portion of which (0.332 g.) was taken up in diethyl ether (4 cc.) and extracted with 5% sodium hydroxide solution. Evaporation of the ether yielded an oil from which a light colored distillate (0.269 g.) was obtained upon distillation (135–160° (0.1 mm.)). *Anal.* Calcd. for $C_{13}H_{18}O_4$: OR as OCH_3, 39.1. Found: OR as OCH_3, 38.8.

A portion (0.237 g.) of the methylated product was dispersed in 2% sodium hydroxide solution (50 cc.) and the mixture warmed on a steam-bath. A solution of 4% potassium permanganate was added dropwise with stirring until the permanganate color persisted for several minutes. After heating for an additional two hours, a few cc. of methanol was added to decompose the excess permanganate. The solution was filtered and the alkaline filtrate extracted four times with diethyl ether, acidified and then extracted five times with diethyl ether. The latter five extracts were combined and on evaporation gave a brown semicrystalline material (0.118 g.) which upon recrystallization from water and then from ethanol gave veratric acid (0.032 g.), identified by its melting point and mixed melting point.

Ultraviolet Absorption Spectrum of the Free Ketone.[15]—A sample of the free ketone (0.0039 g.) was dissolved in 10 cc. of absolute ethanol and a portion (1.3 cc.) was diluted with absolute ethanol (8.7 cc.) giving a 0.0051% solution. The absorption curves obtained from the solution with a Hilger Spekkerphotometer and a Hilger E2 quartz spectrograph showed a single well-defined maximum at 1060 fresnel units ($E_{\text{max.}}$ = 1.66) and a minimum at 1145 fresnel units ($E_{\text{min.}}$ = 1.06), after which the curve rose sharply to the limit of the photometric range (1224 f at E = 2.0).[16]

Oxidation with Chromic Acid.—A modification[9] of the Kuhn and L'Orsa method[17] was used. This modification involves an acetyl determination on the distillate which serves as a check on the first titration of the acetic acid. Titration of the acetic acid produced by the oxidation of the semicarbazone (0.1648 g.) of the new phenolic constituent (X) required 10.60 cc. of 0.103 *N* alkali (corrected for blank) which is equivalent to 39.8% acetic acid or 93.2% of the theoretical amount for 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone semicarbazone.

Summary

1. Two new products, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone and 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, have been isolated from the ethanolysis products of spruce wood.

2. Their existence in the ethanolysis mixture is in accordance with previous predictions relating to their derivation from more reactive lignin progenitors, the latter possessing the function of plant respiratory catalysts.

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[15] Carried out by Mr. R. F. Patterson.

[16] Patterson and Hibbert, unpublished results.

[17] Kuhn and L'Orsa, *Z. angew. Chem.*, **44**, 847 (1931).

Montreal, Canada Received March 11, 1943

[Contribution from the Division of Industrial and Cellulose Chemistry, McGill University]

Studies on Lignin and Related Compounds. LXX. Hydrogenolysis and Hydrogenation of Maple Wood

By John R. Bower, Jr.,[1] Lloyd M. Cooke and Harold Hibbert

Earlier work[2] has shown that, using a copper chromite catalyst, high yields (up to 78% of propylcyclohexyl derivatives are obtainable by high-pressure hydrogenation of monomeric propyl phenol derivatives related to the proposed C_6–C_3 lignin structure.[3] It was further shown[2] that hydrogenation of 3-(4-hydroxycyclohexyl)-1-propanol over copper chromite at 250° in dioxane solution resulted in the loss of at least 60% of the primary hydroxyl groups and formation of 4-*n*-propylcyclohexanol, one of the principal products obtained from the hydrogenation of lignin.[4] This result, together with those obtained in recent investigations[5] on the chromic acid oxidation of wood and extracted lignins, indicates the essentially complete absence of terminal methyl groups in native lignin and has emphasized the importance of determining the extent to which terminal —CH_2O— units present in native lignin undergo conversion into entities with terminal methyl groups during hydrogenation.

Preliminary work was undertaken with 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, a typical propyl phenolic substance containing both a primary and a phenolic hydroxyl group. Hydrogenation of this pure substance in dioxane solution over copper chromite gave an 81% yield (minimum value) of 4-*n*-propylcyclohexanol (24%) and 3-cyclohexyl-1-propanol (76%). The former, a previously-investigated hydrogenation product of lignin

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[1] This paper represents part of a thesis submitted to the Faculty of Graduate Studies of McGill University by John R. Bower, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy, November, 1942.

[2] Cooke, McCarthy and Hibbert, This Journal, **63**, 3052 (1941).

[3] Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942).

[4] (a) Cooke, McCarthy and Hibbert, This Journal, **63**, 3056 (1941); (b) Godard, McCarthy and Hibbert, *ibid.*, **63**, 3062 (1941); (c) Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938).

[5] MacGregor and Hibbert, unpublished results.

and maple wood,[4] was readily identified by comparison of the melting point (129–130°) and mixed melting point of its phenyl urethan with that of an authentic sample. 3-Cyclohexyl-1-propanol, a product not hitherto isolated from the hydrogenation products of lignin or wood, was identified by comparison of the melting point (87–88°) and mixed melting point of its phenyl urethan with that obtained from a sample of authentic 3-cyclohexyl-1-propanol synthesized by the hydrogenation of cinnamyl alcohol over copper chromite.

In view of these results, the previous low yield of 3-(4-hydroxycyclohexyl)-1-propanol (1.29% of wood weight[4b]) obtained in the hydrogenation of maple wood seemed surprising and a re-investigation of these products was undertaken. Extracted maple wood was hydrogenated under conditions identical with those employed by Godard, *et al.*,[4b] and the reaction products separated into water-soluble and water-insoluble fractions. Fractional distillation of the water-insoluble oils, using the newly-developed, spiral screen-packed column[6] (28 theoretical plates as compared with 8 for the Podbielniak wire-spiral type column used previously[4b]) resulted in the separation of the material previously reported[4b] as "4-*n*-propylcyclohexanol" into two distinct products (see fractionation curves, Fig. 1).

Determination of the melting points of their phenyl urethans and of mixtures of the natural and synthetic urethans proved the presence of two propylcyclohexyl derivatives: (a) the previously reported 4-*n*-propylcyclohexanol (2.2%) and (b) a *new* wood hydrogenation product, 3-cyclohexyl-1-propanol (2.8%). The combined yield of these products represents an increase from 4.4%[4b] to 5% of the wood weight over that previously reported.

Fractional distillation of the water-soluble maple wood hydrogenation oils gave the same results as reported previously,[4b] the identical yield of 1.29% of 3-(4-hydroxycyclohexyl)-1-propanol being obtained.

The total yield of identified propylcyclohexyl derivatives isolated from the hydrogenation products of maple wood has been increased to 39.8% of the *methoxyl-free* lignin carbon as compared with the former value of 36%.[4b]

Isolation of the new hydrogenation product in the refractive index range previously assigned to 4-*n*-propylcyclohexanol led to a re-examination by the present authors of the substances isolated previously from the hydrogenation products of various maple ethanol lignin fractions and which have been reported[4a] as 4-*n*-propylcyclohexanol. It was found that the *new* product, 3-cyclohexyl-1-propanol, comprised the upper "flat" of each of the hydrogenation products represented in Fig. 1 of the previous paper,[4a] only the lower "flat" consisting of 4-*n*-propylcyclohexanol. Positive identification was made through their phenylurethans. A comparison of the previously-reported yields[4a] with their corrected values is given in Table I.

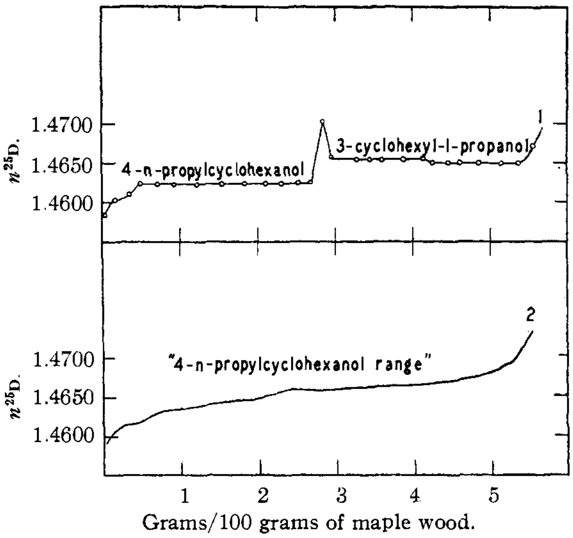

Fig. 1.—Comparative fractionation results of water-insoluble maple hydrogenation products: (1) fractionation through new 28-plate column; (2) fractionation through single-wire spiral Podbielniak column (8 plates).

TABLE I

PREVIOUS[4a] AND REVISED YIELDS OF PROPYLCYCLOHEXYL DERIVATIVES OBTAINED FROM HYDROGENATION OF MAPLE ETHANOL LIGNIN FRACTIONS (WATER-INSOLUBLE PRODUCTS)

Product source	Previously-reported yields[4a] of 4-*n*-propylcyclohexanol,[a] %	Authors' values: 4-*n*-Propylcyclohexanol, %	Authors' values: 3-Cyclohexyl-1-propanol, %
Ethanol lignin	9.9	5.0	4.9
Benzene-soluble lignin	13.5	7.0	6.5
Lignin tars	17.5	12.0	5.5

[a] These values are taken from the "flats" in Fig. 1.[4a]

In the light of the above results it seems highly probable that the material first reported by Adkins and co-workers[4c] as 4-*n*-propylcyclohexanol (obtained by hydrogenation of aspen methanol lignin) was actually a mixture of this compound

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[6] Bower and Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

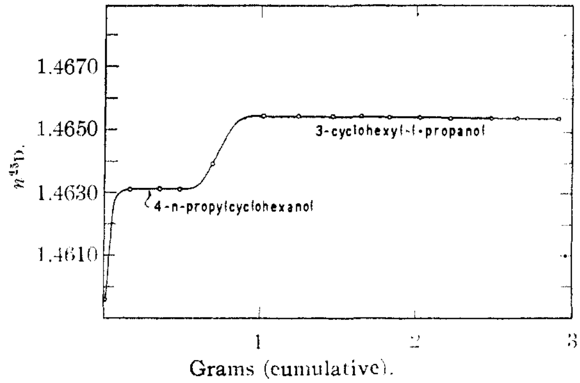

Fig. 2.—Fractionation curve of hydrogenation products of 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone.

with 3-cyclohexyl-1-propanol since they employed for the fractionation the much less efficient Widmer type column.

The isolation of 3-cyclohexyl-1-propanol is of some significance in connection with the structure of lignin. Hitherto the only evidence for the presence of a terminal —CH$_2$O— group on the propylphenol side chain has been the relatively small amount of 3-(4-hydroxycyclohexyl)-1-propanol (20% of isolated propylcyclohexyl derivatives from maple wood) isolated from hydrogenation products. With the isolation of 3-cyclohexyl-1-propanol from maple wood, a minimum of 65% of the isolated propylcyclohexyl derivatives are shown to have the terminal —CH$_2$O— grouping on the side chain. It would also seem probable that in native lignin an even higher percentage of the side chains have this end grouping, since in the hydrogenation of 3-hydroxy - 1 - (4 - hydroxy - 3 - methoxyphenyl)-1-propanone under conditions identical with those used for the hydrogenation of wood and lignin, a considerable portion of the primary hydroxyl is removed with formation of 4-*n*-propylcyclohexanol.

Experimental

Hydrogenation of 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl) - 1 - propane.—3 - Hydroxy - 1 - (4 - hydroxy - 3-methoxyphenyl)-1-propanone (5 g.), synthesized by the method of West and Hibbert,[7] was dissolved in 150 cc. of dioxane and hydrogenated over copper chromite (3 g.) at 280° (initial pressure, cold, 3000 lb./sq. in.) for nine hours. The liquid contents of the bomb, after centrifuging off the catalyst, were subjected to distillation from a Perry–Widmer flask[8] at atmospheric pressure to remove the bulk of the dioxane. The residual product and dioxane (20 cc.) were fractionally distilled through a spiral screen-packed column having an efficiency of twenty-eight theoretical plates.[6] After all residual dioxane had been removed, the remainder of the material (3 g.) was readily separated into two distinct products (A) n^{25}D 1.4631 and (B) n^{25}D 1.4655, in yields of 24 and 76%, respectively (Fig. 2). The phenylurethan of (A) melted at 129–130°; mixed m. p. with the urethan from an authentic sample of 4-*n*-propylcyclohexanol, 129–130°. The phenylurethan of (B) melted at 87–88° compared with the value 87–88° reported in the literature[9] for 3-cyclohexyl-1-propanol; mixed m. p. with an authentic sample 87–88°.

Synthesis of 3-Cyclohexyl-1-propanol.—Kahlbaum cinnamyl alcohol was fractionally distilled at 0.5 mm. and 120–160° bath temperature and a pure sample of 20 g. taken for hydrogenation. This was dissolved in 150 cc. of dioxane and hydrogenated over copper chromite (10 g.) at 270–280° (initial pressure, cold 3000 lb./sq. in.) for six hours. The liquid contents of the bomb, after centrifuging off the catalyst, were transferred to a Claisen flask and concentrated (20 mm. pressure) on a steam-bath for five hours to remove the solvent; yield of product, 16.6 g.; n^{25}D 1.4635. The phenylurethan (36% yield) melted at 87–88° compared with 88° recorded[9] for the phenylurethan of 3-cyclohexyl-1-propanol.

Hydrogenation of Maple Wood.—Solvent-extracted maple wood meal (175 g.) was suspended in 1030 cc. of anhydrous dioxane and hydrogenated to completion over copper chromite catalyst (100 g.) at 280° (initial pressure, cold, 3000 lb./sq. in.) for twenty hours. Total hydrogen absorption was 3.1 moles per 100 g. of wood; the dioxane reaction mixture was colorless. The products were examined by the previous procedure[4b] involving concentration in a Claisen flask, fractionation through a Fenske column[10] and extraction with water. The water-soluble and water-insoluble fractions were fractionated individually through the new spiral screen type fractionating column.[6]

The fractionation curve for the water-insoluble oils (Fig. 1) differed from that obtained previously[4b] in that two distinct "flats" were found in the n^{25}D 1.4600–1.4700 range. Conversion of several test samples from the first "flat" (n^{25}D 1.4625) into their phenylurethans showed the former to be 4-*n*-propylcyclohexanol (m. p. of the phenylurethan 129–130°; mixed m. p. with an authentic sample 129–130°) while the second "flat" (n^{25}D 1.4650–1.4655), treated similarly, proved to be 3-cyclohexyl-1-propanol (m. p. of the phenyl urethan 87–88°; mixed m. p. 87–88°).

The water-soluble oils were fractionated through the same column and gave results practically identical with those obtained previously.[4b] The 3-(4-hydroxycyclohexyl)-1-propanol (1.29%) was identified by the procedure used by the previous investigators.[4b]

Identification of Various Lignin Hydrogenation Products.—Phenylurethans were prepared from samples of the water-insoluble hydrogenation products obtained previously by Cooke, *et al.*,[4a] from ethanol lignin, benzene-soluble ethanol lignin and ethanol lignin tars, respectively. In each case the samples were taken from both the upper

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[7] K. West and H. Hibbert, THIS JOURNAL, **65**, 1170 (1943).

[8] Perry and Hibbert, *ibid.*, **62**, 2561 (1940).

[9] Waser, *Helv. Chim. Acta*, **8**, 117 (1925).

[10] Fenske, Tongberg and Quiggle, *Ind. Eng. Chem.*, **26**, 1213 (1934).

(II, Table II) and lower (I, Table II) "flats" of the fractionation curves as given in Fig. 1, Cooke, McCarthy and Hibbert[4a] in the range $n^{25}D$ 1.4600–1.4700. The melting points of the urethans are given in Table II.

TABLE II

PHENYLURETHANS OF HYDROGENATED LIGNIN FRACTIONS[4a]

Lignin type	Material tested, $n^{25}D$		M. p. of urethan, °C.
Ethanol lignin	I	1.4635	129–130
	II	1.4678	87–88
Benzene-soluble ethanol lignin	I	1.4618	129–130
	II	1.4660	87–88
Ethanol lignin tars	I	1.4615	129–130
	II	1.4675	87–88

Comparison of mixed melting points with the phenyl urethans from the corresponding pure synthetic derivatives proved that each of the products melting at 87–88° (II) was the urethan of 3-cyclohexyl-1-propanol, while those melting at 129–130° (I) were the urethans of 4-*n*-propylcyclohexanol.

Acknowledgment.—The authors wish to acknowledge the kind financial assistance accorded one of them (J. R. B.) by the Canada Paper Company and the Canadian Pulp and Paper Association.

Summary

1. Use of a much more efficient fractionation technique has resulted in the isolation of a new product, 3-cyclohexyl-1-propanol, from the hydrogenation products of maple wood and maple ethanol lignin fractions. Its synthesis was carried out by hydrogenation of cinnamyl alcohol over copper chromite in dioxane solution.

2. The hydrogenation of 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone over copper chromite in dioxane solution gives a mixture of 4-*n*-propylcyclohexanol and 3-cyclohexyl-1-propanol in the ratio of 24 and 76%, respectively. Total yield 81%.

3. The results obtained provide support for the view that the side chains attached to the aromatic nuclei in the structure of native lignin contain the terminal grouping —CH_2OH or —CH_2—O—C—.

MONTREAL, CANADA RECEIVED MARCH 11, 1943

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

Studies on Lignin and Related Compounds. LXXI. The Course of Formation of Native Lignin in Spruce Buds[1]

BY JOHN R. BOWER, JR., LLOYD M. COOKE AND HAROLD HIBBERT

In connection with the question of formation and mode of synthesis of lignin in the plant—the subject of several communications by Hibbert[2]—it is of importance to know at what stage of growth the initial appearance of lignin takes place. In the interesting and instructive experiments carried out by Phillips, *et al.*,[3] using oat shoots as their plant material, it was found that the percentage of lignin (determined by use of fuming hydrochloric acid) in the culms, sheaths, leaves and roots remained at a nearly constant, low level (2–2.5% of the culms, sheaths and leaves; 5.6–6.2% of the roots) during the first six weeks of growth and then increased rather rapidly and uniformly until maturity was reached in fifteen weeks (final lignin values: culms, sheaths and leaves, 11%; roots, 12.5%).

It was desirable to ascertain whether a similar behavior is shown by growing spruce tips and since it has been found that the presence of propylphenol derivatives is definitely associated with the presence of lignin in plant materials,[4] it appeared possible that an analytical determination of such products, in the form of their hydrogenated propylcyclohexyl derivatives, might serve as a method for determining qualitatively, and possibly quantitatively, the amount of lignin present.

In order to establish a reference basis, ethanol–benzene extracted mature spruce wood (35–40 years old) was hydrogenated in dioxane solution over copper chromite catalyst under conditions

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(1) This paper represents part of a thesis submitted to the Faculty of Graduate Studies of McGill University by John R. Bower, Jr., November, 1942, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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

(3) Phillips, Goss, Davis and Stevens, *J. Agr. Research*, **59**, No. 5, 319 (1939).

(4) (a) Cooke, McCarthy and Hibbert, THIS JOURNAL, **63**, 3056 (1941); (b) Godard, McCarthy and Hibbert, *ibid.*, **63**, 3062 (1941); (c) Bower, McCarthy and Hibbert, *ibid.*, **63**, 3066 (1941); (d) Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938); (e) Bower, Cooke and Hibbert, *ibid.*, **65**, 1192 (1943).