denser with a drying tube. The solution was heated on a steam-bath and granulated sodium (2.2 g.) added in small portions during two hours, with vigorous stirring. The reaction mixture became very viscous and another portion of benzene (300 cc.) was added. Iodine (13 g.) dissolved in anhydrous benzene (250 cc.), was added dropwise to the hot, well-stirred mixture during four hours. Stirring was continued for one hour longer and the solution added in a fine stream to water (one liter). The benzene layer was decanted, washed with 5% aqueous sodium thiosulfate (100 cc.) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the resulting oil distilled at 210–216° (0.01 mm.), yielding 23.3 g. (93%).

Anal. Calcd. for $C_{28}H_{34}O_{10}$: OCH_3, 35.1. Found: OCH_3, 34.6.

2,3-Diveratroylbutane (XV).—bis-(Methyl ethyl veratroylacetate) (23 g.) was dissolved in anhydrous ethanol (375 cc.) containing sodium hydroxide (8.5 g.) and the mixture allowed to stand at room temperature during twenty-four hours with occasional stirring. The reaction mixture was cooled and concentrated hydrochloric acid added dropwise until the evolution of carbon dioxide ceased. The mixture was immediately added to cold water (450 cc.), the solution filtered, the oily product dissolved in chloroform–ethanol (1:2, 200 cc.) and charcoal added. The mixture was heated under reflux on the steam-bath during two hours and filtered while hot. The solvent was removed under reduced pressure and the tan-colored crystalline substance which separated was twice recrystallized from hot methanol yielding 8.4 g. (48%), m. p. 189–190°.

Anal. Calcd. for $C_{22}H_{26}O_6$: C, 68.39; H, 6.76; OCH_3, 32.1; mol. wt., 386. Found: C, 68.3; H, 6.9; OCH_3, 31.9; Rast mol. wt., 395.

The bis-2,4-dinitrophenylhydrazone was prepared by the usual method.

Anal. Calcd. for $C_{34}H_{34}O_{12}N_8$: OCH_3, 16.6. Found: OCH_3, 16.6.

Action of 2% Ethanolic Hydrogen Chloride on XIII.—2,2′-Divanilloyl diethyl ether (1.00 g.) was heated under reflux with 2% ethanolic hydrogen chloride (50 cc.) for forty-eight hours in an atmosphere of carbon dioxide. A small amount (0.15 g.) of an amorphous lignin-like substance which separated was removed by filtration. The filtrate was neutralized with sodium ethylate and the precipitated sodium chloride removed by filtration. The solvent was removed under reduced pressure and the product recrystallized from methanol yielding 0.75 g., m. p. 153–154°. A mixed melting point determination with an authentic sample of XIII showed no depression.

Action of 2% Ethanolic Hydrogen Chloride on XIV.—The effect of 2% ethanolic hydrogen chloride on this dimer (XIV) (1.00 g.) was determined as above. The starting material was recovered unchanged in a yield of 0.91 g.

Action of 2% Ethanolic Hydrogen Chloride on XV.—In this reaction 1.00 g. of dimer (XV) was used and the amorphous product weighed 0.79 g.

Acknowledgment.—The authors gratefully acknowledge the kind financial assistance of the Canadian Pulp and Paper Association and the Spruce Falls Power and Paper Company.

Summary

1. Several propylphenol monomolecular compounds related to lignin progenitors were prepared. Some of these were new compounds, while others were prepared by new and better methods.

2. The synthesis of three dimers from these propylphenol units has been carried out.

3. Ethanolysis of the three dimers did not yield the customary monomolecular fission products, obtained by the ethanolysis of wood. This indicates that these synthetic dimers differ from those materials forming the readily hydrolyzable portion of native lignin.

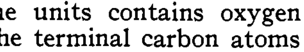
MONTREAL, CANADA RECEIVED APRIL 10, 1947

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

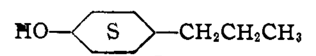
Studies on Lignin and Related Compounds. LXXXVI. Hydrogenation of Dimers Related to Lignin[1]

BY SAMUEL B. BAKER[2] AND HAROLD HIBBERT[3]

Complete liquefaction of spruce wood has been achieved by means of high-pressure catalytic hydrogenation.[4] The protolignin is converted in part to 4-*n*-propylcyclohexanol (I), 3-(4-hydroxycyclohexyl)-1-propanol (II) and 3-cyclohexyl-1-propanol (III) in yields of 9.9, 5.8 and 12.6%, respectively (based on the Klason lignin content of the wood).[4,5,6] These isolated products (I, II, III) serve to establish the propylphenol units in lignin. Further investigations[7,8] have shown that a relatively high proportion of the cyclohexylpropane units contains oxygen atoms attached to the terminal carbon atoms in the side chains.



I



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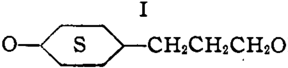

III

According to Hibbert, the experimental results seem to indicate that a large portion of native lig-

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[1] This paper represents part of a thesis submitted to the Faculty of Graduate Studies and Research, McGill University, by Samuel B Baker, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, Oct., 1943.

[2] Present address: Montreal General Hospital, Montreal, Que.

[3] Late E. B. Eddy Professor of Chemistry, McGill University.

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

[5] Bower, Cooke and Hibbert, *ibid.*, **65**, 1192 (1943).

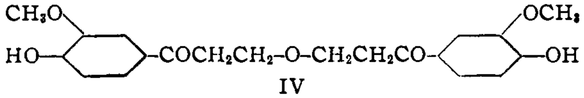
[6] Cooke, McCarthy and Hibbert, *ibid.*, **63**, 3056 (1941).

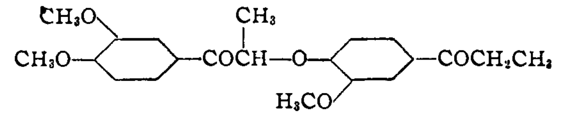
[7] Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938).

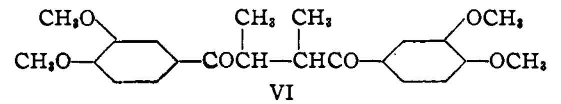
[8] Harris and Adkins, *Paper Trade J.*, **107**, No. 20, 38 (1938).

nin could conceivably consist of complex polymers of the dehydrodiisoeugenol type.[9] This similarity in structure between lignin and the lignans has been noted by Erdtman[10] and Haworth.[11]

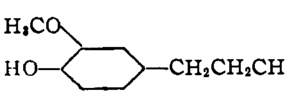
The three dimers, 2,2′-divanilloyl diethyl ether (IV), 1-veratroyl-1-[2-methoxy-4-(propanone-1)-phenoxy]-ethane (V), and 2,3-diveratroylbutane (VI) whose syntheses have been reported previously[9] have been hydrogenated using conditions developed in these Laboratories for the hydrogenation of spruce wood.

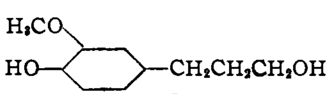

IV

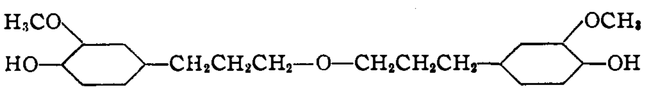

V


VI

Hydrogenation of IV.—Hydrogenation of IV[12] over Raney nickel in aqueous ethanol (1:1), containing 3% alkali, for four hours at 165°, at an initial pressure of 3020 p.s.i., resulted in the hydrogenolysis of the ether linkage to the extent of 60%. Both carbonyl groups were reduced while the aromatic rings remained intact. The remaining 30% consisted of the original dimer in which the only change taking place was that of a reduction of the carbonyl to methylene groups. The products were identified as 4-hydroxy-3-methoxyphenylpropane (VII), 3-(4-hydroxy-3-methoxyphenyl)-1-propanol (VIII) and 2,2′-divanillyl diethyl ether (IX), in yields of 30, 30 and 33%, respectively.


VII

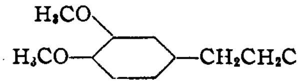

VIII

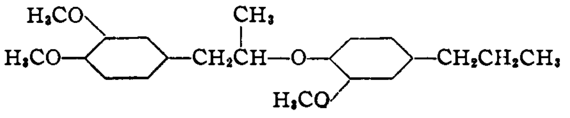

IX

Hydrogenation with the same type of catalyst and medium at 185° for eighteen hours yielded the following cyclohexane derivatives: 4-*n*-propylcyclohexanol (I), and 3-(4-hydroxycyclohexyl)-1-propanol (II), in yields of 46 and 50%, respectively. Evidently chain fission occurred at the ether linkage followed by reduction of the aromatic rings. This type of reaction probably occurs in the hydrogenation of native lignin when spruce and maple woods are hydrogenated.[5,6]

Using copper–chromium oxide as catalyst, hydrogenation of the first dimer (IV) in aqueous ethanol at 150–160° for one hour at an initial pressure of 2980 p.s.i., but in the absence of alkali, gave only one product, 2,2′-divanillyl diethyl ether (IX) in a yield of 95%. Chain fission did not occur under these conditions.

Hydrogen of V.—Treatment[12] of the second dimer (V) under the same conditions using Raney nickel, ethanol–water (1:1), 3% alkali at 165° for four hours and at an initial pressure of 3030 p.s.i. brought about both cleavage of the ether linkage and reduction of the carbonyl groups. The products isolated were 4-hydroxy-3-methoxyphenylpropane (VII), 3,4-dimethoxyphenylpropane (X) and the carbonyl-reduced dimer (XI) in yields of 30% each. The same result was obtained under similar conditions as above but in the absence of alkali.


X


XI

Substitution of copper–chromium oxide catalyst for the Raney nickel, at 150–160° in ethanol for one hour yielded the same products (VII), (X) and (XI) in yields of 40, 40 and 15%, respectively. Hydrogenation of the carbonyl-reduced dimer (XI), under the same conditions of time, temperature and pressure but with copper–chromium oxide catalyst left the product unchanged. The presence of alkali brought about a partial cleavage (15%), the remainder of the saturated dimer (XI) being recovered unchanged. On the other hand, hydrogenation of the latter (XI) over Raney nickel at 160–165° for four hours brought about a cleavage, the reaction products comprising (VII), (X) and (XI) in yields of 25, 25 and 50%, respectively. The presence of the two carbonyl groups appeared to exert a marked effect in the hydrogenation of the dimer over copper–chromium oxide catalyst since cleavage did not occur when the saturated dimer (XI) was hydrogenated, while fission did occur when the unreduced dimer (V) was hydrogenated under the same conditions. When the hydrogenation over Raney nickel was carried out at 185° for eighteen hours, only one product was obtained, namely, 4-*n*-propylcyclohexanol (I) in a yield of 85%. Under these conditions both ether cleavage and reduction of the aromatic rings apparently occurred.

Hydrogenation[12] of VI.—Using Raney nickel catalyst, ethanol–water (1:1), 3% alkali, a

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[9] Baker, Evans and Hibbert, This Journal, **70**, 60 (1948).

[10] Erdtman, *Svensk Papperstidn.*, **44**, 243 (1941); translation in *Pulp and Paper Magazine of Canada*, Feb. (1942).

[11] Haworth, *Nature*, **147**, 255 (1941).

[12] The authors are indebted to Dr. J. M. Pepper, Research Chemist, Dominion Rubber Company, Ltd., for the hydrogenations reported in this paper.

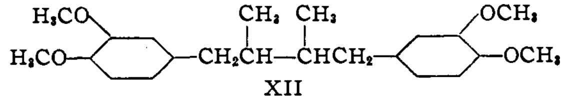
TABLE I

HYDROGENATION OF 2,2'-DIVANILLOYL DIETHYL ETHER

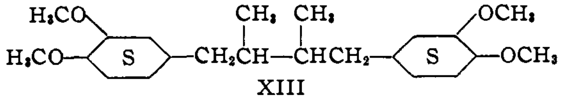
Weight, g.	Solvent, 1:1,100 cc.	Catalyst, g.	NaOH, g.	Time, hours	Temp., °C.	Initial pressure, p.s.i.	Products,[a] g.
1.0	EtOH-H_2O	RaNi 1.0	3.0	4	165	3020	0.85 A
1.0	EtOH-H_2O	RaNi 1.0	3.0	18	185	3000	0.71 B
1.0	EtOH-H_2O	CuCrO 0.5	None	1	150–160	2980	0.88 C

[a] A, B, C refer to Experimental Text.

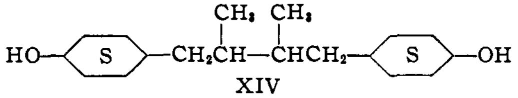
temperature of 165°, time of four hours, and at an initial hydrogen pressure of 2950 p.s.i., the only reaction product obtained was the dimer with the side chain saturated, namely, 2,3-diveratrylbutane (XII). The same result was obtained using copper-chromium oxide catalyst at 150–160° for one hour. This reduced dimer (XII) when hydrogenated over the latter catalyst at 185–190° for twelve hours underwent reduction of the aromatic rings, but no fission occurred. The product isolated was 2,3-bis-(hexahydroveratryl)-butane (XIII). Substitution of the copper-chromium oxide catalyst in the last reduction by Raney nickel gave, under the same conditions, only the one product, namely, 1,4-bis-(4-hydroxycyclohexyl)-2,3-dimethylbutane (XIV). The latter, on hydrogenation at 225–230° over Raney nickel and at 260 and 280° over copper-chromium oxide catalyst, was recovered unchanged with gasification to the extent of 10, 20 and 38%, respectively.



XII



XIII



XIV

These experimental results apparently substantiate Hibbert's theories regarding the types of linkages found in native lignin. It would appear that a portion of the lignin contains easily cleaved linkages, in all probability, ether linkages. The greater portion of the hydrogenated native lignin consists of a complex mixture of dimeric, trimeric, etc., type of substances since hydrogenolysis of a carbon–carbon linkage does not occur even at 280° over copper–chromium oxide catalyst, it seems that the dimers obtained from the hydrogenation of spruce wood do not arise by the cleavage of more complex polymers.

Experimental

Hydrogenation of IV.—2,2'-Divanilloyl diethyl ether (IV) was hydrogenated in a small Parr bomb of 500-cc. capacity under the various conditions given in Table I.

The product (A) (0.85 g.) obtained in the first hydrogenation was dissolved in ethereal diazomethane solution (200 cc.) and the solution allowed to stand overnight at 0°. The solvent and excess diazomethane were removed under reduced pressure and the resulting product re-methylated to completion, as shown by a negative ferric chloride–phenol test. This methylated product was distilled under reduced pressure yielding two fractions (i) and (ii).

(i) **Low-boiling Fraction.**—Bath temperature at 80–90° (0.1 mm.); yield, 0.51 g. The oily product was analyzed to determine whether cleavage of the dialkyl ether linkage occurred. The methods used were methoxyl and Smith–Bryant[13] hydroxyl determinations.

Anal. Calcd. for cleavage mixture: OH, 4.54; OCH_3, 32.9. Found: OH, 4.5; OCH_3, 32.8.

(ii) **High-boiling Fraction.**—Bath temperature at 150–153° (0.01 mm.); yield, 0.28 g.

Anal. Calcd. for $C_{22}H_{30}O_6$: OCH_3, 33.1. Found: OCH_3, 33.1.

The product (B) from the second hydrogenation of 2,2'-divanilloyl diethyl ether was distilled under reduced pressure yielding the two fractions (i) and (ii).

(i) **First Fraction.**—Bath temperature at 115–119° (15 mm.); yield, 0.31 g. The phenyl urethan of this distillate was prepared (m. p. 127–128°) and a mixed melting point determination with the phenyl urethan of 4-*n*-propylcyclohexanol showed no depression.

(ii) **Second Fraction.**—Bath temperature at 119–123° (0.1 mm.); yield, 0.35 g. The product (0.35 g.) was dissolved in a mixture containing chromic oxide (1.1 g.), glacial acetic acid (10 cc.), water (5.5 cc.) and benzene (20 cc.) in a small Erlenmeyer flask. The reaction mixture was shaken at room temperature during nineteen hours, the benzene layer removed and the dark green acid mixture extracted with three portions (10 cc.) of benzene. The combined benzene solutions were washed once with water (15 cc.) to remove suspended chromic acid, then extracted with four portions (10-cc. each) of sodium carbonate solution (10%). The carbonate solution was cautiously acidified with dilute hydrochloric acid and the milky solution extracted with five portions (10 cc. each) of benzene. The combined benzene solutions were dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The yield of the resulting oil was 0.17 g. This oil was dissolved in aqueous ethanol (50%, 1 cc.) and added to a solution consisting of semicarbazide hydrochloride (0.2 g.), potassium acetate (0.25 g.) and water (5 cc.). The solution was heated at 60° for ten minutes and the crystalline product which separated was removed by filtration and recrystallized twice from hot water; yield, 0.09 g., m. p. 200–202°. A mixed melting point determination with an authentic sample of the semicarbazone of 3-(4-cyclohexanone)-1-propanoic acid showed no depression, thereby indicating that the original product, prior to the chromic acid oxidation, was 3-(4-hydroxycyclohexyl)-1-propanol (II).

The copper–chromium oxide catalytic hydrogenation of 2,2'-divanilloyl diethyl ether (1.0 g.) resulted in a product (C) which after complete methylation with diazomethane, was distilled at a bath temperature of 150–154° (0.01 mm.); yield, 0.88 g.

Anal. Calcd. for $C_{22}H_{30}O_6$: OCH_3, 33.1. Found: OCH_3, 33.0.

Hydrogenation of V.—The second dimer (V) was hydrogenated under the various conditions indicated in Table II. The resulting products were isolated by alkaline separation into phenolic and non-phenolic fractions, dis-

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(13) Smith and Bryant, THIS JOURNAL, 57, 61 (1935).

TABLE II

HYDROGENATION OF 1-VERATROYL-1-[2-METHOXY-4-(PROPANONE-1)-PHENOXY]-ETHANE[a]

Dimer, g.	Sat. dimer,[b] g.	Charge solvent, cc.	Ra Ni, g.	CuCrO, g.	Time, hours	Total weight, g.	Sat. dimer, g.	Products,[c] g. RCH_2-CH_2CH_3	Products,[c] g. $R'CH_2$-CH_2CH_3
4.0	..	EtOH–H_2O 1:1, 100	3.5	...	4	3.6	1.1	1.1	1.2
8.2	..	EtOH 150	...	4	1	7.3	1.1	2.9	3.0
...	1.0	EtOH 75	...	0.3	1	0.96	0.96	..	..
...	0.96	EtOH–H_2O 1:1, 100	1.0	...	4	.88	.42	0.23	0.21
1.0	..	EtOH–H_2O 1:1, 100	1.0	...	4	.86	.40	.21	.23
1.0	..	EtOH–H_2O 1:1, 100	1.0	...	1	.91	.59	.12	.10
1.0	..	H_2O 100	1.0	...	4	.92	.40	.23	.21
....	1.0	EtOH–H_2O 1:1, 100	...	0.5	1	.92	.74	08	.07
1.0	..	EtOH–H_2O 1:1, 100	1.0	...	12	.65	Identified as 4-*n*-propylcyclohexanol 117–120° (15 mm.)		

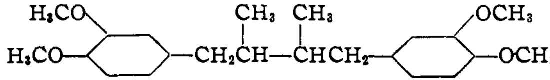
[a] Sodium hydroxide (3 g.) was added to mixture in 1st, 4th, 8th and 9th runs. Pressure was 3000 p.s.i. in each run. Temperature was 150–160° except in the last run, which was 185°. B. p. of sat. dimer was 171–173° (0.01 mm.). B. p. of $RCH_2CH_2CH_3$ was 70–72° (0.01 mm.). B. p. of $R'CH_2CH_2CH_3$ was 83–85° (0.01 mm.). [b] This refers to XI. [c] R and R[1] refer to veratryl and guaiacyl, respectively.

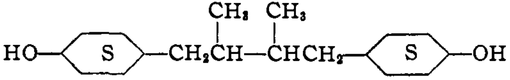
TABLE III

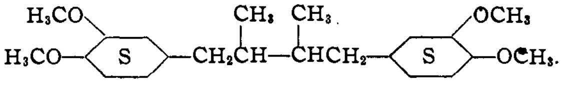
HYDROGENATION OF 2,3-DIVERATROYLBUTANE[a]

Weight, g.	Solvent, cc.	Catalyst, g.	Time, hours	Temp., °C.	Products
5.0 XII	EtOH–H_2O 1:1, 150	RaNi 5	4	165	4.2 g. (91%) distilled[b] at 211–213° (0.02 mm.), m. p. 77–78°. Calcd. for $C_{22}H_{30}O_4$: OCH_3, 34.7; C, 73.74; H, 8.38. Found: OCH_3, 34.6; C, 73.88; H, 8.45.
3.7 Product 1	EtOH–H_2O 1:1, 150	RaNi 3.7	12	185	2.4 g. (83%) distilled[c] at 185–188° (0.01 mm.) Calcd. for $C_{11}H_{34}O_2$: OCH_3, 0.0; OH, 12.0. Found OCH_3, 0.3; OH, 11.8
2.0 Product 2	EtOH–H_2O 1:1, 150	RaNi 2	12	225–230	1.8 g. (90%) distilled[c] at 190–194° (0.02 mm.)
5.0 XII	EtOH 150	CuCrO 2.5	1	150–160	4.3 g. (93%) m. p. 77–78°[b] mixed m. p. with 1, no depression
3.8 Product 4	EtOH 150	CuCrO 1.9	12	185–190	3.3 g. (87%) distilled[d] at 200–205° (0.01 mm.). Calcd. for $C_{22}H_{42}O_4$: OCH_3, 33.6. Found: OCH_3, 33.6
3.3 Product 5	EtOH 100	CuCrO 1.6	12	225–230	2.3 g. (92%) distilled[c] at 180–184° (0.02 mm.)
2.0 Product 6	EtOH 100	CuCrO 1.0	12	260	1.6 g. (80%) distilled[c] at 180–185° (0.01 mm.)
1.3 Product 7	1,4-Dioxane 100	CuCrO 0.65	12	280	0.8 g. (62%) distilled[c] at 194–199° (0.03 mm.)

[a] Sodium hydroxide was added to mixture in 1st, 2nd and 3rd runs. Runs 1, 2, 4, 5 at 3000 p.s.i.; runs 3, 6 at 2450 p.s.i., run 7 at 1800 p.s.i., run 8 at 1650 p.s.i.

[b] Products 1, 4 are identical 

[c] Products 2, 3, 6, 7, 8 are identical 

[d] Product 5 is 

tilled under reduced pressure and finally identified by ultimate analysis. In each case the low-boiling phenolic fractions were shown to be 4-hydroxy-3-methoxyphenylpropane by the formation of the *p*-nitrobenzoate (m. p. 73.5–74.5°). A mixed melting point determination with an authentic sample of the *p*-nitrobenzoate of 4-hydroxy-3-methoxyphenylpropane showed no depression.

The final hydrogenation over Raney nickel resulted in one product only, 4-*n*-propylcyclohexanol. The phenyl urethan (m. p. 127–128°) was prepared and a mixed melting point determination with an authentic sample of the phenyl urethan of 4-*n*-propylcyclohexanol showed no depression.

Hydrogenation of VI.—The third dimer (VI) was hydrogenated and the products rehydrogenated under the various conditions given in Table III. Examination of the products indicated reduction of the carbonyl groups, demethylation, demethoxylation and/or ring reduction. However, cleavage of the carbon-to-carbon linkage in the side chain did not occur even at 280°.

Acknowledgment.—The authors gratefully acknowledge the kind financial assistance of the Canadian Pulp and Paper Association and the Spruce Falls Power and Paper Company.

Summary

1. Three dimeric compounds, containing linkages similar to those in the complex structure of

native lignin, have been hydrogenated under similar conditions to those used in the hydrogenation of spruce wood.

2. The ether-linked dimers cleaved at the ether linkage, yielding products similar to those found in the reaction mixture after hydrogenation of spruce wood.

3. The carbon-to-carbon linked dimer did not yield fission products although nuclear reduction occurred. This apparently substantiates the opinions of Hibbert that dimeric, trimeric, etc., substances obtained by the hydrogenation of wood do not arise through the carbon-to-carbon cleavage of similar but more complex polymers. It would therefore appear that these complex substances exist as such in the wood prior to the hydrogenation reaction.

MONTREAL, CANADA RECEIVED APRIL 10, 1947

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

Studies on Lignin and Related Compounds. LXXXVII. High Pressure Hydrogenation of Maple Wood[1]

BY JAMES M. PEPPER[2] AND HAROLD HIBBERT[3]

Although abundant evidence is available[4] which points to the now well-recognized essentially aromatic character of native lignin, the actual yield, to date, of identified products, is in no case very large. By means of the ethanolysis procedure[5] all of the identified lignin products obtained from maple wood are *propylphenol* derivatives but amount to only 9.75% of the original lignin (Klason basis).[6] From nitrobenzene oxidation studies[7] much larger amounts of aromatic compounds are obtained, the total mixed aldehydes (vanillin and syringaldehyde) have been isolated in yields of 43% of the lignin, but in this case it must be remembered that these derivatives have only a C_6–C skeleton and as such cannot be used as positive evidence for the presence of a C_6–C–C–C lignin monomer. Much higher yields of C_6–C–C–C compounds have been obtained by means of the high pressure hydrogenation technique[4] but in every such case these have been *propylcyclohexyl* derivatives, and, although it is improbable that these could arise from any source except a propylphenyl unit, it still remained necessary to isolate the *aromatic* C_6–C–C–C units in high yields to justify the several formulas for native lignin that have been proposed.[4,8]

In a previous communication[9] a new technique has been described by which, under greatly milder conditions of hydrogenation and hydrogenolysis, propylphenol lignin derivatives have been isolated and identified. The apparent advantages of such a method include, apart from the value of the results obtained, the use of a starting material containing *all* of the lignin *in situ* and the stabilization, by reduction, of any reactive groups formed during the pressure cook thereby preventing any subsequent polymerization which might otherwise occur. It was thought that if it were possible to remove the entire lignin fraction from the wood by this means greatly increased yields of aromatic lignin products could be obtained. To effect this a detailed study of the conditions of isolation was undertaken and subsequently when it was found possible to isolate all the lignin as a chloroform-soluble product, characterization of this material was commenced in an attempt to increase the yield of aromatic derivatives.

Preliminary Experiments.—A concurrent investigation[9] had shown that for the hydrogenation of maple wood in a neutral medium (ethanol–water (1:1)), the optimum conditions for lignin removal were 165–170° for four hours at an initial pressure of 3000 lb./sq. in. Such a medium, after the cooking procedure, had a *p*H of 5.5, and this slight acidity may have been sufficient to bring about an effective hydrolysis of any existent lignin–carbohydrate complex. This fact initiated a series of experiments[10] to study the effect of *p*H on the lignin removal by this newly developed technique. Complete solution of the lignin was obtained in both acidic and basic media. The extensive use of an acid medium (hydrochloric acid) was not favored for the following reasons: (a) poisoning of the catalyst (Raney nickel) which does not take place in alkali; (b) the tendency toward increased polymerization which is minimized in alkali due to the blocking of the phenolic hydroxyl groups, and (c) the increased tendency toward formation of hydroaromatic derivatives at a lower temperature.[11]

Dioxane was chosen to replace ethanol in the final large-scale hydrogenation experiments in

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(2) Present address: Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

(3) Late E. B. Eddy Professor of Industrial and Cellulose Chemistry, McGill University, Montreal, Quebec.

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(10) Pepper and Hibbert, unpublished results.

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