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Studies on Lignin. X. The Identity and Structure of Spruce Lignins Prepared by Different Methods

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The numerous investigations relating to the structure of lignin have been carried out on products prepared by a variety of different processes involving the use of extraction media of widely varying chemical characteristics. These media can be divided into two classes: (I) those capable of functioning as solvents for the lignin and (II) reagents capable of dissolving the cellulose. Class I can be divided into two groups Ia and Ib.

To Class Ia belong such solvents as alcohols,[1] polyalcohols, chlorohydrins[2] and phenols[3] used in conjunction with a catalyst such as hydrochloric acid; while Class Ib includes caustic alkalies.[4] Class II comprises solvents such as solutions of cuprammonium hydroxide,[5] strong mineral acids (HCl and H_2SO_4)[6,7] and trichloroacetic acid.[8]

The question as to the identity of the lignin, isolated by these various methods, with the "native lignin," as present in the original wood, still remains a matter of great uncertainty. Furthermore, no evidence has been adduced, as yet, to show that the lignins isolated by the various methods bear any direct relationship to one another.

The reason for this is to be found in the very reactive nature of the lignin complex and its tendency to undergo marked alteration in structure under the influence of chemical reagents.

Previous investigations have indicated that the use of alcohols and polyalcohols gives a lignin which has apparently undergone little or no structural change during the process of isolation.[2] It therefore seemed of interest to investigate more fully the properties and structure of "methyl alcohol lignin" and to compare this with "glycol lignin" on the one hand and, on the other hand, with lignin isolated by the use of (a) concentrated mineral acid, for instance hydrochloric ("Willstätter lignin")[6] and (b) a solution of cuprammonium hydroxide ("Freudenberg lignin").[5]

In a previous preliminary communication[9] it was found possible, on the basis of the analytical data obtained from an intensive study of carefully purified "glycol lignin" and "methyl alcohol lignin" to establish with reasonable certainty the empircal formula for "native lignin" as

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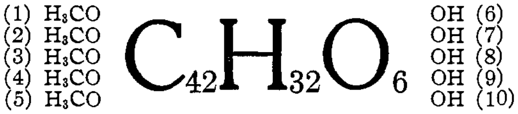
(1) E. Hägglund, *Cellulosechemie*, **8**, 69 (1927); **9**, 49 (1928).
(2) H. Hibbert and co-workers, *Can. J. Research*, **2**, 357, 364 (1930).
(3) R. O. Herzog and A. Hillmer, *Cellulosechemie*, **6**, 169 (1925).
(4) C. Dorée and L. Hall, *J. Soc. Chem. Ind.*, **43**, 257 (1924).
(5) K. Freudenberg, *Ber.*, **62**, 1814 (1929).
(6) R. Willstätter, *ibid.*, **46**, 2403 (1913); **55**, 2637 (1922).
(7) P. Klason, *Cellulosechemie*, **4**, 81 (1923).
(8) H. Hibbert, unpublished results.
(9) F. Brauns and H. Hibbert, *Pulp and Paper Mag. Can.*, **34**, 187 (1933).

$(C_{47}H_{52}O_{16})_x$ or $[C_{42}H_{32}O_6(OH)_5(OCH_3)_5]_x$. The smallest "building unit" is, accordingly



$$\begin{matrix}(1)\ H_3CO\\(2)\ H_3CO\\(3)\ H_3CO\\(4)\ H_3CO\\(5)\ H_3CO\end{matrix}\ C_{42}H_{32}O_6\ \begin{matrix}OH\ (6)\\OH\ (7)\\OH\ (8)\\OH\ (9)\\OH\ (10)\end{matrix}$$

with a molecular weight of 872.

The essential feature of this is the experimental establishment for *the first time* of a definite "building-unit" molecular weight representing the smallest unit possible which satisfies the analytical data corresponding with the introduction of *one* methoxyl group by the use of diazomethane.

It seemed probable that a connecting link between these two types of lignin might be established by their conversion into phenol condensation products, the analysis and properties of which should yield valuable information along structural lines.

This conclusion was based on the marked solubility shown by "glycol" and "methyl alcohol lignin," on the one hand, as compared with the insoluble character of "Willstätter" and "Freudenberg lignin" on the other, and the fact that both types give well-characterized, homogeneous soluble phenol condensation products in remarkably high yield.

Using this as a guiding principle it has been possible to prove definitely the structural identity of the lignin isolated by the use of the markedly different reagents grouped under Class I and Class II above.

Discussion of Results

Structural Identity of "Glycol" and "Methyl Alcohol Lignins."—In Table I are given the methoxyl values of various derivatives prepared from these two types of lignin. The methoxyl content of "glycol lignin," after treatment with diazomethane, is seen to increase from 16.8 to 21.0% and, on complete methylation, to 31.6%. The completely acetylated "glycol lignin" contains 14.1% OCH_3, or a ratio of (OCH_3) to (CH_3CO) of 1:1; in other words, for each methoxyl group there is one acetyl group present. Furthermore, acetylation of "glycol lignin" premethylated with

TABLE I

METHOXYL CONTENT OF GLYCOL AND METHYL ALCOHOL LIGNIN AND OF THEIR DERIVATIVES

Compound	Glycol lignin	MeOH lignin
Extraction medium	Glycol + HCl	MeOH + HCl
A, original lignin	16.85	21.2
B, fully acetylated product	14.1	17.9
C, original lignin (A) methylated with diazomethane	21.0	24.9
D, acetyl derivative of (C)	17.5	21.7
E, fully methylated lignin prepared from (D)	31.6	32.4
Ratio of methoxyl to acetyl in (B)	1:1	6:4
Ratio of methoxyl to acetyl in (D)	6:4	7:3

diazomethane (product C) gives a product (D) containing 17.5% OCH_3 and containing a ratio of methoxyl to acetyl of 6:4.

"Methyl alcohol lignin," on methylation with diazomethane, shows an increase in methoxyl value from 21.2 to 24.9%, while on complete methylation the value obtained is 32.4%.

The fully acetylated "methyl alcohol lignin" has a methoxyl value of 17.9%, the ratio of (OCH_3) to CH_3CO being 6:4. The acetylation of "methyl alcohol lignin" premethylated with diazomethane (C) gives a product (D) containing methoxyl and acetyl in the ratio 7:3.

It follows from these analytical data, in particular from the ratios shown, that the smallest "native lignin" building unit must contain a total of ten hydroxyl groups five of which are methylated.

From the combustion analyses of the fully methylated derivatives (E), Table I, from their methoxyl contents, and from the ratio of methoxyl to acetyl present, it is possible to calculate their empirical formulas, which, as shown in Table II, are $C_{54}H_{66}O_{17}$ and $C_{52}H_{62}O_{16}$ for fully methylated "glycol" and "methyl alcohol lignin," respectively.

TABLE II

ANALYSES AND FORMULAS OF FULLY METHYLATED GLYCOL AND METHYL ALCOHOL LIGNIN

Compound, fully methylated	Glycol lignin	MeOH lignin
Carbon, %	65.65	66.2
Hydrogen, %	6.74	6.6
Methoxyl, %	31.6	32.4
Calcd. formula	$C_{54}H_{66}O_{17}$	$C_{52}H_{62}O_{16}$
Extended formulas:		
Fully methylated lignin derivs.	$C_{44}H_{36}O_7(OCH_3)_{10}$	$C_{42}H_{32}O_6(OCH_3)_{10}$
Original lignin derivs.	$C_{44}H_{36}O_7(OH)_5(OCH_3)_5$	$C_{42}H_{32}O_6(OH)_4(OCH_3)_6$

Since there are ten methoxyl groups in each fully methylated product their formulas are represented by $C_{44}H_{36}O_7(OCH_3)_{10}$ and $C_{42}H_{32}O_6(OCH_3)_{10}$, respectively.

It also follows that on complete methylation of the "glycol lignin" *five* methoxyl groups are introduced as compared with *four* in the case of the "methyl alcohol lignin." Deducting the new methoxyl groups from the respective formulas for the fully methylated compounds, there are obtained for "glycol lignin" and "methyl alcohol lignin" the formulas $C_{44}H_{36}O_7(OH)_5(OCH_3)_5$ and $C_{42}H_{32}O_6(OH)_4(OCH_3)_6$, respectively.

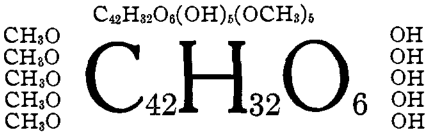
It is apparent that the former differs from the latter with respect to the (OCH_3), (OH) and the remaining radicals ($C_{44}H_{36}O_7$ and $C_{42}H_{32}O_6$), respectively.

Expanding the two formulas further to give $C_{42}H_{32}O_6(OH)_4(OCH_3)_5$-$OCH_2CH_2OH$ and $C_{42}H_{32}O_6(OH)_4(OCH_3)_5OCH_3$ it is evident that in the "methyl alcohol lignin" the glycol radical has been replaced by a methoxyl group. In other words, on extracting spruce wood meal with glycol, the hydrogen in one of the hydroxyl groups in the lignin is replaced by the glycol radical (C_2H_4O), while in "methyl alcohol lignin" the same hydrogen has been replaced by a methyl group.

Of the five free hydroxyl groups present in the "native lignin," one is characterized by its acidic property in that it undergoes methylation with diazomethane, and the methylated product so obtained is insoluble in sodium hydroxide solution.

The formula of the native lignin is readily deducible from that of the "glycol" and "methyl alcohol lignin" in that it is only necessary to deduct the number of C and H atoms present in the radicals C_2H_4O and CH_2 from the respective formulas. In both cases the same structural formula is obtained, *viz.*

$$C_{42}H_{32}O_6(OH)_5(OCH_3)_5$$



$$\begin{matrix}CH_3O\\CH_3O\\CH_3O\\CH_3O\\CH_3O\end{matrix}\;C_{42}H_{32}O_6\;\begin{matrix}OH\\OH\\OH\\OH\\OH\end{matrix}$$

in which, as stated above, one hydroxyl group is known to possess an acidic, probably phenolic or enolic character, while a second hydroxyl group is characterized by ease of reaction with alcohols and hydrochloric acid.

Corresponding with this formula the methoxyl content of "native lignin" should be 17.5%, which agrees very well with the value calculated from the methoxyl content of the wood meal and its percentage of lignin and is also in agreement with the methoxyl content of Willstätter and Freudenberg lignin, the latter prepared by a preliminary mild hydrolysis with 1% sulfuric acid followed by extraction with cuprammonium hydroxide solution. The methoxyl content of "Willstätter lignin" varies from 14.2 to 15.8% depending on the mode of preparation. Assuming that it loses one methoxyl group due to the action of the strong hydrochloric acid during the course of preparation, this would lead to a structural formula $C_{42}H_{32}O_6(OH)_6(OCH_3)_4$ containing four methoxyl groups and a methoxyl content of 14.2%. As shown later, however, a "Willstätter lignin" if prepared at a low temperature and under mild conditions[10] has a higher methoxyl value (16.5% instead of that usually found (14.6%)). This surprising variation is due to contamination of the true Willstätter lignin with a by-product amounting, in general, to about 4–10%, left as an insoluble methoxyl-free residue in the conversion of both "Willstätter" and "Freudenberg" lignin into their phenol condensation products, so that the true methoxyl value is 17.5%.

On complete methylation the Freudenberg and Willstätter lignins are converted into products having a methoxyl content in each case of 32.2%, while the value calculated on the basis of the formula for fully methylated "native lignin" is 32.9% (Table II, $C_{42}H_{32}O_6(OCH_3)_{10}$). In other words,

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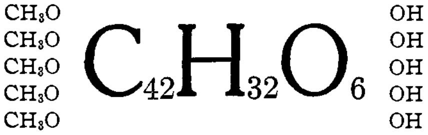
(10) L. Kalb and Lieser, *Ber.*, **61**, 1021 (1928).

hydroxyl groups are neither formed, nor removed, in the isolation of lignin by the alcohol extraction, or by the Willstätter or by the Freudenberg process.

If the formula suggested above for "native lignin" (Table III) is correct, it should be possible to deduce from it the structure of other types of lignin, *e. g.*, "phenol lignin."

TABLE III

Glycol lignin
$C_{42}H_{32}O_6(OH)_4(OCH_3)_5OCH_2CH_2OH$
Methyl alcohol lignin
$C_{42}H_{32}O_6(OH)_4(OCH_3)_5OCH_3$



$$\begin{array}{c}CH_3O\\CH_3O\\CH_3O\\CH_3O\\CH_3O\end{array} C_{42}H_{32}O_6 \begin{array}{c}OH\\OH\\OH\\OH\\OH\end{array}$$

Native lignin

Relation of "Phenol Lignin" to "Native Lignin."—Several papers dealing with the properties of phenol lignin have been published recently[3] but it seemed advisable to repeat and extend the work. In an investigation carried out by a co-worker, Miss Koerber, it was found that the phenol lignin obtained by extracting spruce wood meal with phenol (using hydrochloric acid as catalyst) could be separated into two approximately equal fractions (a) an ether-insoluble (OCH_3, 10.1%) and (b) ether-soluble (OCH_3, 5.4%).

In Table IV the analytical data relating to the former product (a) and its derivatives are shown. It can be seen that methylation with diazomethane yields a methylated product (C) with a methoxyl content of 21.6% from which, on further and complete methylation with dimethyl sulfate and sodium hydroxide, a fully methylated "phenol lignin" (E) (OCH_3, 28.2%) is obtained.

TABLE IV

METHOXYL CONTENT OF PHENOL LIGNIN AND DERIVATIVES PREPARED FROM SPRUCE WOOD MEAL, WILLSTÄTTER AND FREUDENBERG LIGNIN

	Spruce meal			
Phenol lignin made from.....	Ether-insol.	Ether-sol.	Willstätter	Freudenberg
A, original compound........	10.1	5.3	12.3	12.0
B, acetylated................	7.8	..	9.6	..
C, meth. with diazomethane..	21.6	21.5	23.8	..
D, acetylated (C)...........	19.0	..	21.0	..
E, fully methylated..........	28.2	..	28.0	..
Ratio of methoxyl to acetyl in: B.....	1:2	..	5:7	..
Ratio of methoxyl to acetyl in: D.....	3:1	..	5:1	..

Acetylation of the ether-insoluble phenol lignin gives an acetyl compound (B) in which the ratio of methoxyl to acetyl groups is 1:2. The ether-insoluble phenol lignin, premethylated with diazomethane, yields on acetylation an acetyl derivative D having a ratio of methoxyl to acetyl of 3:1. This change in the ratio from 1:2 to 3:1, following methylation with diazomethane, indicates the presence of some new "free phenol hydroxyl groups" in the ether-insoluble phenol lignin.

The high yield of "phenol lignin" obtained (about 140%) shows that a large amount of phenol must have reacted with the lignin. It seems probable that *one* molecule of the phenol reacts in the same manner as glycol or methyl alcohol, giving rise, presumably, to formation of a phenol-ether. Apparently the remaining phenol molecules, reacting with the lignin, enter the lignin molecule in such a way that the phenolic hydroxyl groups remain free and the question thus arises as to the number of phenol groups so introduced.

The actual number entering into nuclear condensation with the lignin molecule was determined experimentally in the following way. "Glycol lignin," "glycol lignin" methylated with diazomethane, as well as the fully methylated "glycol lignin" were condensed separately with phenol and hydrochloric acid under the same usual operating conditions. The products thus obtained were then subjected to (a) methylation with diazomethane (b) complete methylation and (c) acylation. The methoxyl content of these products together with the ratio found for methoxyl to benzoyl shows that three new phenolic hydroxyl groups have been introduced into the respective phenol-glycol-lignin condensation products.

Three phenol molecules have evidently undergone nuclear condensation with the lignin molecule, whereby their respective hydroxyl groups remain uncombined, so that it was then possible to prepare from them well-characterized derivatives, homogeneous in character and remarkably light in color.

The analyses of the latter are also given in Table V, and, on the basis of the data shown, it is possible to calculate the formula for the original "phenol lignin," obtained directly from spruce meal (Table V).

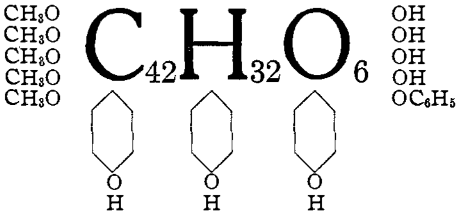
TABLE V

METHOXYL CONTENT OF THE PHENOL GLYCOL LIGNIN CONDENSATION PRODUCTS AND THEIR BENZOATES

Phenol deriv. of	Orig. prod.	Benzoyl deriv.	Ratio of methoxyl to benzoyl
Glycol lignin	13.1 (12.95)[a]	7.52 (7.6)	5:8
Glycol lignin meth. with diazomethane	16.1 (15.4)	9.52 (9.58)	6:7
Fully meth. glycol lignin	24.5 (24.45)		

[a] The figures in parentheses are the values calculated on the basis of the formula.

Phenol lignin



$$(CH_3O)_5\,C_{42}H_{32}O_6\,(OH)_4(OC_6H_5)(C_6H_4OH)_3$$

The theoretical methoxyl content of phenol lignin, as calculated from the formula given, is 12.6% whereas that actually found in ether-insoluble phenol lignin is only 10.1% and in the ether-soluble fraction 5.3%. If it is assumed, however, that in the preparation of phenol lignin from spruce wood meal, *one* methoxyl group is split off, a product would be obtained having the theoretical methoxyl value 10.1% and, as a matter of fact, all of the analytical values found for the various derivatives prepared from the ether-insoluble phenol lignin are then in agreement with the above formula (see Table IV).

The ether-soluble phenol lignin (CH_3O, 5.4%) apparently has the same fundamental building unit, since, on methylation with diazomethane, it yields the same product as the ether-insoluble (Table IVC). It differs from the ether-insoluble lignin in its methoxyl content only, in that it contains two instead of four methoxyl groups.

Application to Other Types of Lignin.—If it be correct that one type of lignin only is present in spruce wood, then the "Willstätter" as well as the "Freudenberg" spruce lignin should each possess the same building unit. On conversion of either into the characteristic ether-insoluble phenol condensation products, they should give in both cases an identical product corresponding with that prepared from glycol lignin with the single difference that the glycol radical has been replaced by a phenoxy group. This conclusion is based on the assumption that no side changes occur during the condensation reaction.

It was found experimentally that Willstätter lignin (OCH_3, 15.3%) gives, in quantitative yield, a phenol lignin with a methoxyl content of 12.3% (calculated 12.6%), leaving an undissolved residue amounting to from 8 to 10%. This insoluble residue is practically free from methoxyl and represents the impurity in the Willstätter lignin referred to above. The methoxyl content (12.3%) of the phenol lignin made from Willstätter lignin indicates that the true value of the methoxyl content of pure Willstätter lignin must be about 17.5%, that is, a value identical with the theoretical value as calculated from the methoxyl content of spruce wood meal taking into account the percentage of lignin present (see Table IV).

These facts find further confirmation in the analysis of the fully methylated products prepared (a) from ether-insoluble phenol lignin obtained directly from spruce meal and (b) from Willstätter phenol lignin, respectively, indicating the same methoxyl content (28.2 and 28.0%, respectively, Table IVE).[11]

Summary

1. Lignin has been isolated from spruce meal by the following methods: (a) action of glycol and hydrochloric acid; (b) use of methyl alcohol and hydrochloric acid; (c) extraction with phenol and hydrochloric acid; (d) Willstätter method; (e) Freudenberg method. The lignin isolated in each case was subjected to careful purification.

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[11] The authors desire to reserve the right of applying the technique described above to other types of lignin.

2. Well-characterized derivatives of each of these types of lignin have been prepared by methylation and acylation, respectively.

3. Each lignin type yields a well-characterized lignin–phenol condensation product, the analysis of which shows that they are derived from a common lignin building-unit.

4. This building-unit, representing the *native lignin* present in spruce wood, has the empirical formula $C_{47}H_{52}O_{16}$ or $C_{42}H_{32}O_6(OH)_5(OCH_3)_5$. Of the five free hydroxyl groups at least three are aliphatic in character, while one of the remainder is of an acidic type, either phenolic or enolic. The fifth hydroxyl group differs markedly from the remaining four and is characterized by its reactivity toward alkylating reagents such as hydrochloric acid and alcohols, phenols, etc.

5. The phenol condensation products from Willstätter and Freudenberg lignin are shown to possess the structure $C_{42}H_{35}O_6(OH)_4(OCH_3)_5(OC_6H_5)(C_6H_4OH)_3$.

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Note

Benzyl Levulinate

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In continuation of the studies of alkyl levulinates,[1,2] the benzyl ester has now been prepared. Of several methods tried, the following gave the best results. A mixture of 52 g. of levulinic acid, 160 g. of benzyl alcohol and 440 g. of toluene was treated with a current of dry hydrogen chloride until 7 g. was absorbed. The solution was boiled under reflux for twenty-four hours, whereupon the toluene was removed by distillation from an oil-bath at 125° and the residue fractionated under reduced pressure. A yield of about 65 g. of pure benzyl levulinate, b. p. 181–183° (17 mm.) was thus obtained. Sapon. eq. calcd. for $C_{12}H_{14}O_3$: 272.2; found 270.7. d_4^{20} 1.0935; d_4^{25} 1.0895; n_D^{20} 1.5090; n_D^{25} 1.5070.

The ester was characterized by a variety of hydrazones,[3] obtained in

Hydrazone		M. p., °C.		Analyses, %	
				Found	Calcd.
Phenyl-	Rhombic plates	91–92	N	9.46	9.73
p-Tolyl-	Rectangular plates	99–100	N	9.03	9.17
p-Chlorophenyl-	Rectangular tablets	106–107	Cl	10.73	11.26
p-Bromophenyl-	Rectangular plates	103	Br	21.31	21.40

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(1) Sah and Ma, THIS JOURNAL, **52**, 4880 (1930); **54**, 3271 (1932).

(2) Schuette and Cowley, *ibid.*, **53**, 3485 (1931); Cowley and Schuette, *ibid.*, **55**, 387 (1933).

(3) Sah and Lei, *Sci. Rep. Nat. Tsinghua Univ. A*, **2**, 1, 7 (1933).