individual anionic substances, or groups of anionic substances, of characteristic electrophoretic mobilities. The peak to the left of the sample section arises as a result of the presence of neutral substances carried toward the cathode by endosmotic flow. In B-6 and B-8 the number of anionic components is found to increase as is indicated by the increasing number and decreasing sharpness of the peaks in the patterns compared with those observed for such pure substances as the products of condensation of formaldehyde with *p*-phenolsulfonate.[17] Since the average molecular weight of the components in these fractions is in the range expected for a mixture of monomeric, dimeric and trimeric lignin sulfonate molecules, efforts are now being made to isolate and identify some of these substances so that a better understanding will be at hand of the nature of the structural units and of the way they are combined in the lignin polymer.

[17] F. R. Stults, R. W. Moulton and J. L. McCarthy, *Chem. Eng. Prog. Symp. Ser.*, **48**, (4) 38 (1952).

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE STATE UNIVERSITY OF NEW YORK, COLLEGE OF FORESTRY, CHEMISTRY DEPARTMENT]

Lignin Structure. VIII.[1] Characterization of Ethanol Spruce Lignin Prepared by a New Method

BY HERBERT G. ARLT, JR., KYOSTI SARKANEN AND CONRAD SCHUERCH

RECEIVED OCTOBER 15, 1955

When spruce wood meal is treated with 0.2 *N* hydrogen chloride in a four to one mixture of chloroform and ethanol at 60°, 20% of the lignin is converted to ether-soluble oils and 60% to ether-insoluble powders. About 16% of the lignin remains in the wood. The lignin oils are somewhat low in methoxyl, in part because of carbohydrate impurities. The light tan powders, however, have a methoxyl to carbon ratio close to theoretical for a propylguaiacyl polymer and their average empirical formula can be calculated as $C_9H_{8.0}O_{2.6}(OC_2H_5)_{0.41}$. The average ethoxyl to phenol ratio is 1.16 or near the theoretical for simple alcoholysis of alkyl aryl ethers. If ethanol is subtracted from the empirical formula, the resulting formula is nearly identical with Erdtman's theoretical value for protolignin derived from data on lignin sulfonates.

Since lignin in wood, or the lignin remaining after wood polysaccharides have been dissolved, is insoluble in all solvents—presumably because of its network structure—it is important that some reaction used to obtain soluble products be thoroughly understood if the original structure is to be elucidated. After over a century of research on lignin, there is still no reaction suitable for its isolation from wood for which a balanced equation can be written with any assurance.[2] This article is a portion of a continuing study to determine whether or not lignin alcoholysis can be so described. It includes two independent preparations and characterizations of ethanol spruce lignin prepared under the relatively new conditions reported once previously.[3]

In essence, this preparation is a stepwise alcoholysis of Norway spruce wood meal in a good solvent system—anhydrous chloroform ethanol in a volume ratio of four to one—using 0.2 *N* hydrogen chloride as catalyst. The ethanol spruce lignins are isolated by filtration of the liquor, washing, concentration and precipitation into ether or preferably petroleum ether. Three or four fractions are obtained by successive treatments of the wood meal.

The lignin powders from a three or four step alcoholysis represent a minimum of 57% of the methoxyl of the original wood. The oils obtained from the precipitation liquors correspond to those from which Hibbert's school has previously obtained propylguaiacyl monomers.[4] These oils amount to about 25% of the original methoxyl. Less than 17% of the lignin (measured as methoxyl) remains in the residual wood meal. The ethanol lignin powders have been characterized by determination of methoxyl, ethoxyl and phenolic hydroxyl, by carbon and hydrogen analyses and by ultraviolet spectra.

An advantage of this preparation lies in the high yield of organic solvent-soluble lignin products corresponding to more than 80% delignification. The conditions of reaction—high dilution, low concentration, good solvent, absence of water and a stepwise isolation—have furthermore been chosen to lessen the probability of side reactions (Table I) and to simplify the interpretation of the reaction.

The ultraviolet absorption spectra of the three powders S 1, S 2 and S 3, obtained in one series of alcoholyses, are very similar and typical of ethanol spruce lignins.[5] They all exhibit a maximum at the 282 mμ region with nearly the same absorptivity (4.4–4.9 l. (mol. $CH_3O)^{-1}$ cm.$^{-1}$). From S 1 to S 3 the absorptivity gradually increases at the 250–270 and 290–320 mμ regions, rendering the 282 mμ maximum less sharp and possibly indicating increased structural complexity in the later fractions.

Similarly the analyses of the powders listed in Table II agree with each other within reasonable limits. The carbon and hydrogen values, while varying more than would be permissible for samples of a crystalline compound, are not greatly divergent considering that the products are amorphous mixtures of structurally related polymer fragments. The alkoxyl contents of the products

---

[1] Previous papers in this series include footnotes 3, 6, 7, reference 2 of Table I, THIS JOURNAL, **72**, 3838 (1950); *ibid.*, **75**, 707 (1953); "Chemistry in Canada," April, 1953, p. 35.

[2] The greatest headway on this problem seems to have been made on the technically important sulfonation of lignin, one excellent study of which has been reported by H. Erdtman, B. O. Lindgren and T. Petterson, *Acta Chem. Scand.*, **4**, 228 (1950). The extent of the concomitant hydrolysis, however, remains obscure.

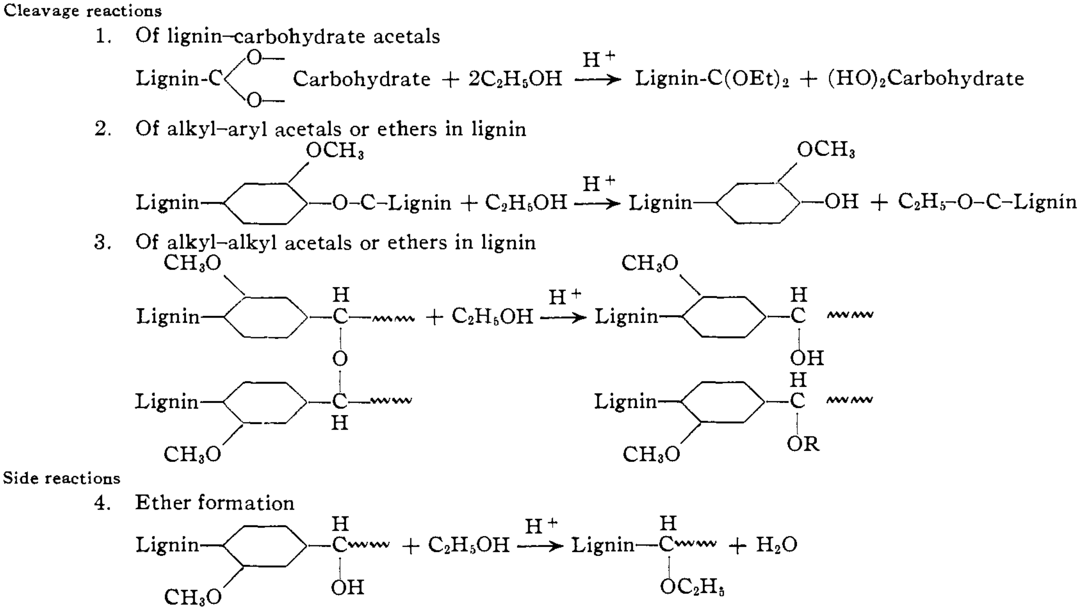
[3] C. Schuerch, THIS JOURNAL, **74**, 5061 (1952).

[4] A. B. Cramer, M. J. Hunter and H. Hibbert, *ibid.*, **61**, 509 (1939).

[5] R. F. Patterson and H. Hibbert, *ibid.*, **65**, 1869 (1943).

TABLE I

ASSUMED REACTIONS IN ETHANOL LIGNIN PREPARATION[a]



5. Repolymerization or condensation (as through benzyl hydroxyls).

[a] Representative references for the above reactions are: (1) B. Holmberg and S. Runius, *Svensk Kem. Tid.*, **37**, 189 (1925). (2) C. Schuerch, THIS JOURNAL, **73**, 2385 (1951); (3) B. O. Lindgren, *Acta Chem. Scand.*, **5**, 616 (1951); (4) B. Holmberg and S. Heden, *Svensk Kem. Tid.*, **48**, 207 (1936); (5) E. Adler and J. Gierer, *Acta Chem. Scand.*, **9**, 84 (1955); (6) W. B. Hewson, J. L. McCarthy and H. Hibbert, THIS JOURNAL, **63**, 3041 (1941).

TABLE II

ANALYSES AND EMPIRICAL FORMULAS OF ETHANOL SPRUCE LIGNINS

Fraction	Yield, % K.L.	Carbon, %	Hydrogen, %	Methoxyl, %	Ethoxyl, %	Phenolic hydroxyl, %	Ratio[a] methoxyl, / C_{10} carbon	Ratio moles ethoxyl / moles phenolic	Formula
A-1	29.0	62.17	6.92	11.9	9.87	2.68	0.209	1.39	
A-1 Reppt.	23.6	62.96	6.25	14.2	8.15	3.04	.242	1.01	$C_9H_{8.1}O_{2.6}(OMe)_{.93}(OEt)_{.37}$
A-2	16.5	62.52	5.96	14.0	8.86	2.88	.242	1.16	$C_9H_{7.4}O_{2.7}(OMe)_{.93}(OEt)_{.41}$
A-3	11.3	63.32	5.95	14.8	7.26	3.09	.250	0.89	$C_9H_{7.4}O_{2.6}(OMe)_{.96}(OEt)_{.32}$
A-4	7.0	62.30	5.99	15.1	6.10	3.04	.256	0.76	$C_9H_{7.8}O_{2.7}(OMe)_{.99}(OEt)_{.28}$
S-1	28.0	62.86	6.45	13.80	10.80	2.75	.242	1.48	$C_9H_{8.2}O_{2.6}(OMe)_{.93}(OEt)_{.50}$
S-2	14.2	63.40	6.46	14.55	9.36	3.02	.249	1.17	$C_9H_{8.2}O_{2.5}(OMe)_{.96}(OEt)_{.43}$
S-3	14.7	62.57	6.23	14.55	8.69	3.11	.251	1.05	$C_9H_{8.0}O_{2.7}(OMe)_{.97}(OEt)_{.40}$

[a] Calculated as % methoxyl/% total carbon − % carbon added by extractant.

show a fair regularity of trend. Those samples later in each series are somewhat higher in methoxyl largely because of a lower ethoxyl content.

The methoxyl to "skeletal" (C_{10}) carbon ratio in[6] all cases approximates that expected of a propylguaiacyl polymer (0.258), the deviation being at most 6% in the earlier fractions except Fraction A1 before reprecipitation. This powder and the lignin oils were both low in methoxyl, but this was at least in part due to the presence of carbohydrate impurities. If any lignin–carbohydrate compounds exist in these isolated lignins, the oily fraction most probably contains them. Low methoxyl contents have generally been observed on low molecular weight lignin fractions.[6]

The ratios of ethoxyl to phenolic groups in these products and the weighted average for each series are sufficiently close to one to suggest that the cleavage of an alkyl–oxygen–aryl linkage (reaction 2, Table I) may be a reaction of major importance in the early stages of the alcoholysis of lignin, if the original phenolic content of spruce wood is assumed to be small enough to be ignored.[7] It can be the *sole* reaction only if the excess ethoxyl in the powders is balanced by excess phenolic groups present in the oils or residual wood meal. It may be significant that the fractions which are dissolved first include the largest amount of oils and the highest ethoxyl to phenol ratio in the powders. It is, however, surprising that the phenolic contents[8] of all fractions are so similar, while the ethoxyl content varies substantially, if the formation of both is governed by the same reaction.

Another explanation for the fact that the ethoxyl

---

(6) C. Schuerch, THIS JOURNAL, **73**, 4997 (1951).

(7) On oxidation of diazomethane methylated spruce wood, Richtzenhain finds less than 6% of the lignin as products with the phenolic hydroxyl methylated, a result in rough agreement with our assumption; *Svensk Papperstidn.*, **53**, 644 (1950).

(8) K. Sarkanen and C. Schuerch, *Anal. Chem.*, **27**, 1245 (1955).

to phenol ratio is significantly greater than one is that other reactions like three and four of Table I are also occurring.

Finally there is no clear trend of an increase in carbon content (or ethoxyl-free carbon content) such as would be expected if condensation (reaction five) were occurring throughout the ethanolysis.

Empirical formulas for these preparations have been calculated on the usual assumption that they are propylguaiacyl polymers (Table III). Since two of the most probable reactions of alcoholysis (Table I, reactions two and three) require the addition of the elements of ethanol to protolignin during reaction, by subtraction the corresponding formula of protolignin should approximate

$$C_9H_{7.6}O_{2.6}(OCH_3)_{0.95}$$

This value agrees well with a formula for "lignin" calculated by Erdtman, *et al.*,[2] from data obtained from lignin sulfonic acids[9]

$$C_9H_{8.2}O_{2.6}(OCH_3)_{0.94}$$

and by Freudenberg[10] for cuproxam–lignin.

$$C_9H_{7.88}O_{2.51}(OCH_3)_{0.92}$$

If reactions which remove hydroxyl groups have occurred, such as those numbered four and five in Table I, the oxygen content of protolignin must be still higher. Specifically, if each ethoxyl has replaced a hydroxyl, there must be very close to four oxygen atoms per monomer unit in the original protolignin. Therefore, this work constitutes further evidence that most of the native spruce lignin polymer contains an average of 3.5 or more oxygen atoms per monomer unit.

Experimental

Preparation of Spruce Ethanol Lignins.—Samples A 1–4 and S 1–3 were prepared essentially as described previously,[3] but with these modifications: before alcoholysis, air-dried Norway spruce wood meal (40–80 mesh; Klason lignin, on a moisture free basis 27.4%) was dried by treating with absolute ethanol two or three times in a closed reaction vessel followed by vacuum filtration and vacuum drying at 40°.

Ethanol lignin samples of series A were isolated by precipitation of a washed, dried and concentrated solution into ten parts of petroleum ether (b.p. 30–60°), solution in chloroform (5 ml./g.), filtration and reprecipitation into ten parts of petroleum ether. Sample A-1 was purified further by precipitation into diethyl ether and then petroleum ether as before from chloroform. This second purification was necessary since sample A-1 contained 2.9% pentosans.

The series S samples were prepared as above and isolated by filtration and precipitation into twenty parts of ether and one precipitation into ten parts of petroleum ether from chloroform. The final precipitation into petroleum ether was necessary to remove adsorbed ether which could not be completely removed by drying 72 hours at 40° under vacuum. The results are recorded in Table III.

Table III

Methoxyl Balance

Sample	Weight	Methoxyl content %	Methoxyl content by wt.
Spruce wood meal	200	4.0	[a]8.00
Series A			
A-1	20.5	11.9	2.44
A-2	10.0	14.0	1.40
A-3	6.4	14.8	0.95
A-4	3.9	15.1	.59
A-5	1.5	est. 15	.23
Combined ether-soluble oils, Series A	[b]31.0	5.5	1.71
Residual wood meal, Series A	93.7	1.2	1.12
Sum of all samples, Series A			8.44
Spruce wood meal, Series S	200		[a]7.67
S-1	16.0	13.8	2.21
S-2	7.7	14.5	1.12
S-3[c]	8.0	14.6	1.17
Combined ether-soluble oils, Series S	19.7	10.6	2.09
Residual wood meal, Series S	101.0	1.3	1.31
Sum of all samples, Series S			7.90

[a] The difference in the moisture content of the two air-dried spruce meal samples is responsible for the difference in their methoxyl content. [b] This sample contains solvent. [c] Isolated after ethanolysis for 72 hr., all other samples for 48 hr.

Analysis of Samples.—Samples were dried at least 72 hours *in vacuo* at 40° usually over phosphorus pentoxide. The methoxyl content was determined by the method of G. Gran,[11] and the total alkoxyl by bromine absorption. The percentage ethoxyl was calculated from the differences between total alkoxyl and methoxyl.

Phenolic hydroxyl was found by a conductometric procedure[8] developed earlier in this Laboratory.

Ultraviolet spectra were taken on a Beckman D.U. spectrophotometer of solutions of sample S 1 and S 2 in 95% ethanol with 2% dioxane added and of S 3 in pure dioxane. Concentrations were 15 to 20 mg. per liter. The values of absorptivity (1. (mol. $CH_3O)^{-1}$ cm.$^{-1} \times 10^{-3}$) of S 1, S 2 and S 3 in sequence are given for the wave lengths 210 mμ 20.6, 19.8, —; 240 mμ 7.67, 8.06, 8.76; 260 mμ 2.73, 3.07, 3.51; 285 mμ 3.80, 3.92, 4.23; 300 mμ 2.42, 2.72, 3.01; 320 mμ 1.89, 1.88, 2.25; 350 mμ 0.59, 0.61, 0.74.

Acknowledgment.—The authors gratefully acknowledge the fellowship for Kyosti Sarkanen, granted by the Research Corporation.

Syracuse, New York

---

[9] Unfortunately, this agreement is somewhat less convincing when it is remembered that the hydrolysis occurring during the sulfonation reaction can not be evaluated and has therefore not been taken into account in the calculations of Erdtman.

[10] A review of this work is given in Hägglund's "Chemistry of Wood," Academic Press, Inc., New York, N. Y., 1951, pp. 276, 284, 286.

[11] G. Gran, *Svensk Papperstidn.*, **57**, 702 (1954). Trimethylamine in isopropyl alcohol is used to absorb volatile iodides. Tetramethylammonium iodide precipitates and is determined separately.