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Reaction of Hardwood Lignin with Hydrogen

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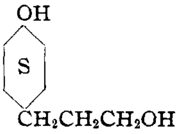
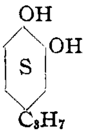
Lignin was found to react with hydrogen over copper-chromium oxide, absorbing one mole of hydrogen for each 25 g. of lignin. The reaction takes place in dioxane solution at 250–260° under 200–350 atmospheres of hydrogen during a period of about eighteen hours. The mixture of products of the reaction is colorless or faintly yellow.

There was obtained from the hydrogenation of 80 g. of hardwood lignin 22 g. of methanol, 9 g. of an alcohol, b. p. 92–95° (7 mm.), about 3 g. of a glycol, b. p. 107–110° (1 mm.), 20 g. of a glycol, b. p. 125–127° (1 mm.), 18 g. of a mixture of compounds, b. p. 130° (1 mm.) to 260° (1 mm.), 4 g. of intermediate fractions and 5 g. of compounds boiling above 260° (1 mm.).

The alcohol has been identified as 4-*n*-propylcyclohexanol-1, (I). The analysis of the glycols for carbon and hydrogen corresponds to the formula $C_9H_{18}O_2$. The one present in the larger amount contains a primary hydroxyl group and has been oxidized to a keto acid, $C_9H_{14}O_3$. The glycol is stable toward hydrogenolysis so that it cannot be a 1,2- or 1,3-glycol, but the secondary hydroxyl may be in either of the three positions on the cycle. The secondary hydroxyl is tentatively placed in the 4-position as in formula II, *i. e.*, it is 3-(4-hydroxylcyclohexyl)-propanol-1. The second glycol has been characterized as 4-*n*-propylcyclohexanediol-1,2 as shown in formula III. These three compounds together with the methanol in the dioxane fraction constituted over 70% of the total weight of lignin subjected to hydrogenation.


I


II


III

The analysis for carbon and hydrogen of the mixture of products distilling above 130° (1 mm.), corresponds to the formula $(C_6H_{11}O)_n$. This material does not contain methoxyl groups and the boiling range of the portion distilled (*i. e.*, about 75% of the fraction) indicates that n has a value of 3 to 5. The analysis for carbon and hydrogen corresponds almost exactly to an average composition of $C_{18}H_{32}O_3$ or $C_{24}H_{42}O_4$.

The products boiling above 130° (1 mm.) were dehydrated over alumina at 400° and then hydrogenated over Raney nickel. A mixture of hydrocarbons was obtained of the formula C_nH_{2n-2} or C_nH_{2n-4} boiling over a wide range above 70° (1 mm.). Most of these hydrocarbons distilled in the range 90° (1 mm.) to 140° (1 mm.). These facts indicate very clearly that there are in lignin, units containing more than nine carbon atoms, for the C_nH_{2n-2} hydrocarbon 1,2-dicyclohexylethane containing fourteen carbon atoms, distilled under exactly the same conditions, boiled at 80–81° (1 mm.).

It remains to be considered what structures for lignin are in harmony with the results of hydrogenation and hydrogenolysis just summarized. A variety of compounds have been investigated with respect to their behavior toward hydrogen over copper-chromium oxide at elevated temperatures and pressures, *i. e.*, esters, alcohols and glycols (Folkers, Wojcik, Connor and Sprague), sugars (Zartman), ethers (Van Duzee and Musser), furans (Burdick) and benzopyrans (Mozingo).[1]

For the present purpose these studies may be summarized as follows: an oxygen to carbon linkage is very labile toward hydrogenolysis over copper-chromium oxide at 250° if it is (a) in the 1,2-position with respect to a double bond in the 3,4-position, *i. e.*, $\overset{4}{C}=\overset{3}{C}-\overset{2}{C}\ldots\overset{1}{O}-$; (b) in the 1,2-position with respect to an oxygen to carbon linkage in the 4,5-position, *i. e.*, $-\overset{5}{O}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}\ldots\overset{1}{O}-$. An oxygen to carbon linkage is labile, but not so markedly so as in (a) and (b), if it is in the 1,2-position (c) with respect to a 3,4-carbon to oxygen linkage, *i. e.*, $-\overset{4}{O}-\overset{3}{C}-\overset{2}{C}\ldots\overset{1}{O}-$, or (d) with respect to a double bond in the 4,5-position, *i. e.*, $\overset{5}{C}=\overset{4}{C}-\overset{3}{C}-\overset{2}{C}\ldots\overset{1}{O}-$.

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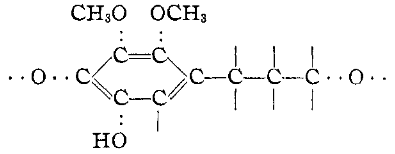
(1) The papers published prior to 1937 are summarized and correlated in a monograph: (a) Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, Madison, Wisconsin, 1937; (b) Folkers and Adkins, THIS JOURNAL, **54**, 1651 (1932); (c) Connor and Adkins, *ibid.*, **54**, 4678 (1932); (d) Wojcik and Adkins, *ibid.*, **55**, 1293 (1933); (e) Zartman and Adkins, *ibid.*, **55**, 4559 (1933); (f) Wojcik and Adkins, *ibid.*, **55**, 4939 (1933); (g) Burdick and Adkins, *ibid.*, **56**, 438 (1934); (h) Sprague and Adkins, *ibid.*, **56**, 2669 (1934); (i) Van Duzee and Adkins, *ibid.*, **57**, 147 (1935); (j) Musser and Adkins, *ibid.*, **60**, 664 (1938); (k) Mozingo and Adkins, *ibid.*, **60**, 669 (1938).

It is readily seen that if lignin consisted of the units of the type IV joined through oxygen, as suggested by Freudenberg many years ago, it would give the alcohols and glycols reported above. The linkages at which hydrogenolysis might occur are indicated by dotted lines. However, carbon to carbon linkages may also be cleaved by hydrogen so that the predominance of nine carbon units in the products does not necessarily indicate that they were joined through oxygen in the lignin. For example, propylene glycol is the chief product of the hydrogenolysis of sugars. It is therefore possible that lignin consists of long carbon chains containing benzenoid nuclei. The products isolated as described above show very definitely that units containing at least as many as eighteen carbon atoms do occur in lignin. The presence of such units in lignin has been postulated by Freudenberg and by Hibbert[2] but as far as we know no one has ever isolated from lignin a compound containing more than a nine carbon unit. Incidentally, it may be pointed out that the very high yield of methanol suggests that it did not come entirely from methoxyl groups, but also from carbon to carbon cleavage. Methanol is so produced in the hydrogenolysis of sugars.



IV

The analysis of the type of lignin submitted to hydrogenation corresponds to the formula $C_{60}H_{59}O_{18}$. Eight of the carbons and oxygens are present in methoxyl groups, while there are two hydroxyl groups capable of methylation; therefore the formula may be written as $(C_{42}H_{33}O_8(OCH_3)_8(OH)_2)_x$. One oxygen is present as a carbonyl group.[3] It is apparent that there are more oxygens in lignin than can be accounted for in hydroxyl and methoxyl groups and in joining nine carbon atom units together. The presence of even larger carbon units makes it necessary to postulate the presence of cyclic ethers presumably of the furan or pyran type. It is possible that the oxygens are in carbonyl (or the corresponding enols) rather than in cyclic ethers, although the ether, for various reasons, seems the more probable linkage. The proportion of carbon to oxygen in lignin, disregarding the hydroxyl, methoxyl and carbonyl oxygen, is six to one. This is the same proportion of carbon to oxygen found in the product boiling above 130° (1 mm.).

The capacity of lignin to take up hydrogen is perhaps best indicated by the fact that a given weight of lignin will take up more hydrogen than the same weight of ethylene or benzene. If lignin consisted of nine carbon atom units such as IV, and contained the methoxyl, hydroxyl, carbonyl and ether oxygens indicated by analysis, it would not take up as much hydrogen in the process of conversion to the alcohols, glycols and ethers, as has been found to be true. This fact should be considered in formulating a structure for lignin.

The proportion of the lignin converted to the nine carbon alcohol and glycols, as compared with the proportion converted to products boiling above 130° (1 mm.), is not necessarily an indication of the proportion in lignin of nine carbon units as compared with larger units. For if hydrogenation of unsaturated linkages precedes hydrogenolysis of carbon to carbon or oxygen to carbon linkages, then cleavage (hydrogenolysis) may not ensue, because the unsaturated groups which facilitate cleavage are no longer present. If hydrogenolysis takes place first, then hydrogenation will ensue. Thus the proportion of the products may be a function of the relative rates of hydrogenation and hydrogenolysis and may not be due to differences in structure. The relative rates of hydrogenation and hydrogenolysis are often quite sensitive to small changes in experimental conditions. In fact, in some hydrogenations of lignin we have obtained a larger proportion of the higher boiling products.

Experimental Part

Preparation of Lignin.—Freshly cut aspen (*populus tremuloides*) wood was made into coarse sawdust and while still green extracted continuously with cold ethyl alcohol for six days, and with an ethanol–benzene mixture (1:2) for two days in a Lloyd extractor. The extracted wood (450 g.) containing 22% lignin was then air dried and refluxed for three days with 4.5 liters of methanol (99%) containing 3% hydrogen chloride by weight. The methanol solution was removed and concentrated to about two volumes and then poured into 10 liters of cold water. The lignin (60–65 g.) thus thrown out was filtered from the solution. The lignin, after air drying in the dark for one day, was again dissolved in 750 ml. of methanol and precipitated by pouring into 10 liters of water, air dried and

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(2) For recent references to lignin see Freudenberg, Meister and Flickinger, *Ber.*, **70**, 500 (1937); Leger and Hibbert, THIS JOURNAL, **60**, 565 (1938); Freudenberg, *Papier-Fabr.*, **36** (Tech. Tl.) 34 (1938); *C. A.*, **32**, 2909 (1938); Hibbert, *Can. J. Research*, **16**, 71 (1938).

(3) E. E. Harris, THIS JOURNAL, **58**, 894 (1936); also a paper given before the Cellulose Division at the American Chemical Society meeting in Pittsburgh, 1936.

then dissolved in 300 ml. of glacial acetic acid. The insoluble fractions were discarded. The glacial acetic acid solution was poured into 20 liters of water, and after filtering was washed until free of acetic acid. It was first air dried and dried at 35° (5 mm.) overnight. The yield was 59 to 60 g. of a very light tan colored powder. The yield may be increased to about 90 g. if the sawdust is subjected to repeated treatments.

Reaction of Hydrogen with Lignin.—The most favorable conditions for the reaction of hydrogen with lignin yet found were those used for the experiment described in the text above. Eighty grams of lignin was dissolved and made up to a volume of 800 ml. with dry dioxane. This solution was submitted to hydrogenation in six portions. Each portion was placed with 7 g. of copper–chromium oxide in a reaction vessel having a void of 270 ml.[4] Hydrogen was admitted to a pressure of 220 atm. and the reaction vessel then heated to 260° within fifty minutes. The maximum pressure was about 400 atm. The pressure dropped about 50 atmospheres (calcd. to 23°) during the course of four or five hours and then about 50 atm. further within the next ten or twelve hours. Agitation of hydrogen, catalyst and lignin products was continued until after the absorption of hydrogen had stopped; this involved a total reaction time of eighteen to twenty-two hours.

Lignin obtained from wood by the soda process or the sulfuric acid method has also been hydrogenated with somewhat similar results.

Separation of Products.—The catalyst was removed by centrifuging and the products of the six hydrogenations combined. The methanol–dioxane–water fraction was then removed through a Widmer column. The materials boiling above 100° (740 mm.) (59 g.) were then distilled without a column, the lower portion (35 g.) at 65–130° (1 mm.) and the higher (18 g.) at 130–270° (1 mm.), an electrically heated oil-bath was used for the former and a Wood's metal bath for the latter. The fraction, b. p. 65–150° (1 mm.), was carefully fractionated and refractionated through a "modified Widmer column" using the column and technique recently described.[5]

The methanol–dioxane–water fraction, boiling below 100° at 740 mm., was dried over oven-dried anhydrous potassium carbonate for several days, then decanted and fractionated through a Widmer column having a spiral 30 cm. in length. The part boiling below 75° at 740 mm. was dried and refractionated; 22 g. boiled between 64 and 66° (740 mm.), d^{20}_{4} 0.803, $n^{25}_{\rm D}$ 1.338.

Characterization of Products.—A sample of 4-*n*-propylcyclohexanol-1, I, was prepared by the following series of reactions. Phenyl propionate was rearranged to *p*-hydroxypropiophenone, m. p. 150°, b. p. 185° (8 mm.) by the method given in "Organic Syntheses" for hydroxyacetophenones.[6] Thirty grams of the ketone in 90 ml. of ethanol was hydrogenated over Raney nickel within thirty minutes between 100–200°. The resulting 4-*n*-propyl-cyclohexanol-1, $n^{25}_{\rm D}$ 1.4617, b. p. 92–93° (7 mm.), was obtained in almost quantitative yield. The α-naphthylurethan was prepared and found to melt at 136° (from petroleum ether, b. p. 90–100°) while the phenylurethan from the same solvent melted at 131°.

The alcohol, $n^{25}_{\rm D}$ 1.4615, from lignin had the same boiling range as 4-*n*-propylcyclohexanol-1, gave an α-naphthylurethan, m. p. 134°, and a phenylurethan, m. p. 129–130°. The mixed melting points with the authentic samples prepared as above were 134° for the α-naphthylurethan, and 130–131° for the phenylurethan.

A sample of 4-*n*-propylcyclohexanediol-1,2 (b. p. 107–110° at 1 mm.), III, was prepared by rearranging catechol propionate to 3,4-dihydroxypropiophenone,[7] m. p. 145°, b. p. 220° (10 mm.), and then hydrogenating to the desired compound as in the case of 4-*n*-propylcyclohexanol-1. The bis-α-naphthylurethan prepared from the glycol had a m. p. of 218–219° (from 95% alcohol) while that for the glycol from lignin had a m. p. of 218–219°. The mixed m. p. was 218–219°. The boiling ranges of the two samples of glycol were the same and the refractive indices were similar, *i. e.*, $n^{25}_{\rm D}$ 1.4769 for the authentic sample and $n^{25}_{\rm D}$ 1.4801 for the glycol from lignin.

The glycol, b. p. 125–127° (1 mm.), II, was oxidized to a keto acid by the following procedure. The glycol (4.6 g.) was added slowly to a mixture containing 18 g. of sodium dichromate, 15 g. of sulfuric acid and 90 ml. of water. The temperature rose through heat of reaction to 65°. Stirring was continued until the temperature dropped to 45°. The mixture was then cooled and extracted with 25 ml. of 10% sodium hydroxide. The solution was then acidified with hydrochloric acid, extracted with ether, dried over sodium sulfate and distilled There was obtained 0.35 g. of a solid acid having a neutral equivalent of 169 as compared to a calculated value of 170 for $C_9H_{14}O_3$.

The glycol (4.7 g.) was also oxidized by shaking at room temperature for eleven hours with a mixture of chromic oxide (12 g.), acetic acid (100 g.), water (50 ml.) and benzene (100 ml.). The layers were separated, and the water layer washed with two 20 ml. portions of benzene. The combined benzene layers were extracted with three 25-ml. portions of 10% sodium hydroxide. The alkaline solution was acidified with hydrochloric acid, saturated with sodium sulfate and extracted six times with benzene. The benzene solution was dried over sodium sulfate. After evaporation of the benzene there was 1.1 g. of solid keto acid. This was distilled at 1 mm. and the product had a m. p. of 55–60° and a neutral equivalent of 171. The boiling point by a micro method was apparently about 280° (740 mm.).

A 2,4-dinitrophenylhydrazone, (from alcohol) m. p. 80°, of the keto acid was prepared by the method of Allen.[8] A 3,5-dinitrobenzoate, m. p. 130–144°, of the glycol, was also prepared. The amounts of these compounds available did not permit a rigorous purification.

Eleven grams of a fraction from lignin, b. p. 150–260° (1 mm.), was heated under hydrogen for four hours at 400° with 1 g. of alumina (*ex* aluminum isopropoxide) distributed over 5 g. of Italian pumice. The liquid product was then hydrogenated over Raney nickel at 200° for three hours under 300 atm. of hydrogen. Upon fractionation of

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(4) The catalyst was prepared as described on p. 13 of reference 1a and the reaction vessel was the one described as number 11 on p. 31. The method of agitation by rocking is shown on p. 38. The Journal reference for catalyst preparation is Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

(5) Smith and Adkins, *ibid.*, **60**, 657 (1938).

(6) Miller and Hartung, "Organic Syntheses," Vol. XII, John Wiley and Sons, Inc., New York, N. Y., 1933, p. 90.

(7) Rosenmund, *Ber.*, **61**, 2601 (1928).

(8) Allen, THIS JOURNAL, **52**, 2957 (1930).

TABLE I

ANALYSES OF VARIOUS COMPOUNDS

Name		B. p. or m. p. °C.	Mm.	Formula	Analyses, % Calcd.	Found
4-Pr-cyclohexanol-1 (I)		92–93	7	$C_9H_{18}O$	C, 76.0	75.9
					H, 12.7	12.6
α-Naphthylurethan of I	M. p.	136		$C_{20}H_{25}NO_2$	N, 4.50	4.65
α-Phenylurethan of I	M. p.	131		$C_{16}H_{23}NO_2$	N, 5.40	5.36
3-(4-Hydroxycyclohexyl)-propanol-1 (II)		125–127	1	$C_9H_{18}O_2$	C, 68.3	68.5
					H, 11.4	11.5
3,5-Dinitrobenzoate of II	M. p.	130–144		$C_{23}H_{22}N_4O$	C, 50.6	50.7
					H, 4.0	4.2
					N, 10.4	9.9
Keto acid from II	M. p.	55–60		$C_9H_{14}O_3$	C, 63.5	63.2
					H, 8.2	8.3
3,5-Dinitrophenylhydrazone of the keto acid	M. p.	90–93		$C_{15}H_{18}N_4O_6$	N, 16.0	15.1
4-Pr-cyclohexanediol-1,2 (III)		107–110	1	$C_9H_{18}O_2$	C, 68.3	68.3
					H, 11.4	11.3
bis-α-Naphthylurethan of III	M. p.	218–219		$C_{31}H_{32}N_2O_4$	N, 5.65	5.56
Residue from hydrogenation of lignin	Above	130	1	....	C, ..	72.9
					H, ..	10.8
Hydrocarbons from residue above		100–115	1	....	C, ..	86.6
					H, ..	12.5

the product 6 g. of material boiling over the range from 70° (1 mm.) to 140° (1 mm.) was obtained. Analysis of these fractions showed the compounds to be hydrocarbons.

A similar residue (15 g.) from the hydrogenation of lignin but which contained 5 g. of material boiling above 260° (1 mm.) was put through the same process. About 5 g. of hydrocarbons was obtained. The analysis for a portion of this product boiling 100–115° (1 mm.) is given in the table. The analysis for the mixture from the hydrogenation of lignin boiling above 130° (1 mm.), which was submitted to dehydration, is also given in the table.

The authors are indebted to E. E. Bowden for the syntheses of *p*-hydroxypropiophenone and 3,4-dihydroxypropiophenone needed for the syntheses of 4-*n*-propyl cyclohexanol-1 and 4-*n*-propylcyclohexanediol-1,2, respectively, and to H. A. Campbell for the analyses of various compounds and products.

Summary

Lignin, extracted from aspen and dissolved in dioxane, reacted with hydrogen so that one mole was taken up by 25 g. of lignin. Four products, *i. e.*, methanol, 4-*n*-propylcyclohexanol-1, 4-*n*-propylcyclohexanediol-1,2 and 3-(4-hydroxycyclohexyl)-propanol-1 have been separated and identified. The weight of methanol isolated and the combined weight of the three nine carbon atom compounds identified were about 28 and 44%, respectively, of the weight of the lignin submitted to hydrogenation. The highest yields, previously reported, from a hardwood lignin by any treatment were 4% for methanol and 9.5% of aromatic compounds isolated after methylation. It has been shown that there are units of fifteen or more carbon atoms in the higher boiling products These products appear to be hydroxy saturated ethers.

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