acterized as 4-*n*-propylcyclohexanol[19] by conversion of three representative samples to the phenyl urethans (yield 11–28%), m. p. 127°, mixed m. p. with authentic sample, 127°.[16]

Acknowledgment.—The authors wish to thank the National Research Council of Canada for the award of a studentship to one of them (H. P. G.) and also the Canadian Pulp and Paper Association for their kind financial assistance. The authors wish also to express their indebtedness to Dr. L. M. Cooke and Mr. J. R. Bower, Jr., for kind help in the preparation of this manuscript.

Summary

1. Samples of spruce and maple wood were suspended in dioxane and hydrogenated over copper chromite catalyst using an initial pressure of 3500 lb./sq. in. and a temperature of 280° and complete conversion of the wood into dioxane soluble products and gases effected, thus providing, for the first time, a method for the complete liquefaction of wood.

2. From the reaction mixture, 4-*n*-propylcyclohexanol and 3-(4-hydroxycyclohexyl)-propanol-1 have been isolated in yields of 19.5 and 5.8% (based on Klason lignin content of wood), respectively. Using as a basis for calculation the carbon values of these isolated units and of the "methoxyl-free protolignin" content of the wood, the combined yield of propylcyclohexane derivatives represents a recovery of 36%.

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[19] Upon refractionation of the 4-*n*-propylcyclohexanol (Column D) 75% of the material was collected between n^{25}_{D} 1.4630 and 1.4670.

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

Studies on Lignin and Related Compounds. LXIII. Hydrogenation of Wood (Part 2)

BY JOHN R. BOWER, JR., JOSEPH L. MCCARTHY AND HAROLD HIBBERT

It has been shown in the preceding paper[1] that maple wood can be completely converted, by high-pressure hydrogenation over copper chromite catalyst, into a mixture of dioxane-soluble oils (and gases) containing (a) 4-*n*-propylcyclohexanol and 3-(4-hydroxycyclohexyl)-propanol-1 both of which undoubtedly originate from protolignin (since they have been obtained by direct hydrogenation of isolated lignins[2]), and (b) unidentified distillable oils, originating from either lignin or carbohydrates which are not readily separable by fractional distillation.[3] Although the complete separation and identification of all the wood hydrogenation products will, no doubt, ultimately be accomplished, the present investigation was limited to an attempt to isolate (and, thereby eliminate) woodmeal hydrogenation products of non-lignin origin by comparing the fractionation results from maple holocellulose hydrogenation products with those previously obtained from maple wood.[1]

Maple holocellulose, prepared according to Van Beckum and Ritter,[4] on hydrogenation under the same conditions as those used for maple wood,[1] reacted with approximately 2 moles of hydrogen per 100 g. of material and was completely converted to dioxane-soluble products and gases. However, since the reaction solution was brown in color (as contrasted with a colorless product from maple wood) and the catalyst considerably reduced, the latter could have been poisoned[5] and, accordingly, the crude reaction mixture was retreated with fresh catalyst under the same conditions. Additional hydrogen (0.5 mole/100 g.) was absorbed during eight hours, the total amount being 2.5 moles (compared with approximately 3.1 moles/100 g. for maple wood) and the now colorless reaction mixture was fractionated by the procedure employed previously[1] in the case of maple woodmeal. The results obtained with the two products are shown in Table I.

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[1] Godard, McCarthy and Hibbert, THIS JOURNAL, **63**, 3061 (1941).

[2] (a) Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938); (b) Cooke, McCarthy and Hibbert, *ibid.*, **63**, 3056 (1941).

[3] This difficulty was not unexpected since Zartman and Adkins [THIS JOURNAL, **55**, 4559 (1933)] have shown that a wide variety of products are formed by hydrogenation of the simplest carbohydrates.

[4] (a) Van Beckum and Ritter, *Paper Trade J.*, **104**, 253 (1937); **105**, 277 (1937). (b) Although the Van Beckum–Ritter holocellulose procedure is essentially a method for the quantitative estimation of the carbohydrate content of wood, it has been applied here as a means of preparing larger quantities of "lignin-free wood."

[5] Difficulty was experienced in removing all traces of chloride (probable catalyst poison) from the holocellulose even when it was re-washed with boiling ethanolamine, hot and cold ethanol, and water, and despite the fact that 5% of the holocellulose itself was dissolved during the treatment. Consequently it was decided to proceed with the examination of the twice-hydrogenated product.

TABLE I

COMPARISON OF HYDROGENATION PRODUCTS FROM MAPLE HOLOCELLULOSE AND MAPLE WOOD

	Holocellulose			Wood		
Fraction	Temp., °C.	Press., mm.	Yield, %[a]	Temp., °C.	Press., mm.	Yield, %[a]
I, b. p. <101° (760 mm.)						
(a) Methanol	60–66	760	1	65–67	760	6–7
(b) Ethanol	75–79	760	5	79	760	14
(c) Water[b]	88–88.4	760	24	88–88.4	760	17
II, b. p. >101° (760 mm.)						
(Separated into water-insoluble Fraction III and water-soluble Fraction IV)						
III, b. p. >101° (760 mm.), water-insoluble						
(a) $n^{25}\mathrm{D}$ 1.4100 to 1.4275	...	...	None	to 95	100	3.5
(b) $n^{25}\mathrm{D}$ 1.4275 to 1.4625	70–125	20	1.7	to 76	20	3.6
(c) 4-*n*-Propylcyclohexanol ($n^{25}\mathrm{D}$ 1.4625 to 1.4680)	...	...	None	80	20	4.4
(d) $n^{25}\mathrm{D}$ 1.4680 to 1.5100	70–190	1	3.3	65–190	1	3.0
(e) Resin	>190	1	1.4	>190	1	3.6
(f) Cold trap			0.3			1.2
IV, b. p. >101° (760 mm.), water-soluble						
(a) Water-immiscible[c]			2			2.1
(b) $n^{25}\mathrm{D}$ 1.4375 to 1.4525	40–80	1	1.3	50–80	1	1.2
(c) $n^{25}\mathrm{D}$ 1.4525 to 1.4860	80–125	1	1.2	80–127	1	1.2
(d) 3-(4-Hydroxycyclohexyl)-propanol-1 ($n^{25}\mathrm{D}$ 1.4865)	...	...	None	129–130	1	1.6
(e) Resin	>125	1	0.5	>130	1	...
(f) Cold trap			0.2			2.4

[a] Grams per 100 g. of *wood*. [b] Water in dioxane–water azeotrope. [c] Steam distillation.

Fractional distillation and quantitative analysis of the dioxane and lower-boiling products (Fraction I) indicated the formation of approximately 24% water,[6] 1% methanol and 5% ethanol from holocellulose as compared with 17, 6 and 14%, respectively, from wood.[7]

The high-boiling products (above 101° (760 mm.), Fraction II) were separated into water-insoluble (Fraction III) and water-soluble (Fraction IV) portions, and the aqueous solution of the latter was distilled. The first portion of the distillate contained a water-immiscible oil (IVa) (probably steam distilled) indicating that a like material obtained in the same yield (2%) from maple wood was of carbohydrate origin. Since the fractionation results for the higher-boiling, water-soluble portion (IVb and IVc) are similar to those from the corresponding maple wood hydrogenation products[1] (except that no 3-(4-hydroxycyclohexyl)-propanol-1 was obtained from the former), and since the total amounts of these products (2.5% of original maple wood) were small and almost equal in each case, it would appear that no material of lignin origin, other than 3-(4-hydroxycyclohexyl)-propanol-1, exists in the *water-soluble* maple wood hydrogenation products.

The *water-insoluble* products (Fraction III) on fractional distillation gave no 4-*n*-propylcyclohexanol (IIIc) (a hydrogenated lignin product[2]) in contrast with the 4.4% obtained from maple wood. The properties of the remainder of the higher-boiling products (IIId) were almost identical with those from maple wood, indicating the absence of any substantial amount of unidentified lignin derivatives in this fraction from the wood. The lower-boiling, water-insoluble holocellulose products (IIIb) obtained only in limited amounts (1.7%) showed widely varying refractive indices and, in general, boiled at a much higher temperature than the corresponding hydrogenation fractions (7.1%) from maple wood (IIIa and IIIb). It would thus appear that this last-named fraction (representing 27% of the Klason lignin content of maple wood) came largely from the *protolignin* in the wood and an investigation concerning its constitution is now in progress.

Experimental

Preparation of Maple Wood Holocellulose.—The holocellulose analytical method of Van Beckum and Ritter[4] was adapted to the large scale preparation of holocellulose. Maple wood (200 g., 7% H_2O) was placed in an 8-in. Büchner funnel, moistened with water and then, with a moderate vacuum applied, chlorine was led on to the wood through an inverted glass funnel. The treatment (with occasional stirring) was continued for five to ten minutes until no further color change of the wood was apparent,

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(6) 24 g. water per 78 g. holocellulose. Since maple wood contains 78% holocellulose, the 24 g. of water represents 24% by weight of the original maple wood.

(7) The yields of water from the holocellulose and woodmeal hydrogenations were corrected for their initial moisture contents.

and the reaction product washed on the funnel successively with 95% ethanol (400 cc.), hot ethanolamine (75°, two 500-cc. portions of a 3% solution in 95% ethanol to remove the chlorinated lignin), 95% ethanol (two 500-cc. portions), and cold water and then the woodmeal transferred to a fresh filter. This cycle of operations was repeated seven times until the residual product remained white after chlorination and washing with ethanolamine. The maple holocellulose was finally washed with ethanol and vacuum-dried; yield, 120 g.; Klason lignin, 0.0%.

Separation and Fractionation of Holocellulose Hydrogenation Products (see table).—The combined dioxane solutions of the maple holocellulose hydrogenation products (from 75 g. of maple holocellulose) were concentrated in a Claisen distilling flask, approximately one-fifth of the solvent being removed at atmospheric pressure (under carbon dioxide atmosphere) to avoid loss of low-boiling products (Fraction I), and the remaining dioxane removed under vacuum (20 mm. at 75°), leaving 12.4 g. of residual oils (Fraction II). The combined low-boiling distillates were then re-fractionated (450 mm. × 10 mm. vapor-jacketed Fenske column/760 mm.) in order to separate any higher-boiling material entrained in the first distillation, to isolate quantitatively the dioxane–water azeotrope (145 g. containing 24 g. of water[2b]), and finally to remove the low-boiling alcohols (b. p. <80° (760 mm.)) prior to a quantitative determination of the methanol (1 g.) and ethanol (5 g.) content according to the method of Cooke.[8] The small residual higher-boiling concentrate (11 cc.) (b. p. >101° (760 mm.) and containing a small amount of dioxane) thus obtained was added to the original liquid concentrate (Fraction II) and the mixture dissolved in 35 cc. of pentane. This solution was then extracted successively with 100, 50, 30, 25 and 20 cc. portions of water giving water-insoluble (Fraction III) and water-soluble (Fraction IV) fractions.

The latter product (IV) was now fractionated through the above-mentioned Fenske column, whereby an initial fraction of dioxane–water, a small amount of a water immiscible "oil" (probably entrained), and a residual oil (3.18 g.) were obtained. The last-named, on fractionation through a Podbielniak column (900 × 3.8 mm.), distilled to the extent of approximately 85% at 40–125° (1 mm.), in the manner indicated in the table.

The water-insoluble oils (Fraction III, 6.71 g.) were fractionated similarly, b. p. 70–180° (20 to 1 mm.), the results being summarized in the table; approximately 83% was distillable.

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Summary

1. Maple wood holocellulose was hydrogenated under the same conditions as used for maple wood by Godard, McCarthy and Hibbert.[1]

2. By comparison of the fractionation results thus found with those obtained for maple wood, it was possible to (a) eliminate the necessity of investigating many difficultly separable (maple wood) fractions shown to be of no interest as sources of lignin products, and (b) indicate a fraction of probable lignin origin.

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[8] Cooke, McCarthy and Hibbert, THIS JOURNAL, **63**, 3052 (1941).

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF CALIFORNIA]

Sulfophenylarsonic Acids and Certain of their Derivatives. V. *p*-(*p*-Sulfophenyl)- and *p*-(*p*-Sulfonamidophenyl)-phenylarsonic Acids[1]

BY JOHN F. ONETO AND E. L. WAY

The following paper deals with the preparation of a number of sulfo- and sulfonamido derivatives of *p*-(phenyl)-phenylarsonic acid. This acid was obtained, (1), by application of the Scheller reaction[2] to *p*-aminobiphenyl and, (2), as a by-product from the preparation of phenylarsonic acid by the Bart reaction. The isolation and purification of the acid in the latter instance was essentially the method described by Schmidt.[3]

Chart A indicates the structures and preparation of the parent compounds, *p*-(*p*-sulfophenyl)-phenylarsonic acid, (II), and *p*-(*p*-sulfonamidophenyl)-phenylarsonic acid, (V).

Chart B illustrates the procedures carried out in determination of the relative positions of the substituent sulfo- and sulfonamido- groups in the para arsonated biphenyl nucleus. The resulting *p*-phenylbenzenesulfonyl chloride (VIII) proved to be of particular value in this instance because of its ease of purification, sharp melting point and stability toward hydrolysis.

We were unable to obtain (II) or (V) by appli-

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[1] Supported by grants from John Wyeth and Brother, and from the Research Board of the University of California.

[2] Scheller, French Patent, 624,028, *Chem. Zentr.*, **98**, II, 229 (1927).

[3] Schmidt, *Ann.*, **421**, 169 (1920).