed from the latter during the usual ethanolysis extraction of wood.

4. The guaiacyl derivatives are more stable under conditions of ethanolysis than their syringyl analogs.

5. Maple ethanol lignin (various fractions) was shown to undergo reconversion into simpler

products by the action of ethanolic hydrogen chloride, the extent of the reconversion decreasing with increasing complexity of the lignin fraction.

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

Studies on Lignin and Related Compounds. LVII. Mechanism of the Ethanolysis Reaction

BY WILLIAM B. HEWSON, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

By treating maple wood with ethanol–hydrogen chloride, 30% of the lignin (Klason) can be isolated as water-soluble "distillable oils" (containing "lignin building units" of the propylphenol type[1]) while the remainder of the lignin either is isolated as a water-insoluble amorphous material, or else remains in the wood. In the present investigation an attempt was made to remove *all* of the lignin from wood in the form of "distillable oils" or, failing this, to ascertain the factors interfering with such an accomplishment.

Accordingly, maple woodmeal was treated, under various conditions, with ethanol and hydrogen chloride, the ethanol reaction mixture separated, and the woodmeal residue examined for unremoved lignin. The ethanol solution was neutralized, concentrated and poured into water, and the insoluble lignin removed. Concentration of the aqueous solution brought about separation of the "lignin tar," while benzene extraction of the aqueous solution yielded the water-soluble lignin or crude "distillable oils."

An attempt (Table I) was first made to decrease the proportion of residual lignin (Klason), amounting to about 30% when forty-mesh maple woodmeal was used,[2] by increasing the surface area of the wood by grinding in a ball mill. This effected only a slight improvement in lignin removal and no marked change in yield of "distillable oils" (Expts. 9–11). Results with maple wood in the form of "Asplund" fiber, produced by disk grinding[3] of maple chips (in which the middle lamella lignin[4] should be freely accessible to the extractant), gave a similar negative result (Expt. 12). A slightly higher yield of "distillable oils" was obtained in one case (Expt. 13) in which a somewhat larger solvent-to-wood ratio was used, a factor known to bring about this effect.[5] In Expt. 15, using ordinary woodmeal (40 mesh), the ethanolysis was carried out with simultaneous grinding in a ball mill and using a higher acid concentration to compensate for the lower temperature conditions. The yield of "distillable oils" was much lower. No change was found in the ethanolysis of younger wood, for example one year old maple woodmeal (Expt. 14). Factors other than the physical nature of the wood thus appear to be operative in controlling the delignification and yield of "distillable oils."

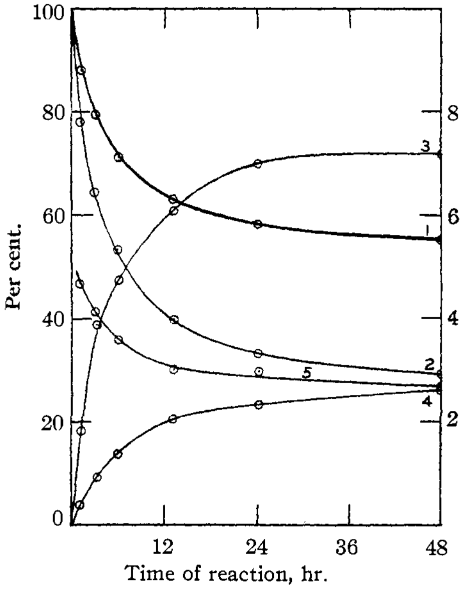

Fig. 1.—(1) Yield of residual wood; (2) original lignin in residual wood; (3) original lignin isolated as ethanol lignin and "lignin tar"; (4) original lignin isolated as "distillable oils"; (5) ratio of (ethanol lignin + "lignin tar")/"distillable oils," scale on right.

In Expts. 1–6, Fig. 1, the ethanolysis reaction was carried out for varying periods of time (1–48 hr.). The residual lignin (Curve 2) decreased progressively to a final constant value, equal to about

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[1] See review by Hibbert, *Paper Trade J.*, **113**, no. 4, 35 (1941).

[2] Brickman, Pyle, McCarthy and Hibbert, THIS JOURNAL, **61**, 868 (1939).

[3] Asplund, U. S. Patent 2,008,892, July 23 (1935).

[4] Bailey, *Ind. Eng. Chem., Anal. Ed.*, **8**, 52 (1936).

[5] K. A. West, Hawkins and Hibbert, unpublished results.