

was isolated by alcoholic extraction, while after thirteen months decay by *Lenzites sepiaria*, 18.3% was obtained.

3. The lignin liberated from its association in the wood by the enzymatic activity of the micro-

organisms was found to be identical with the Native Lignin of the wood.

4. The nature of the linkage between lignin and cellulose in softwood is discussed.

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Experiments on the Fractionation of Isolated Wood Lignins

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The separation of the bulk of lignin from the carbohydrate portion of wood material is invariably accomplished by the use of chemical reagents which alter the structure of the original material. The soluble lignin derivatives so obtained have usually been separated by physical methods: fractional precipitation from solution,² partitioning between neutral solvents,³ or diffusion experiments.⁴ The fractions isolated by a single method have usually been fairly similar in analysis, and the assumption has therefore been general that "protolignin" is a polymer system based on a single repeating structure. The following results indicate that at present such a conclusion is based on incomplete evidence.

When maple hydrol lignin⁵ was subjected to a systematic fractionation by partial solution and precipitation, a series of fractions was obtained differing substantially in molecular weight but little in alkoxy content. When, however, individual fractions were then subjected to a chemical separation, counter-current extraction against alkali and alkaline buffers,^{6,7} the substrates were found to consist of mixtures of materials with widely different partition coefficients and alkoxy contents.⁸ In this case the original similarity in analysis of different molecular weight fractions obviously had little structural significance. Similar separations were also achieved using ethanol spruce and ethanol maple lignins.

The initial experiments, outlined in Table I, are in part a confirmation of the work of Brewer, Cooke and Hibbert⁵ who reported that hydrol lignin was prepared in good yield, was aromatic

in nature, contained both ether-soluble and ether-insoluble constituents, and was stable to ordinary laboratory manipulations. The ether-soluble portion, as these authors report, consisted largely of distillable monomers, together with some non-distillable resin, and could be separated into alkali-soluble and insoluble material.

TABLE I

RECOVERY OF HYDROL LIGNIN FROM	MAPLE	WOOD ^a
	G.	% ^b
A. Ether-soluble		
1. Alkali soluble, distillable	22.7	21.8
2. Alkali soluble still residue	9.05	8.68
3. Neutrals	6.35	6.1
B. Ether-insoluble	34.0	32.6
C. Recovered from aqueous residues	3.65	3.5
D. Lignin in wood residue	...	20.4
Total		93.1

^a Weight 540 g. containing 19.3% of Klason lignin.

^b Of original Klason lignin. These values are undoubtedly high since no corrections were applied, and the lignin isolated contained the elements of ethanol derived from the hydrogenation medium.

Since dioxane was found to be a better solvent than ethanol for hydrol lignin, a second series of wood hydrogenations was carried out in which the usual solvent, 50% ethanol, was largely replaced by 50% dioxane (Method II, Experimental Section). Although the product obtained appeared identical with hydrol lignin in alkoxy content and fractionation characteristics, the yields were erratic and poor. Ethanolysis of the protolignin appeared, therefore, to be involved in the hydrol lignin preparation, and in fact ethoxyl groups were later shown by difference⁹ to be present in the product.

The ether-insoluble fraction of hydrol lignin, a light-colored powder not previously examined in detail, was found in the present research to be in part diffusible through cellophane, and to contain components of differing solubility. A systematic fractional precipitation from solvents by conventional methods, outlined in Fig. 1, separated the material into six fractions (I to VI) which were obtained as powders, and a seventh (VII), the most soluble, as a resin. The alkoxy values

(1) Harold Hibbert Memorial Fellow 1948-1949. Present address: New York State College of Forestry at Syracuse University, Syracuse, New York.

(2) Patterson, West, Lovell, Hawkins and Hibbert, *THIS JOURNAL*, **63**, 2065 (1941).

(3) Lovell and Hibbert, *ibid.*, **63**, 2070 (1941).

(4) Olleman, Pennington and Ritter, *J. Colloid Science*, **3**, 185 (1948).

(5) Brewer, Cooke and Hibbert, *THIS JOURNAL*, **70**, 57 (1948).

(6) Craig, Golumbic, Mighton and Titus, *J. Biol. Chem.*, **161**, 321 (1945).

(7) Golumbic, *THIS JOURNAL*, **71**, 2627 (1949).

(8) Previous workers who have isolated hardwood lignin derivatives of varying methoxyl content include Holmberg (*Arkiv. Kemi, Mineral, Geol.*, **24A**, No. 29 (1947); *C. A.*, **43**, 2767g (1949)), Lieff, Wright and Hibbert, *THIS JOURNAL*, **61**, 1477 (1939)), and Lovell and Hibbert ref. 3.

(9) Cooke and Hibbert, *Ind. Eng. Chem., Anal. Ed.*, **15**, 24 (1943).

of fractions II to VI (listed in Table II) ranged from 24 to 26%, a difference to which little significance was at first attached because of the possibility of some retention of solvent. Fraction I, on the other hand, had a much lower alkoxy content. Since no marked discontinuity was apparent to account for the differences in solubility of fractions II to VI, molecular weight determinations were made. Barger's isopiestic method^{10,11} was used for convenience and because traces of adsorbed solvent should by this method cause the least error. Least soluble fractions I and II had molecular weights too high to be reliably estimated under our conditions, and solutions of I were obviously colloidal. The most soluble portion of hydrol lignin has previously been shown to consist of monomers.⁵ Between these extremes, a regular gradation in the molecular weights of fractions III, IV, V and VI (Table II) made it clear that this property dominated the course of fractionation from inert solvent mixtures.¹²

In order to determine whether the individual molecular weight fractions were chemically heterogeneous, hydrol lignin fractions II, IV and VI (Fig. 1) were partitioned between nearly equal volumes of ethanolic chloroform and ethanolic aqueous alkali, and by employing the counter-current extraction method of Craig⁶ a distribution was found in each case characteristic of a mixture of two different classes of materials: one which entered into chemical combination with the alkali (Table III, Column A), and the other which remained preferentially soluble in the ethanolic chloroform after a three or four-fold extraction with alkali (Table III Columns D and E). The latter, classified as "neutral" in Table III, presumably contains fewer phenolic groups

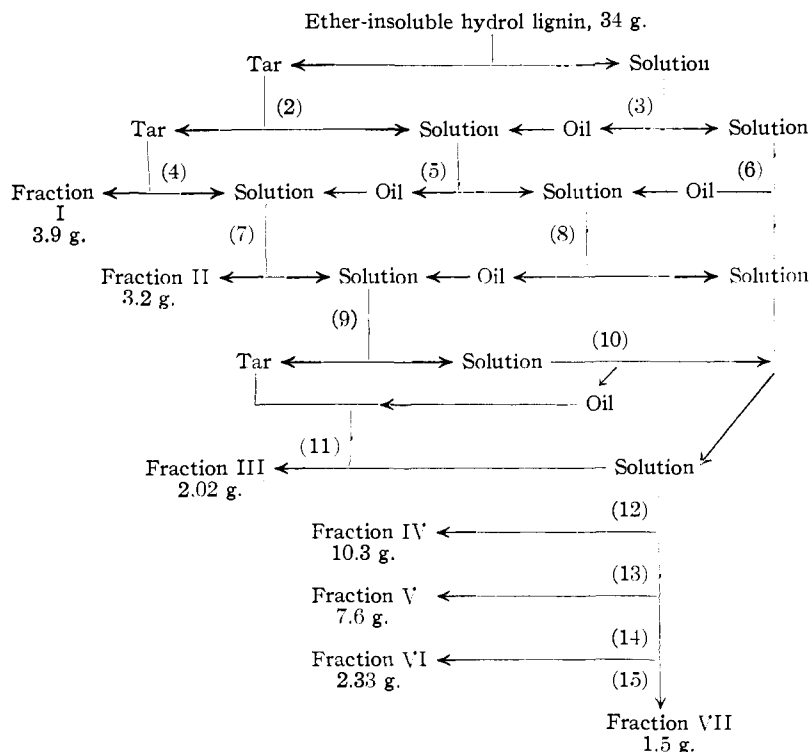


Fig. 1.—Fractionation of ether-insoluble hydrol lignin B with solvents: (1) extracted with 400 ml. of hot ethanol and centrifuged; (2) dissolved in less than 100 ml. of dioxane, and precipitated into 800 ml. of ethanol; (3) chilled and centrifuged; (4) dissolved in a small amount of dioxane and precipitated into 400 ml. of ethanol; (5) evaporated to 250 ml., and a few ml. of ether added; (6) diluted to 400 ml. with ethanol and precipitated in 400 ml. of ether; (7) evaporated to ca. 50 ml. and precipitated in 175 ml. of ethanol; (8) made up to 300 ml. with ethanol and 300 ml. of ether added; (9) oil dissolved in 225 ml. of this solution on heating, and solution cooled to precipitation point; (10) an equal volume of ether added; (11) dissolved in a small amount of dioxane and precipitated with 200 ml. of ethanol; (12) evaporated to 310 ml. and precipitated with an equal volume of ether; (13) evaporated to small volume, and precipitated in ether washings from IV; (14) evaporated to small volume and precipitated in 150 ml. of ether; (15) precipitated from small volume with petroleum ether; total recovery, 30.85 g. or 90.9%.

than the alkali-soluble material. Chemical differences between the alkali-soluble and neutral material are also indicated by the results of total alkoxy and methoxy determinations which are recorded in Table II.

The proportion of neutral material present in the hydrol lignin fractions decreased regularly from fraction II (of highest molecular weight) to IV to VI (of lowest molecular weight). It is interesting that this distribution is that to be expected, if a relatively "neutral" high molecular weight polymer is fragmented during isolation, with the liberation of phenolic groups, and *if little or no repolymerization occurs*.

Molecular weights of the partitioned hydrol lignin samples IVA, IVE, VIA and VIE were determined by Dr. I. E. Puddington of the National Research Council by means of the vapor

(10) Barger, *J. Chem. Soc.*, **85**, 286 (1904).

(11) Caesar, Gruenhut and Cushing, *THIS JOURNAL*, **69**, 617 (1947).

(12) Similarly, the fractional precipitation of ethanol maple lignin has given a high molecular weight fraction low in alkoxy content and a series of fractions of similar alkoxy content and decreasing viscosity (ref. 2). For the similarity of hydrol lignin to ethanol lignin on hydrogenolysis see the section of this paper entitled Appendix.

TABLE II

ANALYTICAL DATA ON FRACTIONS OF HYDROL LIGNIN B (FIG. 1) AND SUB-FRACTIONS (TABLE III)

Fraction no.	Yield, ^a %	Total alkoxy, % ^b	Methoxy, % ^b	Apparent mol. wt. ^d	C, % ^e
I	11.5	18.7	16.5		...
II	9.4	25.8 ^o
IIA ^f		22.7	20.3 ^g
IID ^f		26.6	23.1
III	6.0	25.2		1470-2640	4 ^h
				1470-2480	3 ^h
				1830-4400	2 ^h
IV	30.3	25.2		1445-1625	2 ^h
IVA ^f		24.2	19.75	1560	2.52 ⁱ
				1400	2.30 ⁱ
IVE ^f		27.0	22.4	2230	3.86 ⁱ
				1640	2.58 ⁱ
V	22.4	24.7		730-870	2 ^h
VI	6.9	23.9		< 723	2 ^h
				643-723	1.33 ^h
VIA ^f		24.6	21.3 ^j	940	3.64 ⁱ
				950	2.34 ⁱ
VIE ^f		25.4	20.2	1230	6.3 ⁱ
				1140	4.5 ⁱ

^a Of ether-insoluble hydrol lignin B. Total recovery from fractionation 90.9%. ^b Average values. ^c Concentration of lignin in mol. wt. determination. ^d Apparently colloidal. ^e Individual values discordant at 25.4, 26.1%. ^f Subfractions obtained by partitioning between chloroform-ethanol and aqueous ethanolic alkali (Table III). ^g Individual analyses 19.9, 20.6%. ^h Molecular weights by Barger's isopiestic method against azobenzene, lignin in 0% chloroform-ethanol solution. Molecular weights by this method are sensitive to variations in concentration. The ranges given indicate the limits of precision of the determinations, not the range of molecular weights present. ⁱ Molecular weights by Dr. I. E. Puddington using his vapor-pressure method; acetone solutions of lignin samples at C% concentration (ref. 13). ^j Individual analyses 21.8, 21.0%.

pressure of their solutions in acetone¹³ and are reported in Table II. The agreement between the values obtained for partitioned and unpartitioned materials is fairly good considering the difference in method and conditions employed in the determinations. The fact that the molecular weights of both IVA and IVE are higher than those of either VIA or VIE supports the supposition that the method of partitioning is primarily dependent not on differences in molecular weight but rather on chemical differences.

Because of the similarity of hydrol to ethanol lignin, ethanol lignins from both maple and spruce (Table III, 4 and 5) were partitioned by the same method and found to contain appreciable amounts of both "neutral" and alkali-soluble substances. When the two types were separately refluxed with 2% ethanolic hydrogen chloride in an inert atmosphere for forty-eight hours, the neutral fraction was converted largely into alkali-soluble material (Table III (9)) but from the alkali-soluble material, very little neutral material

(13) Puddington, *Can. J. Research*, **B27**, 151 (1949).

TABLE III

SEPARATION OF ALKALI-SOLUBLE AND NEUTRAL FRACTIONS^a

No.	Lignin sample	Alkali-soluble					Recovery, %
		A	B	C	Neutral		
		D		E			
(1)	Hydrol II	23.6	7.5	7.5	55.3	.. ^b	94
(2)	Hydrol IV	34	8	7	22 ^c	21 ^c	92
(3)	Hydrol VI	44	5	6	8	24.5	87.5
(4)	Benzene-sol. ethanol maple	20	3.2	2.8	6.4	57.3	89.7
(5)	Unfractionated ethanol spruce	51.9	3.8	2.9	5.7	21.3	85.6
(6)	Native spruce	55	4	... ^d	.. ^d	1	60 ^e
(7)	Native aspen	76	2.8	1.1	0.7	1.2	81.8
(8)	(4)A after re-ethanolysis	85	7	92
(9)	(4)E after re-ethanolysis	70	28	98

^a Analytical data on the partitioned fractions are listed in Table II. ^b Omitted. ^c Poor separation of layers at this point. ^d No material precipitated from an ether-ligroin mixture. ^e Low recovery because of solubility in the precipitant. Some color also remained in the aqueous layers of A after acidification and resisted extraction with chloroform-ethanol in the case of samples numbered (4) to (9) above.

was obtained (Table III (8)). Phenolic groups, therefore, are liberated rather than masked during ethanolysis. Since native spruce and aspen lignins (Table III (6) and (7)) were found to be nearly completely alkali-soluble on partitioning, it appears probable that these lignins contain a higher proportion of phenolic groups than does the bulk of protolignin from which the ethanol lignins are derived.

Because the above separation is essentially a division of the components of isolated lignins into two broad classes, the separation was continued by the similar series of counter-current extractions against buffers shown in Fig. 2. It was found possible to separate an alcohol-soluble ether-insoluble hydrol lignin which had been prepared according to Method II (Experimental) into various fractions including one not extracted from chloroform by ethanolic alkali (fr. 1), another extracted from chloroform by alkali but not extracted by a buffer of pH ca. 12 (fr. 3), and another extracted from chloroform by a buffer of pH ca. 9.6, but not extracted by bicarbonate (fr. 7). The most acidic fraction remained preferentially soluble in bicarbonate after a three-fold extraction with ethanolic chloroform (fr. 8).

TABLE IV

PARTITION OF HYDROL LIGNIN AGAINST BUFFERS

Fraction	Yield, g.	Alkoxy, %	Fraction	Yield, g.	Alkoxy, %
1	2.80	26.6	5	0.38	23.4
2	3.35	23.9	6	.15	21.1
3	1.03	24.5	7	.16	21.7
4	0.39	23.5	8	.26	20.6

There was found to be an essentially regular increase in alkoxy content with decrease in apparent acidity of the individual fractions (Table IV). This by no means constitutes an ultimate separation, and there is probably some overlapping of fractions 4 and 5, and 5 and 6 (Fig. 2). It seems clear, nevertheless, that there is an extraordinary mixture of chemical individuals present in a portion of hydrol lignin fairly homogeneous to fractional precipitation.

The relationship of hydrol lignin to protolignin is not yet established, but it appears most probable that the functional groups which are operative in the partitioning experiments are at least in part an artifact of isolation. The difference in methoxyl content of the various fractions, however, may indicate that the original structure or structures of protolignin contain different proportions of guaiacyl and syringyl units. It is possible that, like holo-cellulose, hardwood protolignin is a mixture or combination of chemically related polymers, probably in large part "neutral" in character. The non-phenolic monomers isolated by various workers^{14,15,16} may be an integral part of such a complex.

Experimental

Analytical.—Products were prepared for alkoxy determinations by boiling two hours in ligroin and drying at 50° *in vacuo* overnight. Individual analyses were consistent, but an alkoxy balance on hydrol lignin fractions II, IV, and VI (Fig. 1), before and after partitioning (Table III) indicated a cumulative error for three analyses of +0.7, -0.4, and -1.0% alkoxy. Methoxyl values were obtained by the method of Cooke and Hibbert.⁹

Molecular weights were determined by an isopiestic technique¹⁰ which recently gave satisfactory results with starch nitrates.¹¹ Lignin solutions usually 2% (weight: volume) in chloroform-ethanol (1:1 by volume) and standard solutions of azobenzene were sealed by micro flame in capillary tubes and equilibrated at constant temperature (25 ± 0.1°) for eighteen to twenty-four hours. Details of the method can be found in the above references.

Isolation of Hydrol Lignin from Maple. Method I.—The method of Brewer, Cook and Hibbert was followed⁵;

(14) Hachihamada and Jodai, *J. Chem. Soc. Ind. Japan*, **46**, 507 (1943); *C. A.*, **43**, 2428c (1949).

(15) Bailey and Brooks, *THIS JOURNAL*, **68**, 445 (1948).

(16) Hewson and Hibbert, *ibid.*, **65**, 1173 (1943); and earlier articles by Hibbert and co-workers report a neutral monomeric fraction obtained by ethanolysis.

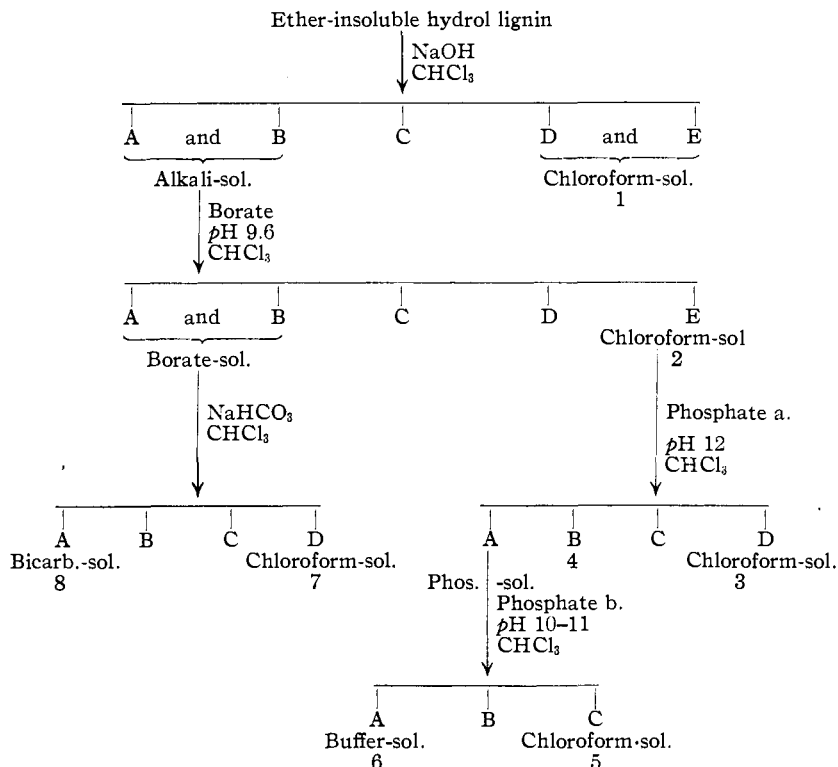


Fig. 2.—Partitioning of hydrol lignin between chloroform and various aqueous alkaline solutions. Horizontal lines indicate individual counter-current extractions; brackets, the recombination of fractions; capital letters, the separating funnels used in each partitioning as in Table III. The substrate used was an alcohol-soluble, ether-insoluble hydrol lignin prepared according to Method II, and isolated by fractional precipitation, and weighing 9.8 g. Lignin samples isolated are labelled with Arabic numerals and data on them are listed in Table IV.

solvent-extracted maple wood meal (90 g., 19.3% Klason lignin) was hydrogenated over Raney nickel (75 g., wet with ethanol) in 1350 ml. of ethanol-water (1:1 by volume) for six hours at 160–180°. The initial hydrogen pressure was 2600 p. s. i. After filtration, the aqueous liquors from six runs were extracted with chloroform as described,⁵ and twice concentrated to small volume and precipitated into ethanol. Two crops of yellow powders were obtained, 18.6 and 12.0 g. in weight, of methoxyl contents 1.8 and 4.3%, respectively. Reconcentration of the mother liquor, and extraction with chloroform yielded 3.6 g. of hydrol lignin (Table I, C).

The combined chloroform solutions from six runs were dried over sodium sulfate, concentrated, and precipitated into 3 l. of ether. After being washed four times on the centrifuge with ether, the ether insoluble fraction of hydrol lignin was recovered as a light brown powder (B, of Table I). Evaporation of the ether solutions gave a chloroform solution from which was obtained, by suitable separation, a neutral oil which was not further investigated (A3 of Table I) and an alkali-soluble oil (31.75 g.). On distillation to 290° at 1 mm., the latter yielded a mixture of oil and crystalline 3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol⁶ of proper melting point, and a non-distillable resin (A2 of Table I).

Method II.—An equal volume of purified dioxane and water (1:1) was substituted for the aqueous ethanol used in method I, but a small amount of ethanol was incidentally introduced with the catalyst. The yields of hydrol lignin were lower and more variable, and 450 g. of maple wood was hydrogenated in order to accumulate 17 g. of

ether-soluble hydrol lignin and 24.1 g. of ether-insoluble hydrol lignin.

Fractionation of Ether-insoluble Hydrol Lignin B with Solvents.—Various fractions derived from 34 g. of starting material (B of Table I) were obtained as indicated in Fig. 1. The products usually separated as resinous oils which were separately dissolved in purified dioxane or in chloroform-ethanol and were reprecipitated into a suitable liquid (ether, ligroin or a mixture of the two). The products were recovered and washed four times on the centrifuge and dried. Fractions I to VI were light colored powders, but fraction VII was a resin similar to the non-distillable resin A2 of Table I. Analytical data for fractions I to VI are in Table II.

Subfractionation by Partition between Chloroform and Aqueous Alkali or Alkaline Buffers.—A mixture of 120 ml. of U. S. P. chloroform, 150 ml. of aqueous sodium hydroxide varying from 0.2 to 1.0 *N* in different experiments, and 150 ml. of ethanol was shaken in a separatory funnel, and two layers of almost equal volume were recovered. These equilibrated layers were the stock solutions for the partitions.

A 4% solution of the lignin sample in some of the equilibrated chloroform layer was placed in the first of five separatory funnels labelled A to E. An equal portion of alkali was placed in each funnel, and funnel A was shaken. After separation, the chloroform layer from A was transferred in order through the funnels to E, equilibrating before each transfer. This was followed by successive extractions of the remaining alkaline solutions in the same order with fresh chloroform, according to the method of Craig⁶ until all five funnels contained two layers; the lignin in funnel A was almost totally alkali soluble, and that in E almost entirely in the chloroform. Acidification and re-extraction gave chloroform solutions of the lignin fractions which were isolated by concentration under reduced pressure and precipitation (Table III), or were subjected to further partitions (Fig. 2) using the following alkaline buffers (the *pH* values of which were taken from tables for more dilute aqueous solutions). **Borate** *pH* 9.6.—500 ml. of 0.4 *M* sodium hydroxide in 90% ethanol and 368 ml. of 0.4 *M* boric acid in aqueous potassium chloride, diluted to 1 liter and equilibrated against 400 ml. of chloroform. **Bicarbonate.**—An aqueous 2.4% solution. **Phosphate a**, *pH* 12.—Anhydrous disodium phosphate, 21.3 g., sodium hydroxide, 6 g., distilled water 772 ml., and ethanol 728 ml., equilibrated against 1210 ml. of chloroform. **Phosphate b**, *pH* about 10 to 11.—750 ml. of 0.15 *N* disodium phosphate, 18.8 ml. of 1 *N* sodium hydroxide and 90 ml. of ethanol. (Extraction of a chloroform-ethanol solution of lignin with this solution resulted in the separation of an oily lignin layer at the chloroform-water interface which was redissolved by the addition of extra ethanol.)

Appendix

Hydrogenation of Hydrol Lignin Fractions.—

Unfractionated ether-insoluble hydrol lignin, 13.8 g., was hydrogenated over 7.0 g. of a copper chromium oxide catalyst in 150 ml. of purified dioxane for six hours at 250° and then five hours at 280°. The catalyst and dioxane were removed and distillation of the product through a Cooke-Bower column¹⁷ gave the expected propylcyclohexanol fraction (*n*_D²⁰ 1.4620–30, mol. wt. (Rast) = 141) and semicrystalline diol fraction (*n*_D²⁰ 1.4860–1.4925) in a combined yield of 3.80 g., distillable greases of increasing viscosity and boiling point, 1.20 g., and a still residue, 1.13 g.

A mixture of fractions IV (8.4 g.) and V (5.4 g.), hydrogenated under the same conditions yielded 5.0 g. of mono and dihydric propylcyclohexane alcohols, 0.67 g. of distillable greases, and 0.5 g.

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

of still residue. Titration of an aliquot of the reaction mixture with Karl Fischer reagent showed that 3.1 g. of water had been formed.

The higher molecular weight fractions of hydrol lignin thus give lower yields of distillable monomers than the lower molecular weight fractions. The yields are in the range obtained also by the hydrogenation of maple wood¹⁸ and ethanol maple lignin fractions.¹⁹

Oxidation of Hydrol Lignin.—Unfractionated ether-insoluble hydrol lignin (2.0 g.) was oxidized with 500 ml. of Fehling solution according to the directions of Pearl.²⁰ The alkali and ether soluble fraction of aliquots withdrawn at one, three and six hours gave no crystalline precipitate when allowed to react with 2,4-dinitrophenylhydrazine. Simple phenolic aldehydes were, therefore, not formed under these mild conditions of oxidation. Apparently a functional group necessary for the production of vanillin and syringaldehyde has been removed during the preparation of hydrol lignin.

Acknowledgment.—The author owes much to the experience of Dr. C. B. Purves in this field and wishes to express his deep appreciation to him for his generous aid and kindly interest in this and related work. To Dr. Puddington for his determination of the molecular weights of several lignin fractions herein reported; to Dr. F. E. Brauns for a sample of native aspen lignin; and to Dr. S. E. Gottlieb of the University of Maryland for a sample of native spruce lignin, the author is also indebted.

Summary

Hydrol lignin is shown to consist of components of differing molecular weight which can be separated by fractional precipitation. The individual fractions so obtained are themselves mixtures of chemically unlike materials which have been partially separated by counter-current extraction against alkali and alkaline buffers.

Ethanol lignins, previously reported to be alkali-soluble have been separated by counter-current extraction into material soluble in alkali and material extractable from alkaline solution. It has been established that, during ethanolysis, the proportion of alkali-soluble material increases. Native lignins are almost completely alkali-soluble. The similarity of hydrol to ethanol lignin is emphasized.

MONTREAL, QUE.

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(18) Goddard, McCarthy and Hibbert, *THIS JOURNAL*, **63**, 3061 (1941), report a yield of 25.3% Klason lignin of mono and dihydric propylcyclohexane alcohols from maple wood.

(19) Cooke, McCarthy and Hibbert, *ibid.*, **63**, 3056 (1941), report an isolation of maple lignin ethanolysis products in five fractions B, C, D, F and G representing 37, 17.7, 2.3, 15, 20.5% Klason lignin, respectively. On hydrogenation, these fractions gave mono and dihydric propylcyclohexane alcohols in yields of 12, 17, 22, 33 and 48%, or a combined yield of 26.7% of the Klason lignin. The similarity of this value to that obtained from the hydrogenation of maple wood appears hard to reconcile with their view that carbon to carbon bonds are formed by polymerization during the ethanolysis procedure.

(20) Pearl, *ibid.*, **64**, 1429 (1942).