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 $\alpha$-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

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[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 $\alpha$-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).

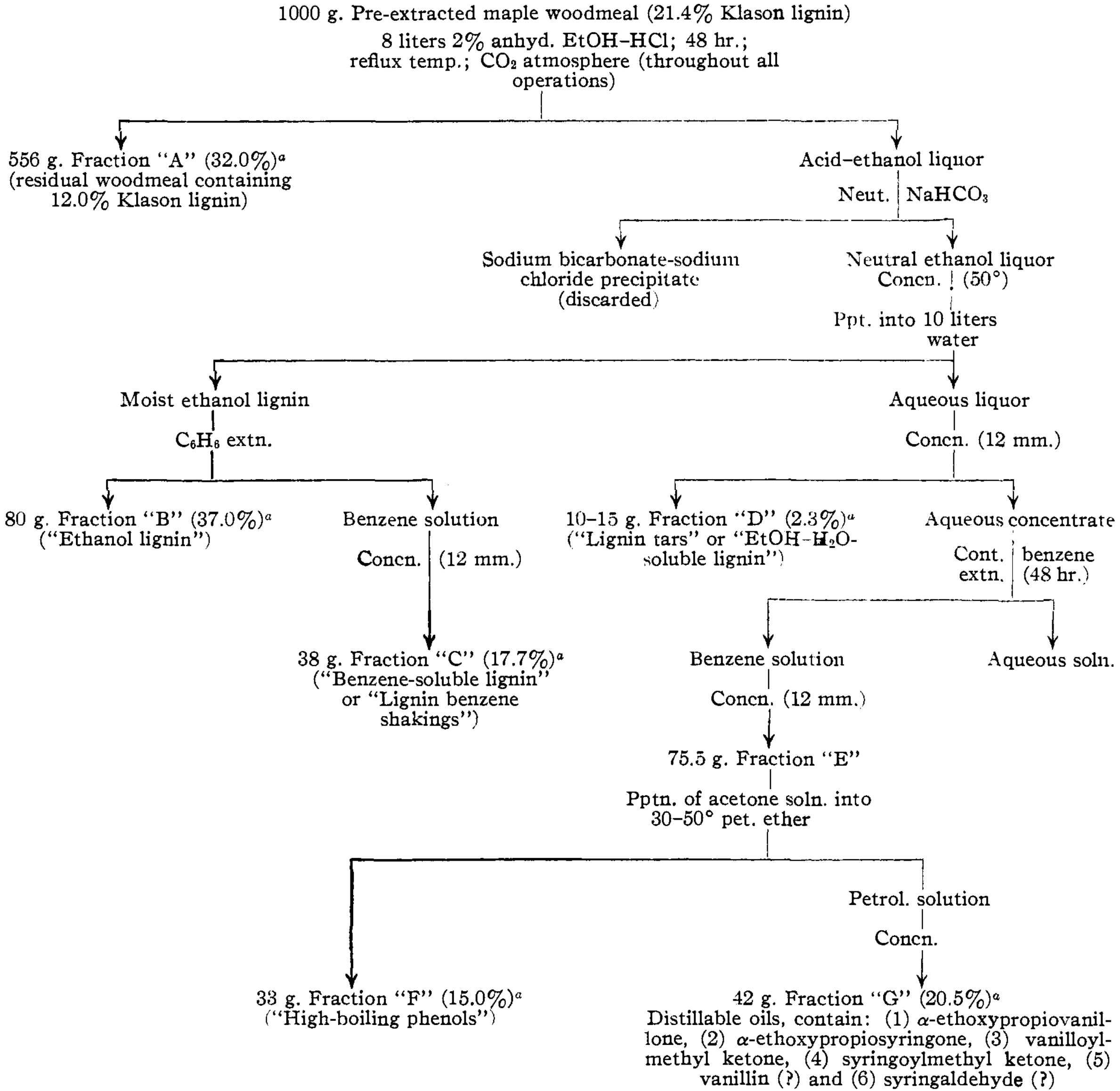
[3] (a) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939); (b) Brickman, Pyle, Hawkins and Hibbert, *ibid.*, **62**, 986 (1940).

[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.

ETHANOLYSIS OF MAPLE WOODMEAL



[a] Per cent. of original lignin (Klason) in extracted maple wood.

panol-1 (2-3% yield). The last-named component is apparently obtained in large quantity (25% yield) from methanol aspen lignin.[5] The water is probably formed by the hydrogenolysis of ether and possibly hydroxyl groups, while the ethanol is undoubtedly formed from ethoxyl groups.[2c,4] The small yield of 3-(4-hydroxycyclohexyl)-propanol-1 can at present be explained only by postulating a difference in structure between *ethanol maple* and *methanol aspen* lignin, and is doubtless the reason the constant-boiling mixture containing 3-(4-hydroxycyclohexyl)-propanol-1 was not encountered previously.[5]

Other smaller amorphous lignin fractions ("C," "D," "F," as well as "B" for a comparative standard; 10-15 g. samples) were hydrogenated under similar conditions (Table II) and the reaction products examined by the method described in the preceding communication,[4] except that the procedure was varied by carrying out a separation of the higher-boiling (b. p. > 101° (760 mm.)) hydrogenation products into water-soluble and water-insoluble fractions. The former, containing 4-*n*-propylcyclohexanediol-1,2 and 3-(4-hydroxycyclohexyl)-propanol-1, never amounted to more than 700 mg. (5%) in these investigations, and is re-

TABLE I

COMPARATIVE YIELDS OF HYDROGENATION PRODUCTS FROM LIGNINS

| Product | Maple ethanol lignin Expt. A (109 g. lignin) Yield, %[b] | Maple ethanol lignin Expt. B (15 g. lignin) Yield, %[b] | Aspen methanol lignin[a] (80 g. lignin) Yield, %[b] |
|---|---|---|---|
| Water | 7.5 | 8.7 | .. |
| Methanol | 10.0 | 13.6 | 26.5 |
| Ethanol | 5.1 | 4.9 | .. |
| 4-*n*-Propylcyclohexanol | 8.0 | 8.1 | 11.0 |
| 4-*n*-Propylcyclohexane-diol-1,2 | 1.9 | 5.4 | 3.2 |
| 3-(4-Hydroxycyclohexyl)-propanol-1 | 3.3 | | 24.0 |
| Unknown compound ($n^{25}_D$ 1.4975) | 3.3 | 2.1 | .. |
| High-boiling resin | 32.0 | 29.5 | 22.0 |
| Total | 71.1 | 72.3 | 86.7 |

[a] Data of Harris, D'Ianni and Adkins.[5] [b] Yields are expressed in weight percentage of lignin hydrogenated.

ported as "Dihydroxy propylcyclohexane derivatives" (Table II) without further separation.

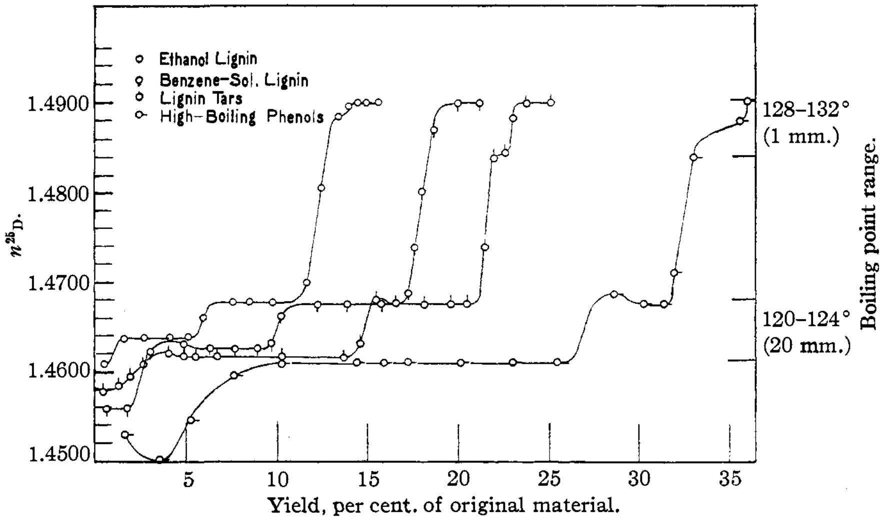


Fig. 1.—Fractional distillation of water-insoluble hydrogenation products from ethanolysis lignin fractions.

TABLE II

HYDROGENATION STUDY OF ETHANOLYSIS LIGNIN FRACTIONS

| Ethanolysis lignin product[a] | Hydrogenation conditions: Sample, g. | Hydrogenation conditions: Reaction time, hr. | Hydrogenation conditions: Hydrogen absorbed, moles/100 g. lignin | Hydrogenation products[b]: Water-soluble product Dihydroxy-propylcyclohexane derivatives, % | Hydrogenation products[b]: Water-insoluble product: Distillable oils, % | Hydrogenation products[b]: Water-insoluble product: Resin, % | Hydrogenation products[b]: Water-insoluble product: Total, % | Oils/Resins |
|---|---|---|---|---|---|---|---|---|
| B, "Ethanol lignin" | 15.0 | 16.0 | 3.9 | 5.4 | 16.0 | 29.5 | 45.5 | 0.55 |
| C, "Benzene-soluble lignin" | 12.2 | 5.0 | 3.8 | 5.2 | 27.4 | 14.8 | 42.2 | 1.9 |
| D, "Lignin tars" | 15.0 | 4.8 | 3.7 | 6.0 | 32.5 | 14.6 | 47.1 | 2.4 |
| F, "High-boiling phenols" | 9.5 | 4.0 | 3.8 | 5.9 | 42.7 | 6.0 | 48.7 | 7.1 |
| G₁, α-Ethoxypropiovanillone | 15.0 | 3.5 | 3.4 | 0.0 | 48.0 | 2.0 | 50.0 | 24 |

[a] See Flow Sheet for origin of fraction. [b] Yield of hydrogenation products expressed as per cent. of weight of lignin product.

The water-insoluble fraction, generally weighing at least 2.0 g. and containing 4-*n*-propylcyclohexanol, the unknown substance ($n^{25}_D$ *ca.* 1.4900) and high-boiling resins, was carefully distilled through a modified Podbielniak fractionating column and the results are shown graphically in Fig. 1. It can be seen that within the boiling point range of 4-*n*-propylcyclohexanol (95–97° (7 mm.)), two substantially constant boiling fractions are present ($n^{25}_D$ 1.4605 to 1.4635 and $n^{25}_D$ 1.4675) which may possibly indicate the presence of *cis-trans* isomers of this substance. The slight rise in refractive index in the initial sample of a fraction varies in degree depending upon the rate of distillation and thus is very probably of no structural consequence.

The yields of hydrogenation products from ethanol lignin ("B") were nearly the same (Table I) when the examination was carried out using either the large- or small-scale technique, thus establishing the validity of the latter. Comparison of the hydrogenated products from various lignin fractions obtained in the same ethanolysis run (Table II) shows that rate of hydrogenation increases (Column 3) as the solubility of the lignin fraction in organic solvents increases, and is especially noticeable with the less readily soluble ethanol lignin, "B." While *total* yield of water-soluble and water-insoluble hydrogenation products remains practically constant, and while the general *shapes* of the fractional distillation curves for the water-insoluble products are essentially the same, there occur with increase in solubility of the lignin fractions ("B" < "C" < "D" < "F") an increase in the yield of distillable, water-insoluble products, a decrease in non-distillable resin, and, consequently, a rapid increase in the ratio of distillable to non-distillable materials.

This relationship is highly significant when considered with respect to the extensive literature information[7] showing that the tendency for hydrogenolysis over copper chromite of –C–C–C– bonds is very slight in comparison with that of –C–O–C– linkages. That under the conditions employed in this investigation –C–O–C– hydrogenolysis occurs readily with the lignin unit, $\alpha$-ethoxypropiovanillone, has already been demonstrated.[4] Apparently with the several amorphous lignins studied a basic difference occurs in the type of linkage existing between their assumed propylphenol building units. The –C–O–C– linkage may predominate in the rapidly hydrogenated soluble lignin fractions ("F" and "G") while the –C–O–C– bond to an increasing degree may bind the units in the less soluble and less easily hydrogenated fractions ("B," "C" and "D"). Supporting this concept are the data given by Adkins[5,8] indicating that the hydrogenated resins (from methanol and alkali lignin) have essentially a hydrocarbon skeletal structure, the simplest nucleus apparently comprising fifteen carbon atoms. While the ortho-type condensation polymer structures for lignin proposed by Freudenberg[9] (two phenylpropane units connected by a dihydrofuran ring) or by Hibbert[10] (formation of furan ring) may exist in the –C–C–C– range of lignin polymers, it must be emphasized[10] that these structures are only partially applicable to hardwood lignins where the presence of the syringyl nucleus would prevent the formation of such a polymer type. The presence of the syringyl nucleus is thus probably a determining factor with respect to the amount of –C–O–C– type polymer present.

Certain hitherto inexplicable changes associated with the ethanolysis of hard- and softwoods,[11] of isolated lignins,[11,12] and of monomeric $C_6C_3$ "lignin building units"[12b] would seem to find a satisfactory explanation in the light of these assumptions. The evidence obtained from these studies of the ethanolysis reaction shows that reversible polymerization–depolymerization and irreversible polymerization reactions are involved. It is of considerable interest, therefore, that the information obtained in the present and preceding hydrogenation studies indicates the presence of –C–O–C– type linkages between the $C_6C_3$ units of the "reversible" polymers and of –C–C–C– unions in the "irreversible" polymers. Thus, with the three amorphous lignin fractions "B," "D" and "F" (possessing apparently an increasing degree of complexity[2c] connoted, as indicated in the present paper, by prevalence of the –C–C–C– type linkage) the yields of simple units on ethanolysis were 30, 22[13] and 10%, respectively (ratio, 3 : 2.2 : 1), while the respective yields of propylcyclohexane hydrogenation products were 43, 32 and 16% (3 : 2.2 : 1.1). In view of the fact that dilute mineral acids catalyze both the formation and hydrolysis of the –C–O–C– type bond (acetal, ether or ester) it is probable that the acetal-type linkage may play a conspicuous role in the ethanolysis polymerization–depolymerization reactions of lignin and lignin units.[14]

## Experimental

**Hydrogenation of Ethanol Lignin: Experiment 1.**—Ethanol lignin ("B") (15 g.) dissolved in 150 cc. of absolute dioxane was hydrogenated over copper chromite (8.8 g.) at 250° for eighteen hours with hydrogen at an initial pressure of 3400 lb./sq. in. During the reaction 3.88 moles of hydrogen (per 100 g. of lignin) was absorbed, and the dioxane solution had become colorless. A similar reaction using 90 g. of lignin was carried out in a 2500-cc. bomb, the products from the two runs combined, and the dioxane solution, after removal of the catalyst by filtration, fractionated through a 30-cm. Widmer column. A total of 145 g. of material (Fraction I) boiling from 63 to 101° (760 mm.) was collected and placed over "drierite." After removal of the remaining dioxane (760 mm.), the orange-colored residual oil (66.6 g.) was distilled from a 125-cc. Claisen flask (10–12 mm.); bath temperature

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

[8] Adkins, Frank and Bloom, THIS JOURNAL, **63**, 549 (1941).

[9] Freudenberg, "Annual Reviews of Biochemistry," Vol. VIII, 1940, p. 95.

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

[11] Hewson, McCarthy and Hibbert, THIS JOURNAL, **63**, 3041 (1941).

[12] (a) Peniston, McCarthy and Hibbert, *ibid.*, **61**, 530 (1939); (b) West, Hawkins and Hibbert, *ibid.*, **63**, 3038 (1941).

[13] Although this determination was made upon an ethanolysis lignin fraction isolated in a slightly different manner than used for Fraction "D," viscometric and solubility characteristics indicated that the two fractions were identical.

[14] It is also important to note that certain unsaturated ethers (*e. g.*, dicinnamyl ether; Meisenheimer and Link, *Ann.*, **479**, 211 (1930)) show remarkable properties with respect to formation and cleavage in the presence of dilute mineral acids. In this connection, the possible roles of coniferyl alcohol and its syringyl analog assume a new importance.

105°. The distillate was dioxane ($n^{25}$D 1.4204); the residue (Fraction II) weighed 55.5 g.

**Examination of Fraction I.**—The material boiling below 101° (760 mm.), after standing over "drierite" for three days, was fractionated carefully in a 24-inch Widmer column.

**Fraction Ia (Methanol).**—Boiling point, 63–66° (760 mm.); $n^{25}$D 1.3520; $\alpha$-naphthylurethan, m. p. 123–124°; mixed melting point, with an authentic sample, 123–124°; yield, 10.6 g.

**Fraction Ib (Ethanol).**—Boiling point, 78–79° (760 mm.); $n^{25}$D 1.3670; $\alpha$-naphthylurethan, m. p. 79–80°; mixed melting point 79–80°; yield, 5.4 g.

**Fraction Ic (Water–Dioxane).**—Boiling point, 86.9–87.2° (760 mm.); $n^{25}$D 1.4079; yield, 40 g. This fraction was shown to be a mixture of water and dioxane by removal of water with both anhydrous cupric sulfate and calcium chloride leaving pure dioxane, $n^{25}$D 1.4200. A synthetic mixture containing dioxane (50 cc.) and water (11.5 cc.) was found to distill at 87.1° with a constant refractive index (25°) of 1.4079. Since a portion of the water was probably absorbed by the "drierite," the yield of 8.0 g. of water represents a minimum value.

**Examination of Fraction II.**—The products boiling from 97.2° (7 mm.) to 185° (0.65 mm.) (21.76 g.) (Fraction II) were refractionated carefully from a 35-cc. vacuum-jacketed Widmer Claisen flask.[15]

**Fraction IIa (4-*n*-Propylcyclohexanol).**—Boiling point, 93–95° (7 mm.); $n^{25}$D 1.4630; phenyl- and $\alpha$-naphthylurethans (m. p. 129–130° and 133–134°, respectively); mixed melting point with phenylurethan from synthetic product 129–130°; yield, 7.5 g.

**Fraction IIb (4-*n*-Propylcyclohexanediol-1,2).**—Boiling point, 106–110° (1 mm.); $n^{25}$D 1.4820; $n^{60}$D 1.4709; $\alpha$-naphthylurethan, m. p. 218–219°; Adkins, 218–219°[5]; yield, 0.92 g.

**Fraction IIc (Designated as Product (X)).**—Four grams of this unidentified fraction (X) was refractionated in a Podbielniak column (90 cm. long, 5 mm. i. d., 8.5 theoretical plates) at 2.0 mm. pressure. After removal of 200 mg. of a material $n^{25}$D 1.4784, a constant-boiling product (125–127° (1 mm.)) $n^{25}$D 1.4860, was first obtained (1.2 g.) following which the distillate began to separate into two layers (wt. 1.6 g.); upper layer, $n^{60}$D 1.4895–1.4900; lower, 1.4825, indicating the presence of at least two components in the original product (X). A resinous product, b. p. above 130° (1 mm.) remained; yield, 33.0 g.

**Experiment 2.**—Ethanol lignin (250 g.) was hydrogenated over copper chromite as described in Expt. 1.

**Fraction II,** composed of products boiling above 101° (760 mm.), was dissolved in an equal volume of ether and the ether solution then extracted ten times with 75-cc. portions of water. The residual ether solution, Fraction III, was dried over sodium sulfate.

The combined aqueous extracts were concentrated to 300 cc. by distillation through an 18-inch Widmer column. The distillate, containing ether, dioxane and water, was not examined further. The aqueous residue (after saturation with sodium sulfate) was extracted continuously with ether for forty-eight hours, dried (sodium sulfate), and the ether removed (reduced pressure) leaving a viscous oil (6.8 g.) (Fraction IV).

**Fraction IV,** containing the water-soluble oils, was separated by fractional distillation (Podbielniak column) into three fractions: namely, 4-*n*-propylcyclohexanediol-1,2 ($n^{25}$D 1.4820, 1.5 g.); 3-(4-hydroxycyclohexyl)-propanol-1 ($n^{25}$D *ca.* 1.4858 (crystallized readily)) (3.1 g.); and a resin (1.49 g.). The 3-(4-hydroxycyclohexyl)-propanol-1 was identified by oxidation to $\beta$-(4-ketocyclohexyl)-propionic acid,[4] semicarbazone m. p. 201–202°; mixed melting point, 201–202°.

**Fraction III** (water-insoluble oils boiling above 101° (760 mm.)) was separated into four fractions by rapid distillation (not fractionation) from a 250-cc. Claisen flask. The following four cuts were made: Fraction IIIa, b. p. below 105° (1 mm.) (4-*n*-propylcyclohexanol); Fraction IIIb, b. p. 100–140° (1 mm.) (boiling range of Product (X)), 15.6 g.; Fraction IIIc, b. p. 140–150° (1 mm.); and Fraction IIId, residue, $n^{25}$D 1.4978, 59.2 g.

**Fraction IIIb** was refractionated in the Podbielniak column but no material corresponding in properties to Compound X (b. p. 125° (1 mm.)), Expt. 1 above, was obtained, showing that one component, 3-(4-hydroxycyclohexyl)-propanol-1, had been removed by the water extraction.

**Hydrogenation of Amorphous Non-distillable Ethanol Lignin Fractions.**—Ten to fifteen gram samples of the amorphous, non-distillable fractions isolated from the ethanolysis of maple wood (Fractions "B," "C," "D" and "F," Flow Sheet) were dissolved in 150 cc. of absolute dioxane and each hydrogenated at 250° with hydrogen at a pressure of 5000–5500 lb./sq. in. using 6–8 g. of copper chromite. The hydrogenation products were separated according to the previous method (Expt. 2) into products boiling above 101° (760 mm.) (Fraction II), water-insoluble (Fraction III) and water-soluble (Fraction IV) fractions.

**Fraction IV,** shown to contain 3-(4-hydroxycyclohexyl)-propanol-1 and 4-*n*-propylcyclohexanediol-1,2 (see above), was found in amounts below 4–5% of the total weight of material hydrogenated. Since it was impractical to fractionate 500-mg. samples, the yields of these two compounds are combined under the heading "Dihydroxy propylcyclohexane derivatives" (Table II).

**Fraction III** (generally 40–50% by weight of the starting material) was fractionally distilled through the Podbielniak column (Fig. 1.). It contained 4-*n*-propylcyclohexanol and the high-boiling resins. In addition, the presence of a compound or compounds, refractive index about 1.4900, was indicated by the nature of the fractionation curves. Approximately 100 mg. of material remained (liquid hold-up) in the column after each fractionation and this weight was added to that of the distillable portion.

The fractional distillations in the Podbielniak column were carried out at a rate of 100 mg. per hour. Initial pressures of approximately 20 mm. were gradually lowered during a fractionation period (24–36 hours) to 1 mm. pressure. Those fractions in the $n^{25}$D 1.4600–1.4700 range distilled uniformly at a temperature of 122° at 20 mm.; those in the $n^{25}$D 1.4900–1.5000 range at 130° (1 mm.). The wire spiral in the column generally became completely dry between the $n^{25}$D 1.4600–1.4700 and the 1.4900–1.5000 ranges.

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

**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. High-pressure, catalytic (copper chromite) hydrogenation of maple ethanol lignin yields water, methanol, ethanol, 4-*n*-propylcyclohexanol, 4-*n*-propylcyclohexanediol-1,2, 3-(4-hydroxycyclohexyl)-propanol-1, an apparently new, unidentified substance, and high-boiling resins in yields of 13.6, 5.0, 8.7, 8.1, 1.9, 3.3, 2.1 and 29.5%, respectively (referred to the weight of the ethanol lignin used). The variation in yield, especially of 3-(4-hydroxycyclohexyl)-propanol-1, as compared with the results obtained by Harris, D'Ianni and Adkins[5] using *aspen methanol* lignin suggests that a difference may exist in the chemical structure of the two types of lignin.

2. Examination of the yields of hydrogenation products from various amorphous fractions of a maple lignin, isolated by ethanolysis, indicates that with increasing solubility of a given lignin fraction and with its increasing susceptibility to depolymerization to simple propylphenol units by ethanolysis there is obtained an increasing yield of water-insoluble, distillable hydrogenation products.

3. This observation is thought to indicate the prevalence of –C–O–C– bonds between the $C_6C_3$ "lignin building units" in those lignin fractions which are easily soluble and cleavable by ethanolysis or hydrogenolysis into simple units; and, on the other hand, an increasing incidence of –C–C–C– bonds in lignin fractions having these characteristics to a lesser extent.

4. Considering the mechanism of the ethanolysis reaction, the extent of occurrence of –C–O–C– bonds between lignin units as compared to –C–C–C– bonds is believed to determine the degree to which polymerization–depolymerization changes can take place, and, in addition, it is suggested that the –C–O–C– linkage involved is possibly of the acetal (ketal) type.

MONTREAL, CANADA RECEIVED AUGUST 25, 1941

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

# Studies on Lignin and Related Compounds. LXII. High Pressure Hydrogenation of Wood Using Copper Chromite Catalyst (Part 1)

BY HUGH P. GODARD,[1] JOSEPH L. McCARTHY AND HAROLD HIBBERT

The isolation of propylcyclohexanol derivatives by means of the hydrogenation of isolated lignins[2] has provided valuable evidence that propylphenol derivatives are the units from which lignin is derived.[3]

This evidence would be stronger if a higher proportion of the protolignin could be converted into identifiable substances. There was reason to believe this might be accomplished by the high pressure catalytic hydrogenation of wood[4] instead of isolated lignins,[2] since protolignin in wood presumably has a relatively simple structure and should thus give larger amounts of simpler hydrogenated products; and also because wood contains *all* of the protolignin, whereas isolated lignins, obtained by mild alcoholic processes, represent only a fraction of this.[5] An investigation of the hydrogenation of wood was undertaken with the object, after separating the hydrogenated carbohydrates by suitable methods, of isolating and identifying lignin hydrogenation and hydrogenolysis products in higher yields.

In preliminary experiments, various samples of spruce and maple wood, suspended in dioxane, were hydrogenated using a copper chromite catalyst, an initial hydrogenation pressure of about 3500 lb./sq. in., and an average temperature of about 280°. The hydrogen reacted quite rapidly at first, then progressively more slowly until the absorption became complete, usually within ten to twenty hours, depending upon the

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[1] This paper is part of a thesis submitted to the Faculty of Graduate Studies, McGill University, by Hugh P. Godard in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, May, 1941.

[2] (a) Harris, D'Ianni and Adkins, THIS JOURNAL, **60**, 1467 (1938); (b) Harris, Saeman and Sherrard, *Ind. Eng. Chem.*, **32**, 440 (1940); (c) Cooke, McCarthy and Hibbert, THIS JOURNAL, **63**, 3056 (1941).

[3] For comprehensive review of the chemistry of lignin see Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941).

[4] Godard, McCarthy and Hibbert, THIS JOURNAL, **62**, 988 (1940).

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