(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—.

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[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).

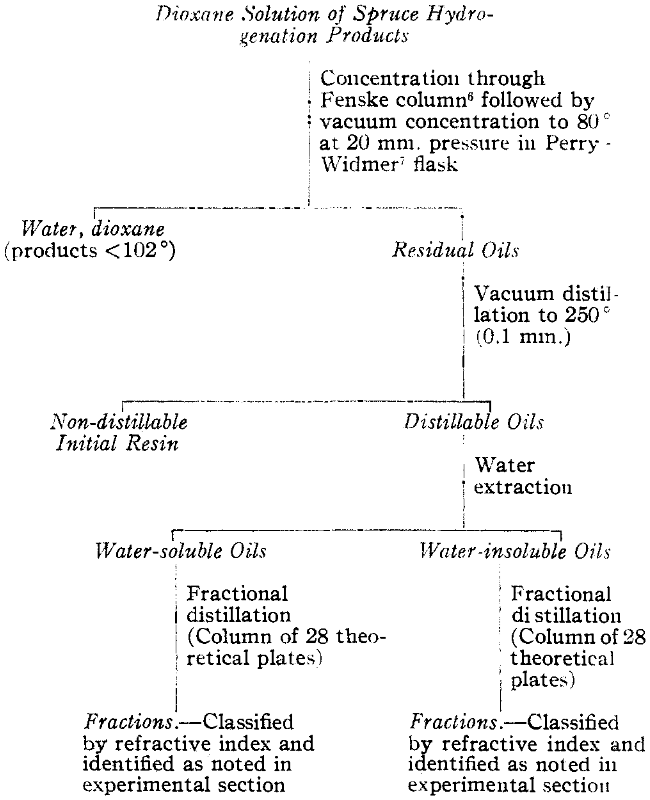
[3] Phillips, Goss, Davis and Stevens, *J. Agr. Research*, **59**, No. 5, 319 (1939).

[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).

previously found suitable for the complete hydrogenation and liquefaction of maple wood[4b,4e] and the water-white liquid reaction products separated into water-soluble and water-insoluble portions according to the previously reported procedure.[4e] Fractional distillation of these two products through the newly-developed, highly efficient, spiral screen-packed laboratory column[5] (28 theoretical plates) yielded the three propylcyclohexyl derivatives (reported previously from maple wood[4e]): 4-*n*-propylcyclohexanol (1.9% of wood weight), 3-cyclohexyl-1-propanol (1.4%), and 3-(4-hydroxycyclohexyl)-1-propanol (0.9%), the combined yield amounting to 4.2% of the original dry wood weight.

FLOW SHEET I

FRACTIONATION PROCEDURE FOR SPRUCE HYDROGENATION PRODUCTS (EXPT. III)



Based on this result, spruce tips (*Stage I*, 2.5 to 3 weeks old) were alcohol-extracted and subjected to hydrogenation under the same conditions. In this case, however, owing to the fact that 50% of the spruce tips were ethanol-soluble (as compared to 1 to 5% for mature woods), the ethanol extract was concentrated to dryness and also hydrogenated. Thus the total hydrogenation products of *Stage I* spruce tips were obtained in two portions. Separation and fractionation of the hydrogenation products from both sources (ethanol-soluble and ethanol-insoluble) showed the complete absence of any of the three known propylcyclohexyl derivatives found in the hydrogenation products of mature spruce wood (Figs. 1 and 2). This was taken as a proof that lignin had not yet been formed, at least in significant amount, in three weeks old spruce tips (*Stage I*).

When dried, unextracted, *Stage II* spruce tips (three and a half to four months old) were hydrogenated under the same conditions, and the products examined similarly, it was found that one of the propylcyclohexyl derivatives, 4-*n*-propylcyclohexanol, previously isolated from mature spruce wood, was present to the extent of 0.8% of the weight of the original material (see Fig. 3, "flat" I). The other two known propylcyclohexyl derivatives were absent. From these results it may be concluded that toward the end of one growing season the amount of lignin present in the spruce tip, as indicated by the presence of propylphenol derivatives, is approximately 20% of that present in mature wood.

To prove that the hydrogenation conditions used had not resulted in an actual destruction of the propylphenol nucleus, a second batch of the unextracted *Stage II* spruce tips was hydrogenated, under the same conditions, in a dioxane medium to which had been added 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (5% of spruce tip weight). Weight of recovered products (Fig. 3, B) showed that a total of 4.4% of propylcyclohexyl derivatives had been obtained. If allowance is made for the loss of oxygen and carbon atoms and gain of hydrogen atoms during the hydrogenation-hydrogenolysis of pure 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone to 4-*n*-propylcyclohexanol (or to 3-cyclohexyl-1-propanol), the maximum theoretical yield of such products would be 3.6 g. from 5.0 g. of the starting material. It is evident, therefore, that the additional 0.8% of 4-*n*-propylcyclohexanol (4.4–3.6%) must have come from the spruce bud material. This figure of 0.8%

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

(6) Fenske, Tongberg and Quiggle, *Ind. Eng. Chem.*, **26**, 1213 (1934).

(7) Perry and Hibbert, THIS JOURNAL, **62**, 2561 (1940).

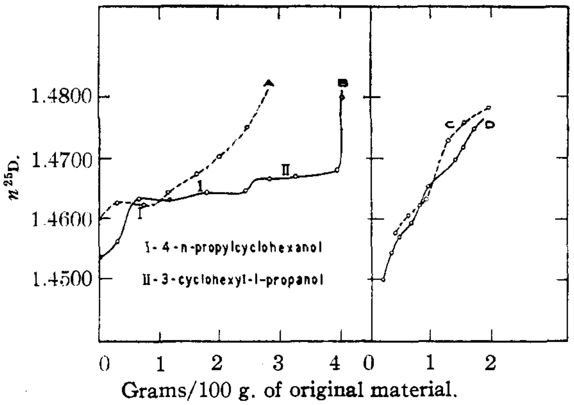

Fig. 1.—Fractionation curves of spruce, "water-insoluble" products showing range of propylcyclohexyl derivatives: (A) *stage II* spruce tips; (B) mature spruce wood; (C) ethanol-soluble *stage I* spruce tips; (D) ethanol-insoluble *stage I* spruce tips.

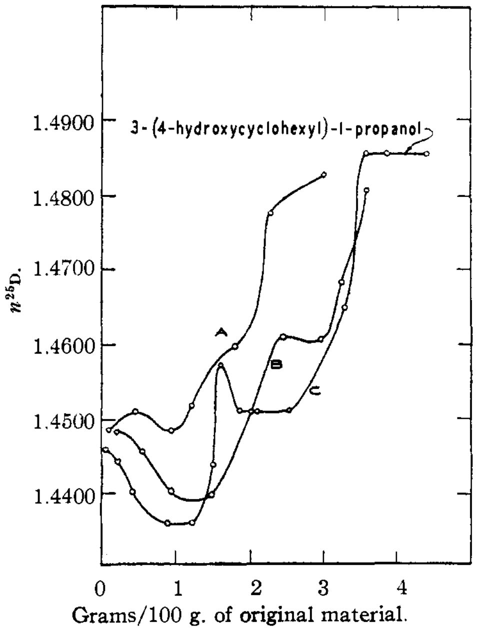

Fig. 2.—Fractionation curves of spruce, "water-soluble" products: (A) *stage I* spruce tips (total); (B) *stage II* spruce tips; (C) mature spruce wood.

is identical with that found for the propylcyclohexyl derivatives obtained from the hydrogenation of *Stage II* spruce tips alone. Thus if hydrogenation has the same effect on both 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and on the propylphenol units present in the spruce tips, it may be assumed that no appreciable decomposition of the latter takes place during the hydrogenation and the conclusions drawn concerning the relative amounts of lignin present, as indicated by the quantity of propylphenol derivatives present, are valid.

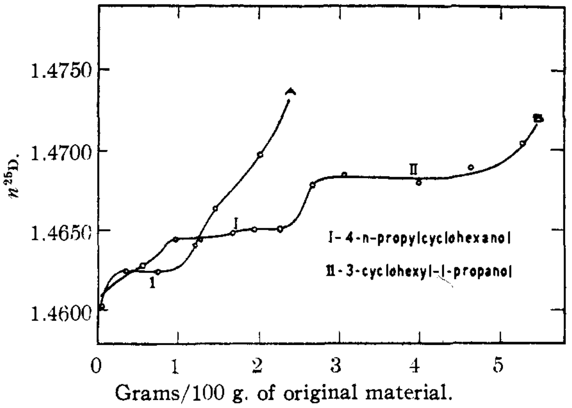

Fig. 3.—Fractionation curves of hydrogenated products of *stage II* spruce and 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (water-insoluble, propylcyclohexyl derivative range): (A) *stage II* spruce alone; (B) *stage II* spruce plus 5% 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone.

Experimental

Hydrogenation of Mature Spruce Wood (35–40 years old).—Solvent-extracted spruce wood meal (175 g.) was suspended in 1030 cc. of dry dioxane and hydrogenated over copper chromite catalyst (100 g.) at 280° (initial pressure, cold, 3000 lb./sq. in.) for twenty-two hours. At the end of this time hydrogen absorption had ceased, the total hydrogen used being 3.2 moles per 100 g. of wood and the reaction products water-white in appearance. They were examined by the same procedure used previously[4b] (outlined in Flow Sheet I).

Fractionation curves for the ranges of known propylcyclohexyl derivatives[4b,4e] are given in Figs. 1 and 2. 4-*n*-Propylcyclohexanol (Fig. 1, B-I, n^{25}D 1.4640) was identified by formation of its phenyl urethan (m. p. 129–130°) and mixed melting point (129–130°).[4e] A similar procedure was used for the 3-cyclohexyl-1-propanol (Fig. 1, B-II, n^{25}D 1.4675); phenylurethan (m. p. 87–88°), mixed melting point 87–88°.[4e] In the case of 3-(4-hydroxycyclohexyl)-1-propanol (Fig. 2, C, n^{25}D 1.4865) the semicarbazone of its keto-acid oxidation product was prepared (m. p. 203–204°[4a]; mixed m. p. with an authentic sample 203–204°).

Hydrogenation of Stage I Spruce Tips

Preparation.—Two and one-half to three weeks old spruce tips (150 g.) were ground under absolute ethanol, the mush transferred to a flask and refluxed with ethanol (6 liters) for twenty-four hours. After filtration the bud meal was dried in a vacuum oven (50°) to 2.3% moisture content. This extraction resulted in the removal of 75 g. of the spruce tips as *ethanol-soluble* material and left 75 g. of extracted residue.

The ethanol extract was concentrated to approximately 200 cc., during which process a gummy, white product separated out on the sides of the flask. Dioxane (1000 cc.) was added and distillation continued until all water and ethanol had been removed, as was evidenced by the collection of pure dioxane (b. p. 101.5°).

Expt. I. Hydrogenation of "Ethanol-insoluble" Stage I Spruce Tips.—Dried extracted spruce bud meal (35 g.)

was hydrogenated in the customary manner using dioxane, 200 cc.; copper chromite catalyst, 20 g.; temp. 280°; time twenty-one hours; initial gas pressure (cold) 3000 lb./sq. in. Hydrogen absorbed, 1.1 moles per 100 g. of bud material. The reaction product had a brownish color. The catalyst was removed by centrifuging, additional catalyst (20 g.) added and the dioxane solution rehydrogenated for eighteen hours: amount of additional hydrogen absorbed, 0.7 mole per 100 g. of bud meal. Product, water-white in appearance. A second similar run was carried out and the reaction products combined and examined by the same method employed for mature spruce wood. On fractional distillation (Figs. 1, D and 2, A) no indication was obtained of the presence of substances within the boiling point and refractive index ranges of the known propylcyclohexyl derivatives.[4e]

Expt. II. Hydrogenation of "Ethanol-soluble" Stage I Spruce Tips.—This material (25 g.), partly in actual solution in dioxane and partly in the form of a white gummy residue (see above),[8] was hydrogenated under the same conditions as in Expt. I. Total volume of solution 235 cc.; copper chromite catalyst 15 g.; hydrogen absorption 4.5 moles per 100 g. original spruce material; appearance of reaction product, water-white. A second identical run was carried out, the reaction products united and subjected to a similar examination procedure (Flow Sheet I). No trace of known propylcyclohexyl derivatives was found (Figs. 1, C and 2, A).

Expt. III. Hydrogenation of Stage II Spruce Tips.—The meal (35 g. dried, unextracted) from three and one-half to four months old spruce tips was hydrogenated in the same manner as Expts. I and II: vol. of dioxane, 200 cc.; catalyst, 20 g.; temp. 280°; time twenty hours; amount of hydrogen absorbed 2.6 moles per 100 g. of material; color of reaction product, brownish. Rehydrogenation as before using 20 g. of fresh copper chromite for five hours left a water-white liquid. There was no apparent further hydrogen absorption.

A second similar run was made and the products united and examined (Flow Sheet I). The material represented by the short "flat" in the distillation curve (0.8% of the weight of dry spruce tips taken) (Fig. 1, A) at $n^{25}\text{D}$ 1.4625, was shown to be 4-*n*-propylcyclohexanol by the melting point (129–130°) of its phenyl urethan and a mixed melting-point (129–130°).

Expt. IV. Hydrogenation of Stage II Spruce Tips in Presence of 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (A).—Two identical hydrogenations were carried out using a mixture of *Stage II* spruce tip meal (35 g. dried, unextracted) and 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (1.75 g.) under the same conditions as in Expts. I, II and III: vol. of dioxane, 200 cc.; catalyst 20 g.; hydrogen absorption per 100 g. of spruce tips was 3 moles, of which 0.18 mole was that required for the hydrogenation of the added ketone (A). The reaction product in each case had a brownish color and was re-hydrogenated for five hours with fresh catalyst (20 g.). No further hydrogen absorption was noted. The two water-white reaction products were united and examined by the same procedure (Flow Sheet I). The analytical results are shown diagrammatically in Fig. 3. Melting points and mixed melting points (129–130°) of phenyl urethans from test samples (lower "flat" (I), $n^{25}\text{D}$ 1.4645, Fig. 3) identified this product as 4-*n*-propylcyclohexanol. Similarly, the material present in the upper "flat" (II) ($n^{25}\text{D}$ 1.4680, Fig. 3) was identified as 3-cyclohexyl-1-propanol by the melting and mixed melting point (87–88°) of the urethans from the various samples.

There was no indication of the presence of any 3-(4-hydroxycyclohexyl)-1-propanol in the hydrogenation products.

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. Spruce buds in two stages of growth and also mature spruce wood have been hydrogenated in dioxane using copper chromite as catalyst. With the younger tips (2.5–3.0 weeks old) no propylcyclohexyl derivatives were found among the hydrogenation products in the reaction mixture, indicating the absence of lignin in the spruce buds. With older material (3.5–4.0 months old, representing completion of first growing season) 4-*n*-propylcyclohexanol was isolated in amount corresponding to about twenty per cent. of the lignin present in mature spruce wood (35–40 years old).

2. Hydrogenation of spruce tips in presence of small amounts of 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone resulted in a quantitative recovery of the latter as 4-*n*-propylcyclohexanol and 3-cyclohexyl-1-propanol, thus proving that the propylphenol nucleus is not cleaved under the hydrogenation conditions used in this investigation.

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 $\text{—CH}_2\text{OH}$ or $\text{—CH}_2\text{—O—C—}$.

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[8] An aliquot of the solution was measured by volume and exactly the same proportion of the gummy residue weighed out and combined with the solution for treatment.