tographic procedure, the product finally crystallized. Pure material was obtained on one recrystallization from acetone and petroleum ether; yield 0.5 g., m. p. 86–88° (cor.), $[\alpha]^{25}_D$ −14.9° (*c* 4.3, U.S.P. $CHCl_3$). The compound reduced hot Fehling solution, gave the Pacsu[19] *keto*-acetate test, and exhibited an absorption band with a maximum at 2840 Å.; log $\epsilon_{max.}$[20] = 1.79 (0.0070 *M* in U.S.P. chloroform, 1 cm. cell, Beckman quartz spectrophotometer, model DU).

Anal. Calcd. for $C_{22}H_{30}O_{15}$: C, 49.43; H, 5.65. Found: C, 49.47; H, 5.94.

D-Manno-L-*fructo*-octose and its Phenylosazone.—Four grams of *keto*-D-manno-L-*fructo*-octose heptaacetate was deacetylated with barium hydroxide as described for *keto*-D-psicose pentaacetate[21] and the resultant colorless, amorphous solid was isolated in the same manner; yield 1.8 g. of amorphous material, $[\alpha]^{26}_D$ +66.4° (*c* 3.2, H_2O, no mutarotation). The substance was water-soluble, possessed a sweet taste, and reduced hot Fehling solution; it was not fermentable by bakers' yeast.

Anal. Calcd. for $C_8H_{16}O_8$: C, 40.00; H, 6.72. Found: C, 39.99; H, 6.76.

The crystalline phenylosazone of this octose was prepared; m. p. 222–223° (dec., cor.), in agreement with the value of 223° (dec.) reported by Fischer and Passmore.[2]

Anal. Calcd. for $C_{20}H_{26}O_6N_4$: C, 57.40; H, 6.26; N, 13.39. Found: C, 57.29; H, 5.96; N, 13.61.

Summary

1. D-Manno-D-*gala*-heptonic acid has been converted to the amorphous D-manno-L-*fructo*-octose, characterized by its crystalline *keto*-acetate and phenylosazone.

2. Crystalline hexaacetyl-D-manno-D-*gala*-heptonic acid, its acid chloride, and 1-diazo-1-desoxy-*keto*-D-manno-L-*fructo*-octose hexaacetate are described.

3. Paralleling the higher aldoses,[6,7] ketoheptoses and ketoöctoses of like configurations in carbons two to six, inclusive, have similar optical rotations.

COLUMBUS, OHIO RECEIVED AUGUST 3, 1949

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(19) E. Pacsu and F. V. Rich, THIS JOURNAL, **55**, 3018 (1933); F. B. Cramer and E. Pacsu, *ibid.*, **59**, 1467 (1937).

(20) $\epsilon_{max.} = E_{max.} \times$ mol. wt./$(C \times D)$; C = g./l., D = cell thickness in cm.

(21) M. L. Wolfrom, A. Thompson and E. F. Evans, THIS JOURNAL, **67**, 1793 (1945).

[CONTRIBUTION FROM THE PULP MILLS RESEARCH PROJECT AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Functional Derivatives of Lignin Sulfonic Acid

BY D. M. RITTER, E. D. OLLEMAN, D. E. PENNINGTON AND K. A. WRIGHT

Methods based upon isolation of quinolinium salts[1] or upon dialysis[2,3] have been found to yield lignin sulfonates of considerable chemical homogeneity. With such material available it appeared desirable to repeat and extend previous work[4] on methylated and acetylated lignin sulfonates. A summary of the derivatives prepared and their composition is given in Table I.

Exhaustive diazomethane methylation of lignin sulfonate ion (I) yielded a product (II), for which the name "hemimethoxy" lignin sulfonate ion is suggested. Through methylation of either (I) or (II) with dimethyl sulfate gave the "permethoxy" lignin sulfonate ion (III). The methoxyl and sulfur contents of (II) and (III) agreed with data obtained by Hibbert and his coworkers[4e] for products obtained in the same two ways and the product made by Freudenberg[4d] was also apparently identical.

The water-soluble product obtained by cautious acetylation with sodium acetate as a catalyst was called the "peracetoxy" derivative. The composition of the "peracetoxy" lignin sulfonate corresponded closely to that expected from lignin sulfonates with the hydroxyl group contents reported by Freudenberg, Lautsch and Piazolo.[5] Acetylation of the "hemimethoxy" lignin sulfonate was accomplished with the sodium acetate catalyst, but with several catalysts listed in Table II, acetylation of the "permethoxy" derivative proceeded only to the degree that methoxyl groups were displaced.

In reactions somewhat analogous to those between ammonium salts of strong acids and diazomethane,[6] the methyl esters (VI), (VII) and (VIII) were prepared from "hemimethoxy," "permethoxy" and "peracetoxy" lignin sulfonic acids (II), (III) and (IV), respectively. In each case the reaction occurred between the solid acid suspended in solutions of diazomethane in solvents for the esters. Esterification of the permethoxy and peracetoxy lignin sulfonic acids was accompanied by some desulfonation, and in the latter case some replacement of acetoxy groups by methoxy groups occurred.

It is well established that there are two steps in the methylation of lignin sulfonates.[4e] On the basis of synthesis the final product obtained with diazomethane, hemimethoxy lignin sulfonate ion (II), is a distinct chemical individual and not merely an intermediate to the permethoxy lignin

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(1) Olleman, Pennington and Ritter, *J. Coll. Science*, **3**, 185 (1948).

(2) Peniston and McCarthy, THIS JOURNAL, **70**, 1327 (1948).

(3) Markham, Peniston and McCarthy, *ibid.*, **71**, 3599 (1949).

(4) (a) Klason, *Ber.*, **53**, 1864 (1920); (b) Heuser and Samuelsen, *Cellulosechem.*, **3**, 78 (1922); (c) Hägglund and Carlsson, *Biochem. Z.*, **257**, 467 (1933); (d) Freudenberg and Sohns, *Ber.*, **66B**, 262 (1933); (e) King, Brauns and Hibbert, *Can. J. Research*, **13B**, 88 (1935); (f) Tomlinson and Hibbert, THIS JOURNAL, **58**, 340 (1936); (g) Erdtman, *Svensk Papperstidning*, **45**, 392 (1942).

(5) Freudenberg, Lautsch and Piazolo, *Cellulosechem.*, **22**, 97 (1944).

(6) Eistert, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, New York, N. Y., 1948, pp. 520, 521.

TABLE I

ANALYSES OF LIGNIN SULFONATE DERIVATIVES

Number	Lignin sulfonate derivative	Analyses, % C	H	OCH₃	S	Ac	Empirical formulas
I	Sodium lignin sulfonate[a]	52.10	4.18	12.8	6.66		$C_9H_{6.75}O_{2.27}(OCH_3)_{0.95}(SO_3Na)_{0.47}$
II	Ammonium "hemimethoxy" lignin sulfonate[b]	52.36	5.95	19.6	6.67		$C_9H_{7.75}O_{1.80}(OCH_3)_{1.52}(SO_3NH_4)_{0.50}$
III	Ammonium "permethoxy" lignin sulfonate[c]	51.90	6.10	26.0	5.18		$C_9H_{7.58}O_{2.17}(OCH_3)_{2.17}(SO_3NH_4)_{0.42}$
IV	Ammonium "peracetoxy" lignin sulfonate[d]	52.40	5.02	9.77	5.52	18.4	$C_9H_{5.92}O_{1.36}(OCH_3)_{0.89}(OAc)_{1.21}(SO_3NH_4)_{0.48}$
V	Ammonium "hemimethoxy acetoxy" lignin sulfonate[e]			17.04		11.5	
VI	Methyl ester of II	55.75	5.88	20.8[f]	5.73		$C_9H_{7.9}O_2(OCH_3)_{1.60}(SO_3CH_3)_{0.42}$
VII	Methyl ester of III	57.68	6.18	25.1[f]	5.56		$C_9H_{7.60}O_{1.50}(OCH_3)_{1.90}(SO_3CH_3)_{0.40}$
VIII	Methyl ester of IV	55.47	6.06	13.1[f]	4.02	14.6	$C_9H_{8.90}O_{1.80}(OCH_3)_{1.12}(OAc)_{0.90}(SO_3CH_3)_{0.38}$

[a] See refs. 1, 2, 3, 4. Na = 4.63. [b] I exhaustively methylated with diazomethane. See Table II. [c] I or II exhaustively methylated with dimethyl sulfate and alkali. [d] Exhaustive acetylation of barium salt of I with sodium acetate as catalyst. [e] Exhaustive acetylation of II as in *d*. [f] After hydrolysis and drying of sample weighed as the ester,

TABLE II

ATTEMPTS TO ACETYLATE PERMETHOXY LIGNIN SULFONATES

Method	Ac, %	MeO, %
NaOAc, Ac_2O, HOAc	4.4	23.5
Ketene	2.0	19.6
AcCl–pyridine	2.7	22.4
Ac_2O–pyridine	3.4	23.8
$AcNH_2{:}BF_3$		23.9
Ac_2O–quinoline	6.7	20.3

TABLE III

METHYLATION OF LIGNIN SULFONIC ACID WITH DIAZOMETHANE

Treatments	MeO content of product	HIO_4 equivalent weight
A. Preparative reaction with excess diazomethane		
1st treatment CH_2N_2 in dioxane		
2nd treatment CH_2N_2 in dioxane	14.8[a]	530
3rd treatment CH_2N_2 in dioxane	17.7[a]	
4th treatment CH_2N_2 in dioxane	19.5[a]	
5th treatment CH_2N_2 in dioxane	18.0[a] 19.6[b]	5000
1st treatment CH_2N_2 in butanol	16.3	900
B. Step-wise methylation with calculated amount of diazomethane		
1st treatment	14.1	490
2nd treatment	14.3	656
3rd treatment	15.1	838
4th treatment	15.5	1024
5th treatment	16.0	1156
6th treatment	16.9	1656

[a] Barium salt. [b] Ammonium salt.

sulfonate ion. The known reactions of diazomethane, as pointed out by Brauns,[7] suggest that this reagent methylates phenolic hydroxyl groups in lignin sulfonic acid. Since reaction with very acidic aliphatic alcohols is possible[6] additional supporting evidence would strengthen the conclusion, and further serve to differentiate between the apparently two kinds of hydroxyl groups. Such verification is furnished in part by the fact that aqueous periodic acid oxidizes unsubstituted lignin sulfonic acid with considerable demethoxylation,[8] as it did also with simple phenolic analogs of lignin,[9] but caused little oxidation of hemimethoxy lignin sulfonic acid, as is shown in Table III.

Additional support for the phenolic character of the hydroxyl groups under discussion was found in the ultraviolet absorption spectra of the lignin sulfonate ion and its functional derivatives. Although these substances had very similar spectra in aqueous solution at *p*H 7, lignin sulfonate ion revealed a weak acidity in 1 *N* sodium hydroxide solution as shown in Fig. 1 but this reversible effect was absent in both the hemimethoxy and permethoxy derivatives as illustrated in Fig. 2. In the former case no estimate of the acid strength was possible because evidence was lacking concerning the absorption of the phenolate ion. Data in Fig. 3 show that the dissociable hydroxyl groups comprise those methylated by diazomethane.

The compositions listed in Table I are approximate to those of derivatives from a parent substance of the average formula $C_9H_{7.5}O(OH)(OCH_3)(SO_3H)_{0.5}$. Slight alteration during the pulping process may account for the fact that the average methoxyl content in each C_9 unit is less than unity, and that the phenolic content is more than that amount. This may also explain why about one in every five C_9 units has an extra oxygen atom not present in a functional group. This latter departure may be better explained, however, as caused by hydration of the lignin sulfonate salts. A similar apparent excess of oxygen and hydrogen was noted in the Kullgren lignin sulfonate from spruce wood,[10] $C_9H_{9.4}O_{2.4}(OCH_3)(SO_3Ba/_2)_{0.3}$, and its further sulfonation

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(7) Brauns, *Paper Trade Journal*, **111**, No. 14, 33–39, Oct. (1940).

(8) Pennington and Ritter, THIS JOURNAL, **68**, 1391 (1946).

(9) Pennington and Ritter, *ibid.*, **69**, 187 (1947).

(10) Erdtman, *Svensk Papperstidning*, **48**, 75 (1945).

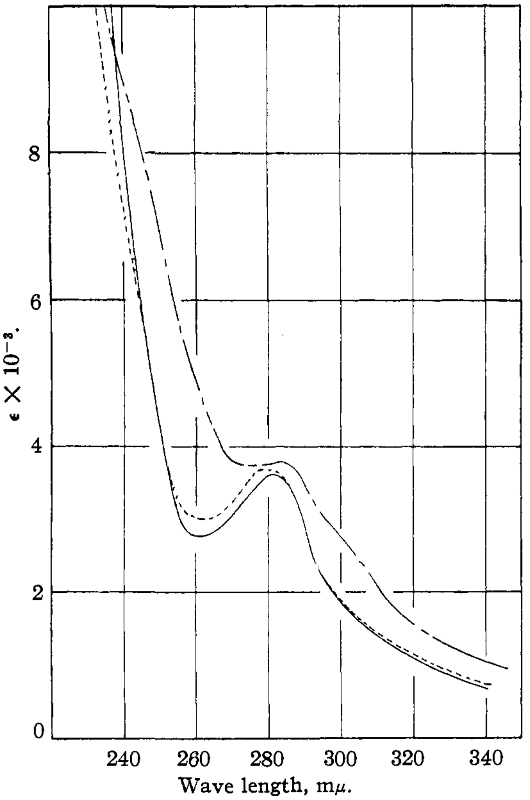

Fig. 1.—Ultraviolet absorption spectra of lignin sulfonic acid: solution at *p*H 7 (—) compared with solution in 1 *N* sodium hydroxide (— — —) and after neutralizing the alkaline solution to *p*H 7 (- - - - - - -).

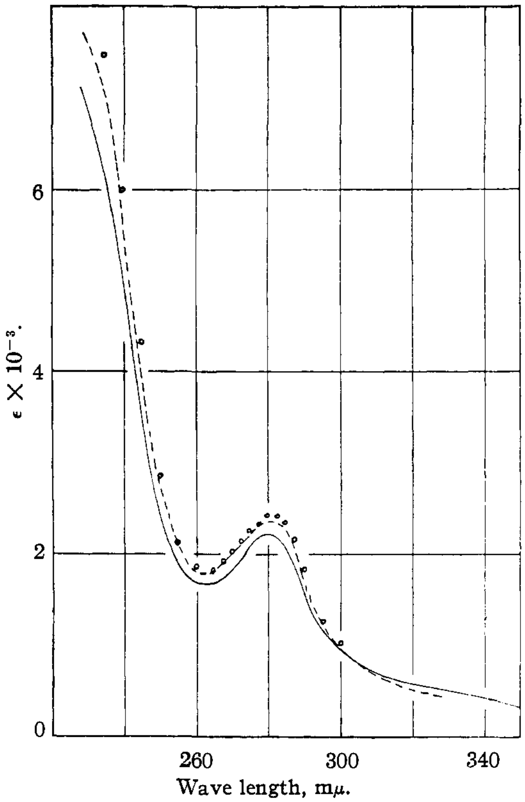

Fig. 2.—Ultraviolet absorption spectra of hemimethoxy lignin sulfonic acid (oooo) and permethoxy lignin sulfonic acid (———) in 1 *N* sodium hydroxide; and of permethoxy lignin sulfonic acid at *p*H 7 (- - - - -).

product, $C_9H_{8.50}O_{2.70}(OCH_3)(SO_3Ba/2)_{0.5}$. Recently barium lignin sulfonate has been shown to exist as a reversibly formed hydrate[11] stable at 60° and containing approximately 1.5 molecules of water for each–$SO_3Ba/2$ group. If the Kullgren barium lignin sulfonates are considered to have been hydrated, the amount of water present can be estimated roughly from the increase in oxygen content with increasing sulfur content. The value found is 1.5 moles of water in agreement with the results of Markham, Peniston and McCarthy. The formulas for the Kullgren acids then reduce to $C_9H_{7.5}O_{0.95}(OH)(OCH_3)(SO_3Ba/2)_{0.3}(H_2O)_{0.45}$ and to $C_9H_{7.0}O_{0.95}(OH)(OCH_3)(SO_3Ba/_2)_{0.5}$-$(H_2O)_{0.75}$. Except at very high sulfur content the lignin sulfonates reported by Freudenberg, Lautsch and Piazolo[5] have formulas essentially in agreement. The unit of structure $C_9H_9O_2$-(OCH_3) found as an average for the lignin sulfonate derivative thus corresponds closely with Holmberg and Gralén's analyses for thioglycolic acid lignin[12] and with the formula $C_9H_8O_2(OCH_3)$ found by Wald, Ritchie and Purves[13] for lignin in wood.

Previously the "extra" oxygen found in (III) over that present in (I) was attributed to hydroxyl groups introduced by opening flavanone rings during acetylation and methylation processes.[14] The methoxyl plus acetyl in the peracetoxy derivative (IV), however, is 2.1 in good agreement with the methoxyl substitution of 2.17 in the permethoxy derivative (III). If new hydroxyl groups were introduced by methylation, they should appear as acetoxyl groups in the analogous acetylation. This does not appear to be the case. Moreover, though attempts to acetylate the permethoxy lignin sulfonate (III) caused displacement of methoxyl groups, no additional hydroxyl groups were located. The methyl esters (VI) and (VII) have compositions whose unassigned oxygen content is similar to that of the parent lignin sulfonate (I), and observation of almost identical ultraviolet absorption spectra for (I), (III) and (V) argues against the occurrence of any major structural change during these transformations. The flavanone hypothesis must therefore be withdrawn as an explanation of the

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(11) Markham, Peniston and McCarthy, THIS JOURNAL, **71**, 3599 (1949).

(12) Holmberg, *Ing. Vetensk. Akad. Handl.*, 131 (1934); Holmberg and Gralén, *ibid.*, 162 (1942).

Although these authors recently preferred the formula $C_9H_9O_2$-(OCH_3) the alternatives which they reject are almost equally acceptable on the basis of the data presented.

(13) Wald, Ritchie and Purves, THIS JOURNAL, **69**, 1371 (1947).

(14) Ritter, Pennington, Olleman, Wright and Evans, *Science*, **107** 20 (1948).

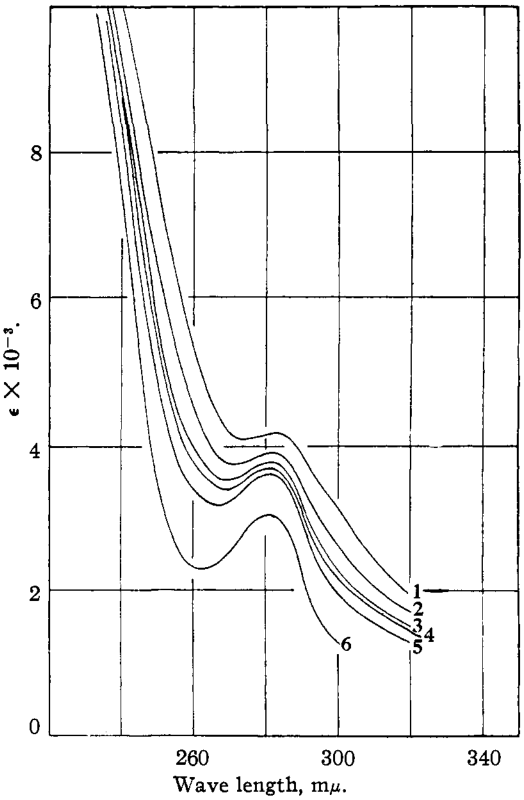

Fig. 3.—Ultraviolet absorption spectra of diazomethane-methylated lignin sulfonates in 1 N sodium hydroxide solution: per cent. methoxyl for curves 1 through 6, respectively, 14.1, 14.3, 15.5, 16.0, 16.9, 18.7 (hemimethoxy lignin sulfonate).

extra oxygen, which now appears associated with the varying degree of hydration of the lignin sulfonate salts. For example, the extra oxygen present in the permethoxy salt (III) and absent in the corresponding methyl ester (VII) is most probably water of hydration of the salt.

Experimental Part

N-Methylquinolinium Lignin Sulfonates.—N-Methylquinolinium iodide was prepared by the action of methyl iodide on quinoline and the salt was converted to the sulfate by reaction with the stoichiometric quantity of silver sulfate. This solution was treated with a slight excess of barium hydroxide, filtered and treated with carbon dioxide to produce N-methylquinolinium bicarbonate. The bicarbonate solution was used to neutralize solutions of lignin sulfonic acid or its methyl derivatives which were prepared by de-ashing solutions of the respective salts. The stoichiometric point was determined to be pH 3.8 by electrometric titration, using the glass electrode. The salt solution was evaporated to dryness to obtain the solid N-methylquinolinium salt. Of these preparations, the N-methylquinolinium salt of "permethoxy" lignin sulfonic acid was found to have the new property of solubility in nitromethane.

Hemimethoxy Lignin Sulfonates.—The ammonium lignin sulfonate used as a starting material was prepared by refining, through quinoline extraction, the quinolinium salts obtained from the sulfite waste liquor left after commercial pulping of Western hemlock *tsuga heterophyla*. The preparation of the sample and demonstration of its chemical homogeneity by fractional diffusion analysis were carried out as described previously.[1] Lignin sulfonates prepared by dialysis[2] can be used as well. The salt, 5.0 g., was dissolved in 100 ml. of water and the solution was diluted with 50 ml. of methanol. A solution of diazomethane in 100 ml. of dioxane was prepared from 10 g. of nitrosomethyl urea and the solution was recovered by phase separation as described in "Organic Syntheses."[15] A test with indicator paper showed that this solution contained a small amount of alkali. The aqueous methanol solution of ammonium lignin sulfonate was cooled to 0° and the diazomethane solution was added as quickly as the violent evolution of nitrogen would permit. The mixture stood overnight and was then evaporated to dryness.

The product was dissolved in water, the solution was de-ashed with "Ionex" no. 2[16] cation-exchange resin and the acid was neutralized with solid lithium carbonate. The lithium salt solution was evaporated to dryness, redissolved in the minimum quantity of water, and the solution was diluted with 30 ml. of dioxane. A phase-separated dioxane solution of diazomethane prepared from 8 g. of nitrosomethyl urea was added. The solution was allowed to stand for several hours; it was made slightly alkaline with lithium carbonate and extracted with ether. The solution was afterward de-ashed, the acid was neutralized with barium carbonate and, after centrifuging, the solution was evaporated to dryness. The methylation was repeated until five treatments had been given.

To obtain uniformly stepwise increments in methoxyl content a series of experiments was carried out in which the calculated stoichiometric quantity of diazomethane was used instead of the excess prescribed for preparative work. The resulting regular decrease in periodic acid consumption as diazomethane methylation proceeds is shown by the results recorded in Table III.

Periodic Acid Oxidation of Lignin Sulfonic Acid and of Phenols.—The reaction of periodic acid with lignin sulfonates and other phenolic derivatives was carried out on a sample of about 35 mg. weight if the equivalent weight toward periodic acid was about 500. The sample was dissolved in 10 ml. of sodium acetate–acetic acid buffer solution (2.0 g. of sodium acetate, 2.0 g. of acetic acid in 100 ml. of water, about pH 4.5); 5 ml. of sodium metaperiodate, approximately 0.0125 N concentration, was added and the flasks were kept at 25° for five hours. In each series of determinations were included several blanks which contained no oxidizable material. After the reaction period the solution was diluted to 100 ml.; 400 mg. of potassium iodide and 0.35 milliequivalent of sodium thiosulfate were added to each flask followed by 1 cc. of 4 N sulfuric acid. As iodine appeared in the flask, it was titrated with 0.01 N sodium thiosulfate so that no more than a slight excess of iodine was ever present. The titration was continued until no iodine appeared in the blank within five minutes after the last discharge of the starch–iodine end-point. This usually occurred about thirty minutes after the start of the titration. Under these circumstances iodine did not react with the lignin sulfonate ion. The results were expressed in terms of an equivalent weight for periodic acid oxidation. A number of results obtained by this method have been published previously.[8,9]

Permethoxy Lignin Sulfonate.—This derivative was prepared by the repeated methylation of sodium lignin sulfonate in alkaline solution using dimethyl sulfate, essentially in accordance with the directions given by King, Brauns and Hibbert.[3e]

Acetylation of Lignin Sulfonates and Their Derivatives.—The acetylation of barium lignin sulfonate was carried out by suspending 6.58 g. of the dry salt ground to a powder in a mixture of 16.5 g. of acetic anhydride and 6.5 g. of glacial acetic acid in which was dissolved 3.2 g. of anhydrous sodium acetate. This mixture was heated on the steam-bath for the five-day period required for solution

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(15) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. XV, p. 3, note 7.

(16) Supplied by Dow Chemical Co., Midland, Michigan.

to occur. The excess acetic anhydride and acetic acid were removed under reduced pressure and the solid was taken up in 100 ml. of water. The resulting solution was de-ashed and neutralized to *p*H 3.0 with barium carbonate. Thereafter it was extracted with ether for four days to remove acetic acid, and during this period the *p*H increased to 5.0.

The "hemimethoxy" derivative was acetylated by this same procedure. Patience had to be exercised while the solid, preferably the lithium salt, dissolved slowly in the sodium acetate-glacial acetic acid solution at room temperature, and heating was avoided until solution was completed. The acetylation product was isolated as described or any excess acetate ion was removed by dialysis. The results of attempts to acetylate permethoxy lignin sulfonate by this method and in several other ways are given in Table II.

Methyl Esters of Lignin Sulfonates

(a) Methyl Permethoxy Lignin Sulfonate.—A permethoxy lignin sulfonate solution was de-ashed and the resulting acid solution was dried by isothermal distillation of the frozen solution. The dry acid, 1.00 g., was finely powdered and suspended in 50 ml. of anhydrous tetrahydrofuran. To this suspension was added approximately 0.35 g. of diazomethane obtained by distillation of a solution in tetrahydrofuran. Both the suspension and the diazomethane solution were cooled at 0° prior to mixing. As soon as the reactants were mixed, nitrogen bubbles began to rise from the surface of the suspended solid and after a few hours a homogeneous solution resulted. After standing overnight the solution was filtered to remove diazomethane polymer and the bulk of the solvent was removed under reduced pressure. The residual tetrahydrofuran solution, about 2 to 3 ml., was poured into 75 ml. of anhydrous ether and about 2 to 3 ml. of wash solvent was used to rinse the distilling flask. The precipitate was washed with ether by decantation and dried in a stream of dry air. The preparation was soluble in tetrahydrofuran, dioxane, nitromethane and chloroform and insoluble in isoamyl ether. When the solid was suspended in 0.5 *N* sodium hydroxide solution, it dissolved completely over a period of three days.

(b) Methyl Hemimethoxy Lignin Sulfonate.—When procedure (a) was attempted an initial evolution of nitrogen soon stopped, and the surface of the reacting solid appeared to become covered with a product insoluble in tetrahydrofuran. A one-quarter volume portion of nitromethane was added; the reaction began anew and, after a few hours, a homogeneous solution resulted. A product was isolated in the same way as described for the permethoxy methyl ester.

(c) Methyl Peracetoxy Lignin Sulfonate.—The general method (b) can be applied to prepare the methyl ester of "peracetoxy" lignin sulfonic acid, a somewhat unstable substance, concentrated solutions of which slowly deposit a solid upon standing.

(d) Lignin Sulfonic Acid.—Application of this method to lignin sulfonic acid was accompanied by initial evolution of nitrogen at the surface of the solid. The reaction soon stopped and no solvent combination was found which caused it to go to completion.

Methoxy Determinations on Sulfonic Acid Esters.—In the semimicro Zeisel determination for methoxyl content only portions of the methyl esters of lignin sulfonic acids were converted to methyl iodide. This result was explored by analysis of known methyl sulfonates. The results are given in Table IV. When the behavior of the sulfonic acid esters in hydrolysis and in alkylation reactions is considered this result is not surprising.[17] The remedy applied was to hydrolyze the esters with ammonium hydroxide and to carry out the methoxyl analyses on the resulting salts.

TABLE IV

METHOXYL DETERMINATIONS ON METHYL SULFONATES

Sulfonate	Methoxyl, % Calcd.	Methoxyl, % Found
Methyl hemimethoxy lignin	5.50	1.00
Methyl permethoxy lignin	5.24	2.70
Methyl peracetoxy lignin	3.88	2.20
Methyl toluene	16.7	8.30
Camphor 10-methyl	12.6	12.4

Spectra of Lignin Sulfonic Acid Derivatives.—The absorption spectra of lignin sulfonic acid derivatives were determined by use of the Beckman ultraviolet spectrophotometer. The spectra were standardized by reference to the curve for potassium chromate in 0.05 *N* potassium hydroxide as published by Hogness, Zscheile and Sidwell,[18] and recordings were made within the optical density range of linear response as determined for the photocell in use during the measurements. In Figs. 1, 2 and 3 $\epsilon = 3100 n\mathrm{D}/C(\mathrm{MeO})$ where n = number of methoxyl groups per C_9 unit, MeO = % methoxyl, C = concn. in g./l., and D = optical density.

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Summary

1. A specially purified lignin sulfonate which fractional diffusion analysis had shown to be chemically homogeneous, yielded a hemimethoxy derivative when methylated with diazomethane, a permethoxy derivative when methylated with dimethyl sulfate and alkali, and a water soluble peracetoxy derivative when cautiously acetylated with sodium acetate as a catalyst.

2. The methyl esters of the three lignin sulfonate derivatives were prepared by the action of diazomethane upon the carefully dehydrated free acids.

3. Systematic and comprehensive analyses of the lignin sulfonate derivatives in the form of the ammonium or barium salts or of the methyl esters were carried out. Assuming that some of the salts contain water of hydration, the results suggested that all of the derivatives originated from a lignin sulfonic acid with the average empirical formula $C_9H_{7.5}O(OH)(OCH_3)(SO_3H)_{0.5}$.

SEATTLE 5, WASHINGTON RECEIVED JANUARY 3, 1949

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[17] Ferns and Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

[18] Hogness, Zscheile and Sidwell, *J. Phys. Chem.*, **41**, 379 (1937).