angiosperms gives yields of a mixture of vanillin and syringaldehyde amounting to 25–45% (Klason lignin basis).

3. In the case of the dicotyledons (maple, aspen, sassafras, jute) the yield is 40–45%, and the ratio of vanillin to syringaldehyde about 1:3. With the monocotyledons (rye straw, corn cobs, bamboo) the yield is lower (25–31%) and the ratio of the two aldehydes about 1:1.

MONTREAL, CANADA RECEIVED JULY 30, 1941

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

Studies on Lignin and Related Compounds. LX. Hydrogenation Studies on Maple Ethanolysis Products (Part 1)

BY LLOYD M. COOKE,[1] JOSEPH L. MCCARTHY AND HAROLD HIBBERT

By treating maple wood with ethanol–hydrogen chloride, Hibbert and co-workers have been able to isolate α-ethoxypropiovanillone,[2] I (Fig. 1), vanilloyl methyl ketone,[3] V (Fig. 1), and their syringyl homologs,[2,3] as well as amorphous lignin fractions which are differentiated by solubility and chemical characteristics.[4] Simultaneously with the isolation of these propylphenol "lignin building units," Harris, D'Ianni and Adkins[5] obtained 4-*n*-propylcyclohexanol, III (Fig. 1), 4-*n*-propylcyclohexanediol-1,2, IV (Fig. 1), and 3-(4-hydroxycyclohexyl)-propanol-1, IX (Fig. 1), by the high-pressure catalytic hydrogenation of a methanol lignin isolated from aspen wood. In view of the close structural relationship apparently existing between the products of lignin ethanolysis and of lignin hydrogenation, a study of the hydrogenation of (a) certain monomolecular constituents of maple lignin ethanolysis products; and of (b) the amorphous maple lignin ethanolysis fractions was undertaken. This paper deals with the hydrogenation of the former and development of a general quantitative technique applicable to small amounts (10–15 g.) of ligneous materials.

The hydrogenation of propylphenol type substances may be expected to occur in a stepwise manner, the individual changes proceeding to a degree determined by the reactivity of the grouping in a particular environment and by catalyst specificity. For example, with vanillin (possibly originating during ethanolysis of wood by cleavage from lignin propylphenol-type substances), high-pressure hydrogenation over copper chromite appeared to bring about a stepwise reduction[6] of the aldehyde to the alcohol, the alcohol to the hydrocarbon, cleavage of the methoxyl grouping, and finally saturation of the ring, to give methylcyclohexanol. Similarly with vanilloyl methyl ketone (V), the work of Adkins and co-workers[7] indicates that with copper chromite catalyst at 250° and 300 atmospheres of hydrogen pressure, its reduction can be expected to proceed rapidly to give 4-*n*-propylcyclohexanol (III) as the major final product, the formation possibly taking place through intermediates VI or IV, or both (Fig. 1).

However, in the case of α-ethoxypropiovanillone (I) there appear to be no good literature examples indicating the probable course of its hydrogenation, although the final formation of 4-*n*-propylcyclohexanol (III), perhaps taking place through 4-*n*-propylcyclohexanediol-1,2 (IV) or else through II or VI (Fig. 1), seems probable.

To determine the actual course followed, α-ethoxypropiovanillone (I) was hydrogenated over copper chromite catalyst at 250° at a hydrogen pressure of 5000 lb./sq. in. and the reaction products (Table I) isolated and identified by use of the new, generally applicable, small-scale technique. The large amount of water and the low yields of methanol and ethanol indicate the probable partial occurrence of reactions of types I → II → III and I → IV → III (Fig. 1) to produce methane[8] and ethane followed by the hydrogenolysis of the newly-formed hydroxyl groups to give

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[1] This paper is part of a thesis submitted to the Faculty of Graduate Studies, McGill University, by Lloyd M. Cooke in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1941.

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

[3] Brickman, Pyle, Hawkins and Hibbert, *ibid.*, **62**, 986 (1940).

[4] (a) Brickman, Pyle, McCarthy and Hibbert, *ibid.*, **61**, 868 (1939); (b) Patterson, West, Lovell, Hawkins and Hibbert, *ibid.*, **63**, 2065 (1941); (c) Lovell and Hibbert, *ibid.*, **63**, 2070 (1941).

[5] Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938).

[6] Godard, Ph.D. thesis, McGill University, 1941.

[7] Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937.

[8] (a) Wojcik and Adkins, THIS JOURNAL, **55**, 1293 (1933); (b) Wojcik, Covert and Adkins, *ibid.*, **55**, 1669 (1933).

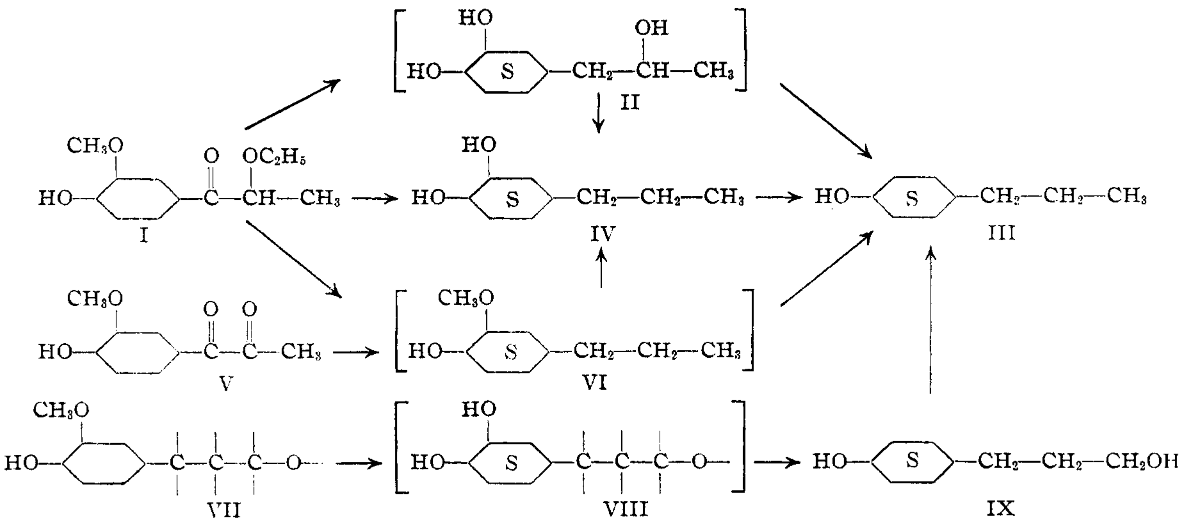

Fig. 1.—Possible steps in hydrogenation of propylphenol lignin units.

water and a methylene grouping.[9] In lignin hydrogenation,[6] these gaseous hydrocarbons are formed to the extent of at least ten per cent. of the weight of lignin treated, and originate, presumably, either through the above type of cleavage of alkoxyl groupings or else by splitting of -C-C- linkages in the side chain of propylphenol lignin building units. The apparent ease with which the ethoxyl grouping is cleaved from α-ethoxypropiovanillone, I→IV→III or I→VI→III (Fig. 1), is probably due to its proximity to an aromatic ring, judging from the emphasis placed by Adkins[7] on the fact that phenyl, hydroxyl, carboxyl, carbalkoxyl, and ethylenic groupings all tend to labilize adjacent -C-O- linkages toward hydrogenolysis.

TABLE I

HYDROGENATION PRODUCTS FROM α-ETHOXYPROPIOVANILLONE

Product	Yields, g.	Yield, %[a]	Yield, % of theoretical[b]
Methanol	1.15[c]	7.66	55
Ethanol	2.50[c]	17.20	86
Water	1.57[c]	10.40	130
4-*n*-Propylcyclohexanol	7.00[d]	46.59	78
Residue	0.60	4.06	

[a] Calculated on weight of original α-ethoxypropiovanillone. [b] Based upon reaction I → VI → III (Fig. 1). [c] Determined by quantitative analyses. [d] Isolated by distillation; characterized by physical properties and derivatives.

The formation of 4-*n*-propylcyclohexanol as the major reaction product definitely establishes the interrelationship (Fig. 1) existing between the products of lignin hydrogenation and lignin ethanolysis. Although the yield was only 78%, no cyclohexane derivatives containing either ethoxyl or isopropyl groupings could be found in the reaction mixture. This fact suggested that intermediates of the general type of II, IV and VI must exist only transitorily in the reaction mixture and that, in general, an ethoxyl grouping in the β-position to an aromatic ring evidently undergoes hydrogenolysis so readily that *all* groupings in the side chains of the simple propylphenol lignin building units isolated thus far may be expected to undergo ready reduction to the saturated propyl derivative, 4-*n*-propylcyclohexanol. Since no cyclohexanediol-1,2 derivative was obtained, it is possible the guaiacyl nucleus is not the precursor of the 4-*n*-propylcyclohexanediol-1,2 which is found, as shown in the following communication, among the hydrogenation products from maple ethanol lignin. This conclusion is based upon the fact that whereas the glycol is obtained (2–4%) by hydrogenation of hardwood lignins which contain both the syringyl and guaiacyl nuclei[10] none of this compound is obtained from α-ethoxypropiovanillone, which contains the guaiacyl nucleus alone. The non-quantitative yield of 4-*n*-propylcyclohexanol is probably due to partial carbon–carbon hydrogenolysis of the side chain of the propylphenol lignin units although little information is available in the literature indicating the degree to which such reactions proceed.

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(9) (a) Connor and Adkins, THIS JOURNAL, 53, 1091 (1931); (b) Covert, Connor and Adkins, *ibid.*, 54, 1651 (1932).

(10) Peniston, Ph.D. Thesis, McGill University, 1939.

The relationships existing during hydrogenation between 4-*n*-propylcyclohexanol and the lignin hydrogenation product,[5] 3-(4-hydroxycyclohexyl)-propanol-1 (IX), are also of interest, especially in view of the probability of the existence in lignin of propylphenol derivatives with terminal oxygen linkages on the propyl side chains.[11] The latter (IX) was synthesized by the method of Bowden and Adkins[12]

For purposes of identification the 3-(4-hydroxycyclohexyl)-propanol-1 was oxidized to the keto acid[5] and the yield increased to 50% (from the 25% previously reported) by reducing the time of chromic acid oxidation from twelve[5] to seven hours. The keto acid was readily convertible to the easily-purified, crystalline semicarbazone derivative (m. p. 201–202°), whereas difficulties were encountered both by Adkins and the present authors in the use of the 2,4-dinitrophenylhydrazone derivative as reference compound.

3-(4-Hydroxycyclohexyl)-propanol-1 (IV) on hydrogenation under the above conditions gave, in a preliminary experiment, 4-*n*-propylcyclohexanol (III) in an indicated yield of around 60%, thus demonstrating the partial instability of the former under the conditions of lignin hydrogenation, and pointing to the existence in lignin of propylphenol derivatives with terminal oxygen linkages in considerably greater proportions than indicated by the quantities of 3-(4-hydroxycyclohexyl)-propanol-1 actually isolated.[5]

Experimental

Hydrogenation of α-Ethoxypropiovanillone.—α-Ethoxypropiovanillone (15 g.), obtained from spruce wood by ethanolysis according to the method of Hunter, Cramer and Hibbert,[2] was dissolved in 155 cc. of dioxane and hydrogenated over copper chromite (8 g.) at 250° with an initial hydrogen pressure of 3000 lb./sq. in. for eight hours, during which time seven moles of hydrogen per mole of compound was absorbed. The liquid contents of the bomb, after removal of the catalyst by filtration, were subjected to distillation through a Widmer column (25 × 1 cm.) at atmospheric pressure. When 50 cc. of liquid (Fraction I) had been collected (b. p. 101°), this portion of distillate was set aside for the water, methanol, and ethanol determinations. A second portion consisting entirely of dioxane (b. p. 101°, n^{25}D 1.4205) was collected and discarded. The residue (Fraction II) was then fractionally distilled at 9 mm. pressure from a Perry flask[13] and, except for a small amount (0.60 g.) of high-boiling resinous material, consisted entirely (7.00 g.) of a liquid boiling at 110–114°, n^{25}D 1.4618. The conversion of a test sample of this material to the phenylurethan (yield, *ca.* 60%) showed that it was 4-*n*-propylcyclohexanol; m. p. of the phenylurethan, 129–130°; mixed m. p. with authentic sample 129–130°.

Fraction I, upon analysis according to the procedure described below, gave the following check results: water, 1.57, 1.54, and 1.62 g.; methanol, 1.13 and 1.15 g.; ethanol 2.46 and 2.56 g. The water was determined by use of calcium carbide[14] and estimation of the liberated acetylene by titration of the copper acetylide formed according to the method of Borellini.[14d]

Determination of Methanol.[15]—The methanol content of the reaction mixture was determined as follows:

Apparatus.—The apparatus consisted of a modified Zeisel apparatus, equipped with a water-cooled reflux condenser, as described by Peniston and Hibbert.[16]

Procedure.—Samples of 80–150 mg. (equivalent to 2.4 mg. of methanol in liquids containing 2–4% methanol) were weighed into a micro container made from a 2-cm. section of 2.5-mm. (i. d.) glass tubing by sealing one end. The container with the sample and a small piece of nichrome wire were placed in the reaction flask (containing 15 cc. of hydriodic acid (b. p. 127° (760 mm.)) and 7.5 g. of analytical phenol) which was then heated to 135–140° (bath temp.). For the first five minutes the condenser was maintained at a temperature of 10–20° and a slow stream of dry carbon dioxide passed through the apparatus, after which the condenser temperature was raised to 45–50° and the carbon dioxide flow increased to 1.5 bubbles per second. Complete absorption (by a solution of trimethylamine (10%) in absolute ethanol) of the methyl iodide was obtained in forty-five to fifty minutes, the total time of operation being approximately one hour. The solvent, containing crystals of tetramethylammonium iodide, was then carefully transferred to a 50-cc. beaker (the absorption tubes being washed with ethanol containing a small amount of water, about 10%) and the combined solutions allowed to stand at room temperature for at least two hours prior to evaporation almost to dryness on the steam-bath. The residue was dried completely in a vacuum desiccator for eight hours, the solid crystalline product extracted with three 3-cc. portions of *absolute* ethanol, and the supernatant liquor removed each time through a suction filter. The solid on the filter paper was washed into the beaker with distilled water, four drops of aqueous nitric acid (1:1) added, and the iodide precipitated by the addition of excess 0.1 *N* silver nitrate, washed, dried and weighed. (One mole of silver iodide represents one of methanol.)

Determination of Ethanol and Methanol.—Using a modification of the procedure of Harris[17] the total meth-

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[11] Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941).

[12] (a) Bowden and Adkins, THIS JOURNAL, **62**, 2422 (1940). (b) See experimental section for a more detailed description of the conversion of ethyl-β-(*p*-methoxyphenyl)-propionate to β-(*p*-hydroxyphenyl)-propionic acid and a correction of the refractive index of ethyl β-(4-hydroxycyclohexyl)-propionate.

[13] Perry and Hibbert, THIS JOURNAL, **62**, 2561 (1940).

[14] (a) Ilosovay, *Ber.*, **32**, 3698 (1899); (b) Willstätter and Maschmann, *ibid.*, **53**, 939 (1920); (c) Schütz and Klauditz, *Z. angew. Chem.*, **44**, 42 (1931); (d) Borellini, *Atti mem. accad. sci. Padova*, **51**, (1934–35); (*C. A.*, **30**, 7495 (1936)).

[15] The details of development of these procedures for the determination of methanol and ethanol will be described in a subsequent publication.

[16] Peniston and Hibbert, *Paper Trade J.*, **109**, No. 17, 46 (1939).

[17] Harris, *Analyst*, **62**, 1729 (1937).

anol–ethanol content of the low-boiling fraction (water, methanol, ethanol and some dioxane) was determined as follows.

Procedure.—A sample containing 0.0–0.5 mg. mole of the alcohols (methanol and ethanol) was placed in a 100-cc. pressure bottle containing 25 cc. of water, 2.0 cc. of concentrated sulfuric acid, and a measured excess (buret) of 0.2 *N* potassium dichromate (about 15 cc.). The pressure bottle was sealed and heated on the steam-bath for thirty minutes, and a weighed quantity of ferrous ammonium sulfate (in excess of that of the unused dichromate) added. The excess of ferrous salt was back-titrated with 0.2 *N* potassium dichromate using potassium ferricyanide solution as external indicator. Under these conditions methanol and ethanol each required four equivalents of dichromate, the methanol undergoing oxidation to formic and the ethanol to acetic acid.

$$\frac{(\text{ml. } K_2Cr_2O_7)(N \text{ of } K_2Cr_2O_7)}{4\ (\text{wt. of sample})} = \text{mg. mole alcohol/g. sample}$$

Knowing the quantity of methanol that of the ethanol was ascertained by difference.

Synthesis of 3-(4-Hydroxycyclohexyl)-propanol-1.—The method of Bowden and Adkins[12] was used with the following modifications.

Preparation of β-(*p*-Hydroxyphenyl)-propionic Acid.—In Experiment I, ethyl β-(*p*-methoxyphenyl)-propionate (25 g.) was heated with constant boiling hydriodic acid (b. p. 127°, 50 cc.) at 90° for fifteen minutes in the apparatus described by Adkins[12] and gave 19 g. of β-(*p*-methoxyphenyl)-propionic acid (identified by reconversion to the ethyl ester; b. p. 126° (1.3 mm.); $n^{25}\mathrm{D}$ 1.5026).

In Experiment II (an improvement on I) ethyl β-(*p*-methoxyphenyl)-propionate (9.6 g.) was treated with 25 cc. of constant boiling hydriodic acid at 95° for forty minutes. At the end of this time *complete solution* of the ester layer had occurred. The reaction mixture was then refluxed for a further twenty minutes (bath temp., 145°). The hot solution was poured into a beaker, the product crystallizing from the aqueous solution on cooling. It was filtered and washed with ice-water; yield of yellow crystalline product, 7.5 g. (93%); recrystallized from water twice, m. p. 127–128° (Adkins,[12] 128–129°).

Preparation of Ethyl β-(4-Hydroxycyclohexyl)-propionate.—Ethyl β-(*p*-hydroxyphenyl)-propionate (39 g.), dissolved in 10 cc. of ethanol, was treated with hydrogen at 200 atmospheres and 210° over Raney nickel (5 g.) for three hours: yield, 37 g.; b. p. 114° (0.6 mm.); $n^{25}\mathrm{D}$ 1.4690; d^{25}_{25} 1.0310; molecular refractivity 53.9; theoretical 53.87. Bowden and Adkins[12] give b. p. 102–103° (0.2 mm.); $n^{25}\mathrm{D}$ 1.5661 and d^{25}_{25} 1.0309 corresponding to a molecular refractivity of 63.2.

Oxidation of 3-(4-Hydroxycyclohexyl)-propanol-1 to β-(4-Ketocyclohexyl)-propionic Acid.—β-(4-Hydroxycyclohexyl)-propanol-1 (500 mg.) dissolved in a mixture containing 1.1 g. of chromic oxide, 10 cc. of glacial acetic acid, 5.3 cc. of water and 10 cc. of benzene was shaken at room temperature for seven hours. The keto acid was isolated according to the procedure described by Adkins[5]; yield of crude acid, 257 mg. (50%). Two hundred milligrams of the keto acid was then distilled in a micro-distillation bulb at 0.025 mm. pressure, the distillate (180 mg.) solidifying to a white camphor-like material on standing, m. p. 62–64°. This material appeared to be hygroscopic. *Neutral Equivalent.* Found, 169.5, 172.1; calcd. 170.1. The semicarbazone of the keto-acid (a new derivative) was prepared as follows. The keto acid (100 mg.), dissolved in 0.8 cc. of 40% aqueous ethanol, was added to a solution of 100 mg. of free semicarbazide (m. p. 94–95°) in 1.5 cc. of a buffered (*p*H 5) aqueous solution. Precipitation occurred immediately and after two crystallizations from water the product melted at 201–202°. *Neutral Equivalent.* Found, 224; calcd., 227.2. *Anal.* Calcd. for $C_{10}H_{18}O_3N_3$: C, 52.6; H, 7.9. Found: C, 52.2, 52.4; H, 8.05, 8.1.

Hydrogenation of 3-(4-Hydroxycyclohexyl)-propanol-1.—3-(4-Hydroxycyclohexyl)-propanol-1 (8.2 g.), dissolved in 90 cc. of absolute dioxane, was hydrogenated over copper chromite (5 g.) at 250° and 5200 lb./sq. in. for sixteen hours. After removal of the catalyst by filtration, the dioxane solution was distilled (760 mm.) from a Perry flask[13] to give 6 cc. of the dioxane–water azeotrope (b. p. 87°, 18.3% H_2O) corresponding to 1.08 g. of water. After the dioxane had been removed completely, the residue was fractionally distilled[13] giving 4.04 g. of 4-*n*-propylcyclohexanol (b. p. 97–98° (7 mm.); $n^{25}\mathrm{D}$ 1.4635); 0.94 g. of 3-(4-hydroxycyclohexyl)-propanol-1 (b. p. 126° (1 mm.), solidified on standing) and 0.62 g. of a residue (which appeared to be the latter compound with a small quantity of resin); material lost (gases or low-boiling) upon hydrogenation, 1.83 g.

Acknowledgments.—The authors gratefully acknowledge the kind financial assistance accorded them by the Spruce Falls Power and Paper Company and the Canadian Pulp and Paper Association.

Summary

1. Using a copper chromite catalyst at 250° and 250 atmospheres pressure, hydrogenation of the lignin ethanolysis product, α-ethoxypropiovanillone, gives a 78% yield of 4-*n*-propylcyclohexanol, a product also obtained by direct hydrogenation of lignin under the same conditions. This observation, along with literature evidence indicating that the lignin ethanolysis product, vanilloyl methyl ketone, should yield the same substance on hydrogenation, establishes a close structural interrelationship between the propylphenol lignin building units isolated by ethanolysis and the hydrogenation products from lignin and wood.

2. The fact that neither 4-*n*-propylcyclohexanediol-1,2 nor hydroxy, ethoxyl, or isopropyl derivatives of this and of 4-*n*-propylcyclohexanes could be isolated from the hydrogenation products of α-ethoxypropiovanillone indicates that, following the initial reaction of the guaiacyl type

unit, the hydrogenation proceeds rapidly to the final stage represented by 4-*n*-propylcyclohexanol. This suggests the guaiacyl nucleus may not be the actual precursor of the cyclohexanediol-1,2 formed by hydrogenation of lignin.

3. The unexpectedly high yields of water, and correspondingly low yields of methanol and ethanol from hydrogenation of α-ethoxypropiovanillone, indicate that the alkoxyl groups cleave to give methane and ethane, in addition to the anticipated methanol and ethanol.

4. The Bowden and Adkins synthesis of 3-(4-hydroxycyclohexyl)-propanol-1 was, in general, confirmed. On hydrogenation with a copper chromite catalyst at 250° using 250 atmospheres pressure, this substance undergoes 60% conversion to 4-*n*-propylcyclohexanol, thus pointing to the existence in lignin of propylphenol derivatives with terminal oxygen linkages in considerably greater proportion than is indicated by the amounts of 3-(4-hydroxycyclohexyl)-propanol-1 actually isolated.

5. Techniques generally applicable to lignin and other organic products have been developed for the examination of small amounts of hydrogenation reaction products. Special analytical methods for methanol and ethanol are given.

MONTREAL, CANADA RECEIVED AUGUST 25, 1941

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

Studies on Lignin and Related Compounds. LXI. Hydrogenation of Ethanolysis Fractions from Maple Wood (Part 2)

BY LLOYD M. COOKE,[1] JOSEPH L. MCCARTHY AND HAROLD HIBBERT

On treatment of maple wood with ethanol–hydrogen chloride (Flow Sheet)[2] about 35% of the lignin is recovered as distillable oils containing simple derivatives of the propylphenol type[3]; and in the preceding paper[4] it was shown that such constituents as α-ethoxypropiovanillone (and probably also vanilloyl methyl ketone) are largely converted (78%) by high-pressure hydrogenation to 4-*n*-propylcyclohexanol, a substance also obtained by direct hydrogenation of a methanol lignin isolated from aspen wood.[5] The ethanolysis reaction, however, also yields amorphous lignin fractions ("B," "C," "D," "F," Flow Sheet) which differ in solubility characteristics[2,6] and the present paper deals with their high-pressure catalytic hydrogenation.

The largest maple lignin fraction, "ethanol lignin" ("B"), was first carefully studied on a large scale (109 g.) for comparison with the nature and yields of products reported by Harris, D'Ianni and Adkins[5] for the hydrogenation of aspen *methanol* lignin. The present hydrogenation reaction was carried out at 250° under 400 atmospheres pressure (copper chromite catalyst), and, by employing the fractionation procedure of those authors,[5] it was possible to isolate and identify (through solid derivatives) water, methanol, ethanol, 4-*n*-propylcyclohexanol, and 4-*n*-propylcyclohexanediol-1,2. In place of their 3-(4-hydroxycyclohexyl)-propanol-1, however, a product boiling within the same narrow range (125–127° (1 mm.)) with an empirical formula of $C_{18}H_{34}O_3$ was obtained. This, after considerable experimentation, proved to be a constant-boiling mixture, separable into the water-soluble 3-(4-hydroxycyclohexyl)-propanol-1 (b. p. 101° (760 mm.)) and an unknown water-*insoluble* component (b. p. 130–132° (1 mm.), $n^{25}D$ 1.4900; C, 80.2; H, 12.3), identification of which is in progress.

A comparison (Table I) of the yields of definitely identified hydrogenation products obtained from aspen methanol lignin[5] with those obtained in the authors' large- and small-scale experiments with ethanol lignin "B" shows a great similarity, but with the difference that ethanol maple lignin also yields water, ethanol, an unidentified component (2–3% yield) and only a *small* amount of 3-(4-hydroxycyclohexyl)-pro-

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[1] This paper represents part of a thesis submitted to the Graduate Faculty of McGill University by Lloyd M. Cooke in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1941.

[2] (a) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509 (1939); (b) Pyle, Brickman, McCarthy and Hibbert, *ibid.*, **61**, 868 (1939); (c) Patterson, West, Lovell, Hawkins and Hibbert, *ibid.*, **63**, 2065 (1941).

[3] (a) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939); (b) Brickman, Pyle, Hawkins and Hibbert, *ibid.*, **62**, 986 (1940).

[4] Cooke, McCarthy and Hibbert, *ibid.*, **63**, 3052 (1941).

[5] Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938).

[6] All ethanolysis lignin fractions discussed in this paper were obtained from *maple* wood.