Lignin. XVI. Synthesis, Nuclear Magnetic Resonance, and Mass Spectroscopy of Several Monomeric and Dimeric Lignin-like Sulfonates[1]

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ABSTRACT: Eight monomeric and seven dimeric lignin-like sulfonates were synthesized. The methods of Gellerstedt and Gierer were used to acetylate hydroxyl and to esterify sulfonic acid groupings in order to cover these polar configurations. The resultant derivatives normally were purified by recrystallization from organic solvents and were studied with respect to the chemical shift of their respective protons in nmr spectroscopy, and with respect to fragmentation patterns in mass spectroscopy. The ranges of τ values of protons in lignin-like sulfonate preparations were compared to those for unsulfonated preparations. In mass spectroscopy, all compounds exhibited peaks for the parent ions in the range of 1–64% abundance relative to the base which was taken to be the most abundant peak. Acetyl, sulfonate, and ether groups proved to be main targets of fragmentation and tended to be eliminated upon electron impact. Cleavage of carbon–carbon bonds was mainly observed for three-carbon-side-chain β-aryl ethers. The general fragmentation pathways have been discussed. In general, the feasibility of application of nmr and mass spectroscopy in structural studies of sulfonated lignin-like model compounds after covering the polar sulfonic acid and hydroxyl groups is demonstrated.

Further knowledge is needed of the structure and reactions of lignin, and the now-reported research has been directed to this end. The basic mechanisms of the sulfonation reactions of lignin have become well established by extensive model experiments and were recently confirmed by the isolation of several sulfonated monomeric phenylpropane derivatives from spent sulfite liquor.[3-8] However, analytical methods attempting to elucidate side-chain structures and types of linkages between the lignin units have not yielded decisive results mainly because of difficulties arising as a result of the polyelectrolytic and polydisperse nature of the material. Lignin sulfonates and sulfonated lignin models commonly have been isolated and characterized as sodium as well as barium or quaternary ammonium salts. Owing to the insolubility in organic solvents and the thermal instability of these derivatives, the procedures of nmr and mass spectroscopy, extensively used in structural studies of organic natural compounds, have not given useful results when applied to lignin sulfonates.

One objective of the present studies, therefore, was to develop procedures for conversion of lignin sulfonates, fractionated into molecular weight groupings, into derivatives with certain desired physical and chemical properties by converting polar groups, and hydroxyl and sulfonic acid groups into esters, without altering the original side-chain structures. Another objective was to collect information concerning the nmr and mass spectroscopic behavior of certain molecular configurations present in the subject molecules, as a basis for later studies of lignin sulfonates themselves.

Although differences of opinion have been reported regarding the possibility of acetylating lignin sulfonates,[9,10] we anticipated that low molecular weight fractions might be acetylated completely by use of the pyridine–acetic anhydride procedure at room temperature. To cover sulfonic acid groupings, conversion to derivatives such as acid chlorides, acid amides and esters was considered. However, previous attempts to characterize acetylated monomeric lignin like sulfochlorides by mass spectroscopy, were unsatisfactory.[11] Thus we sought a satisfactory method for esterifying the labile and reactive sulfonic acid groups, such as those of the benzylsulfonic acid type which may occur predominantly in the α position of side chains of lignin-like molecules.

King, Brauns, and Hibbert[12] reported the preparation in about 10% yield of methyl esters of lignin sulfonates, previously methylated with diazomethane, by reacting the silver salts suspended in dioxane with methyl iodide. Recently Gellerstedt and Gierer,[13,14] applied a similar procedure in order to characterize sulfonated dimeric lignin models prepared in the course of their sulfonation studies, and showed that the original side-chain structures were not changed by the preparation procedures. (After completion of this manuscript the two Swedish authors published a further paper on their studies[15] with sulfonated lignin model compounds.)

The use of nmr spectroscopy as a valuable method to study the overall structure of lignin preparations has been

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(3) (a) V. F. Felicetta and J. L. McCarthy, unpublished results; (b) D. W. Glennie, Ph.D. Thesis, University of Washington, 1955; (c) G. M. Andrus, Ph.D. Thesis, University of Washington, 1957.

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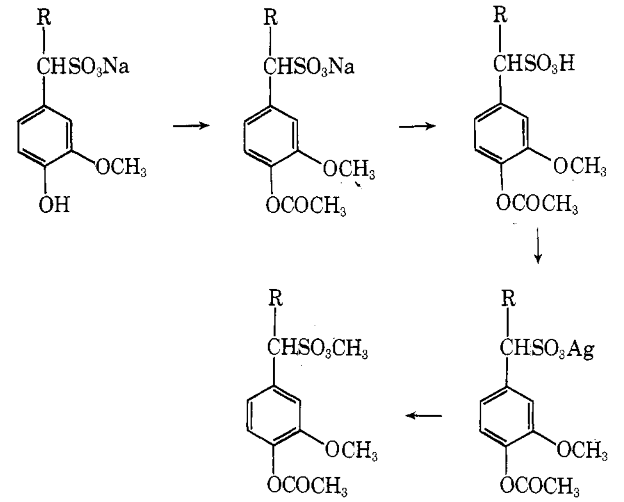


Figure 1. Reactions for preparation of acetylated lignin-like sulfonate methyl esters.

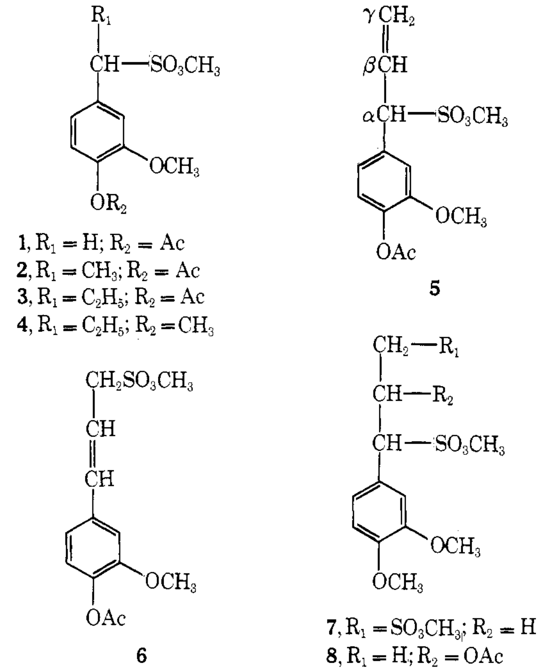
demonstrated by Ludwig, Nist, and McCarthy in this Laboratory.[16,17] When compared to the chemical shifts of lignin-type model compounds, the spectra of the lignin preparations "allowed semi-quantitative estimates to be made on the number of condensed aromatic systems free benzylic hydroxyls, aliphatic and aromatic hydroxyls, and total aliphatic hydrogens."[17] After acetylation, all preparations were found to be sufficiently soluble in deuteriochloroform for nmr determinations. The use of nmr spectroscopy in lignin chemistry has recently been reviewed by Ludwig.[18]

The behavior of monomeric and dimeric lignin structural units in mass spectroscopy has been studied recently.[19,20] General fragmentation patterns and relative stabilities of several types of linkages upon electron impact have been proposed. The data reported increased the understanding of lignin degradation products but, the results cannot be applied in general to sulfonated lignin-like monomers and dimers which might be isolated from spent sulfite liquors. The acetylated and methylated sulfonates appear to be the only known derivatives with sufficient stability and volatility to be successfully studied in mass spectroscopy. Attempts to analyze the acid chlorides were unsuccessful insofar as no parent peaks could be detected in the mass spectra of the sulfonates.[11]

In this context, a number of lignin-like lignin sulfonates were prepared as acetylated and methylated derivatives, and the nmr and mass spectra of these compounds were studied.

Results and Discussion

Synthesis. Attention was devoted mainly to monomeric and dimeric guaiacyl- and veratryl-type sulfonates featuring several side-chain structures of phenolic and nonphenolic lignin-like sulfonate structural units. In general, the appropriate benzyl alcohols were prepared and sulfonated following procedures described in the literature. For acetylation and esterification, the methods reported by Gellerstedt and Gierer[13,14] were used although in somewhat modified form as indicated in Figure 1 and Table I, and described in the Experimental Section.



1, $R_1 = H; R_2 = Ac$
2, $R_1 = CH_3; R_2 = Ac$
3, $R_1 = C_2H_5; R_2 = Ac$
4, $R_1 = C_2H_5; R_2 = CH_3$
5
6
7, $R_1 = SO_3CH_3; R_2 = H$
8, $R_1 = H; R_2 = OAc$

Figure 2. Monomeric lignin-like sulfonate derivatives.

Normally, the sodium sulfonates were acetylated by pyridine–acetic anhydride. The aqueous solution of the free acids—prepared by cation exchange—was neutralized with silver oxide and the silver sulfonates were reacted with methyl iodide in acetonitrile to form the corresponding acetylated methyl sulfonates.

Monomeric Lignin-like Sulfonate Derivatives. Many proposals for the structure of lignin sulfonates have placed a sulfonate group in the α position and thus **1**, **2**, **3**, and **4** of this type were prepared as indicated in Figure 2.

Compounds **5** and **6** were prepared since, in prior research in this Laboratory, the two sulfonated phenylpropane-type monomers **5*** and **6*** (the asterisk after the numeral distinguishes a compound as unacetylated, unesterified sodium sulfonate) were isolated from spent sulfite liquor of preextracted hemlock,[3,4,21-23] and these substances were found to be unsaturated in the side chain. Further studies indicated that these compounds originate from coniferyl alcohol groups in lignin.[22,24] Parrish[8,11] isolated six monomeric lignin sulfonic acids of the syringyl type from cooking liquor of wattle wood (*Acacia mearnsii*) and among them was the syringyl analog to **5*** and **3***.

Parrish[8] also isolated two monomeric disulfonates, the 1,2- and 1,3-disulfonates, which he synthesized by reacting sinapyl alcohol with sulfite ions over a wide pH range (pH 4-7.4). As model for monomeric disulfonates, we prepared **7** following a similar route. This substance was synthesized by refluxing 3,4-dimethoxycinnamyl alcohol in a solution of 10% $NaHSO_3$. Compound **8** was prepared by sulfonation of veratrylpropane-1,2-diol 2-acetate to yield introduction of the sulfo group in α position and deacety-

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Table I
Information Concerning Synthesized Monomeric and Dimeric Lignin-like Sulfonates

			Yield				Anal.				
No.	Compound Name	Formula	Sulfonation (%)	Conversion (%)	Mp (°C)	Mol Wt	C (%)	H (%)	S (%)	Modificn of Std Sulfonation Procedure	Ref to the Synthesis of Starting Materials
1	(4-Acetoxy-3-methoxyphenyl)methanesulfonic acid methyl ester	$C_{11}H_{14}O_6S$	30	60	103–104	F:[a] 274 R:[a] 274	48.30 48.18	5.29 5.14	11.59 11.69	No SO_2 addition, three-hr reflux	
2	1-(4-Acetoxy-3-methoxyphenyl)ethane-1-sulfonic acid methyl ester	$C_{12}H_{16}O_6S$	90	80	75–76.5	F: 288 R: 288	50.28 49.99	5.56 5.59	11.10 11.12	125°	*c*
3	1-(4-Acetoxy-3-methoxyphenyl)propane-1-sulfonic acid methyl ester	$C_{13}H_{18}O_6S$	85	70	82–83	F: 302 R: 302	51.70 51.64	5.98 6.00	10.46 10.60		*d*, *e*
4	1-(3,4-Diethoxyphenyl)propane-1-sulfonic acid methyl ester	$C_{12}H_{18}O_5S$	85	90	Oil	F: 274 R: 274		Not obtained		Room temperature, 3 days	*f*, *g*
4	1-(4-Acetoxy-3-methoxyphenyl)prop-2-ene-1-sulfonic acid methyl ester	$C_{13}H_{16}O_6S$	Obtained from Schubert *et al.* (ref 20)	90	68.5–70	F: 300 R: 300	52.04 51.99	5.52 5.37	10.48 10.68	Ref 20	
6	1-(4-Acetoxy-3-methoxyphenyl)prop-1-ene-3-sulfonic acid methyl ester	$C_{13}H_{16}O_6S$	Obtained from Schubert *et al.* (ref 20)	90	113–115.5	F: 300 R: 300	52.00 51.99	5.48 5.37	10.41 10.68	Ref 20	
7	1-(3,4-Dimethoxyphenyl)propane-1,3-disulfonic acid methyl ester	$C_{13}H_{20}O_8S_2$	70	20	101–102	F: 368 R: 368		Not obtained		No SO_2 addition, three-hr reflux	*h*
8	1-(3,4-Dimethoxyphenyl)propane-2-acetoxy-1-sulfonic acid methyl ester	$C_{14}H_{20}O_7S$	85	70	121.5–123	F: 332 R: 332	50.81 50.59	6.02 6.07	9.29 9.65		*i*
9	1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)ethane-1-sulfonic acid methyl ester	$C_{19}H_{24}O_7S$	80	80	107–107.5	F: 396 R: 396		Not obtained		125°	*c*, *j* (ref *29*)
10	1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxy-4-methylphenoxy)ethane-1-sulfonic acid methyl ester	$C_{20}H_{24}O_8S$	60	30	114–116	F: 424 R: 424	56.79 56.59	5.88 5.70	7.27 7.55		*j*
11	1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)propane-1-sulfonic acid methyl ester	$C_{20}H_{26}O_7S$	45	80	89–90[b]	F: 410 R: 410	58.38 58.52	6.51 6.38	7.58 7.81		*k*
12	1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1-sulfonic acid methyl ester	$C_{20}H_{24}O_8S$	40	30	Oil	F: 424 R: 424		Not obtained			*k*
13	1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)-3-acetoxypropane-1-sulfonic acid methyl ester	$C_{22}H_{28}O_9S$	52	80	102–103[b]	F: 468 R: 468	56.53 56.40	6.31 6.02	6.57 6.84		Ref 26
14	1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxy-4-methylphenoxy)-3-acetoxypropane-1-sulfonic acid methyl ester	$C_{23}H_{28}O_{10}S$	60	30	112–113[b]	F: 496 R: 496		Not obtained			*j* (ref 26)

15	1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)propanone-1-sulfonic acid 3-methyl ester	$C_{20}H_{24}O_8S$	Obtained from Sarkanen and Wallis (ref 28)		160-161	F: 424 R: 424	Obtained by Sarkanen *et al.* (ref 28)	16-hr reflux in 20% $NaHSO_3$
16	1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-methyl-phenoxy)propanol-1-sulfonic acid 3-methyl ester	$C_{20}H_{26}O_8S$	Obtained from Sarkanen and Wallis (ref 28)		Oil	F: 426 R: 426	Obtained by Sarkanen *et al.* (ref 28)	Catalytic reduction of 15 on Pd-C (5%)
17	(2,4'-Diacetoxy-3,3'-dimethoxy-5-propyl-α-methyl)bibenzyl-α'-sulfonic acid methyl ester	$C_{25}H_{32}O_9S$	Obtained from Gellerstedt *et al.* (ref 14)		127-129[b]	F: 508 R: 508	Obtained by Gellerstedt *et al.* (ref 14)	
18	Diacetate of dimethyl dehydrodivanillyl-disulfonate	$C_{22}H_{26}O_{12}S_2$	60	20	148-149	F: 546 R: 546	Not obtained	Room temperature, 7 days

[a] Upper line in column for each substance refers to values found (F), lower line to values required (R). [b] Refers to "A" or erythro form of compound. [c] "Organic Synthesis," Collect. Vol. II, Wiley, New York, N.Y., p 619. [d] B. O. Lindgren, *Acta Chem. Scand.*, **4**, 1365 (1950). [e] E. Adler and J. Marton, *Acta Chem. Scand.*, **13**, 75 (1959). [f] K. Kindler and W. Peschke, *Arch. Pharm.* 352 (1932). [g] E. Adler and H. D. Becker, *Acta Chem. Scand.*, **15**, 849 (1961). [h] K. Freudenberg and G. Schumacher, *Chem. Ber.*, **87**, 1992 (1954). [i] A. B. Cramer, M. J. Hunter, and H. Hibbert, *J. Amer. Chem. Soc.*, **61**, 509 (1939). [j] H. Nimz, *Chem. Ber.*, **102**, 3803 (1969). [k] E. Adler, S. Delin, and G. E. Miksche, *Acta Chem. Scand.*, **20**, 1034 (1966). [l] E. Adler and S. Hernestam, *Acta Chem. Scand.*, **9**, 332 (1955).

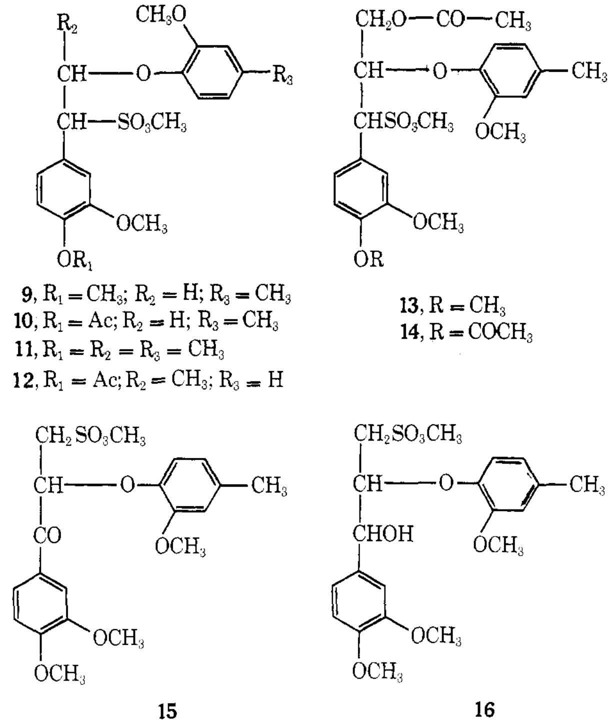

Figure 3. Dimeric β-O-4-type lignin-like sulfonate derivatives.

lation; after reacetylation and esterification the two diastereomeric forms of 8 were formed and these were separated by column chromatography.

Dimeric "β-O-4-" Type Lignin-like Sulfonate Derivatives. The presence of both α- and β-aryl ether linkages between structural units in lignins appears to be well established. The β-ether linkages (β-O-4) are considered to be stable toward hydrolysis under the acidic condition of bisulfite delignification[25] and thus should be of special significance in the structure of lignin sulfonates.

Important evidence for the presence of sulfonated arylglycerol aryl ether configuration in lignin sulfonic acids has resulted from the anaerobic alkaline hydrolysis studies of lignin sulfonates and sulfonated models by Kratzl *et al.*[26,27] These studies indicated that the fragmentation products vanillin and acetaldehyde originate from arylglycerol β-aryl ether type, and consisted of compounds 9–14 as shown in Figure 3. Thus these substances were of interest and were prepared and studied in the present investigation. The preparation of two sulfonic acid esters similar to 9 and 10 has been reported recently.[13]

The literature on the sulfonation of β-guaiacyl ether of α-(4-hydroxy-3-methoxyphenyl)glycerol[26] and of α-(3,4-dimethoxyphenyl)glycerol,[28] indicates that under the conditions of an acid bisulfite delignification, the corresponding α-sulfonic acids were formed which were isolated as Ba salts. In our work, the sodium salts were acetylated and then converted into the methyl sulfonates which were purified by recrystallization from organic solvents.

In the present study, nmr spectra revealed that 11 and 12 were obtained as mixtures of their diastereomers. In both cases the stereoisomer which exhibited the doublet

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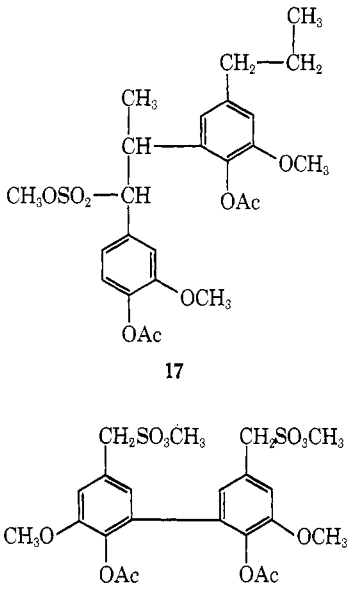


17

18

Figure 4. Dimeric carbon—carbon-linked lignin-like sulfonate derivatives.

for the α-methine proton with the smaller coupling constant (A, probably erythro) was formed in a higher yield than its counterpart (B, probably threo). The ratio of formation between erythro and threo was 3:1 in **11** and 3:2 in **12**. For both erythro forms of **11** and **12**, the coupling constants of the α-methine proton doublet amounted to 4 Hz compared with 7 Hz for the threo forms. Both compounds were prepared from the erythro forms of their corresponding alcohols, obtained by sodium borohydride reduction of the ketones, and the alcohols exhibited the smaller coupling constants in the nmr spectra compared to the threo forms. The separation of the erythro form of **11** was achieved by fractional crystallization.

A crystalline diastereomeric form of **13** was isolated by column chromatography. The nmr spectrum exhibits a doublet for the α-methine proton, which has the same coupling constant as the erythro forms of **11**, **12**, and **14**. No other isomeric form was indicated by examination of the nmr spectrum of the crude reaction mixture, which might be due to overlapping by the multiplet exhibiting the γ-methylene group.

Compound **14** was obtained as a mixture of its diastereomeric forms. Separation of the crystalline erythro form (higher R_f value than threo form) was achieved by column chromatography. Nmr spectroscopy indicated the presence of erythro and threo forms in a ratio of about 3:2. The location and coupling constants for the doublets exhibited by the diastereomeric forms of **14** are very similar to those of **11** and **12**.

Related substances have been reported in the literature and thus were of interest. Sulfonation in γ position of a ketol β-ether analog to **15*** (Figure 3) was reported earlier by Adler *et al.*[28] The methyl ester **16** has recently been subjected to anaerobic, alkaline hydrolysis studies.[29]

Dimeric C—C-Linked Lignin-like Sulfonate Derivatives. Several types of carbon—carbon linkages between lignin structural units have been proposed including pinoresinol-, phenylcoumaran-, and diphenyl-type linkages. The sulfonation of pinoresinol resulted in cleavage of the two cyclic dialkyl ether bonds and sulfonation of one α position.[25]

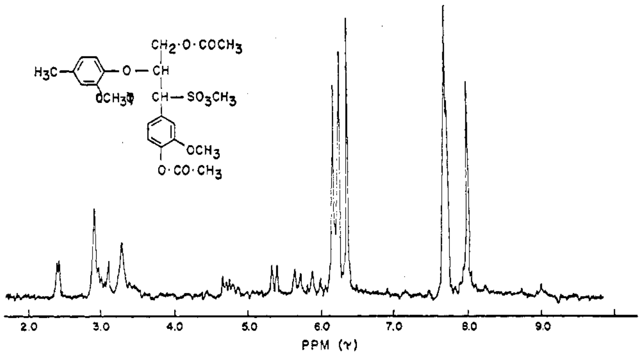


Figure 5. Nmr spectrum of **14**.

Cleavage of a furan ring and sulfonation of the resulting benzyl alcohol was observed in recent sulfonation studies (neutral sulfite delignification) of phenylcoumaran models by Gellerstedt and Geirer[14] who isolated the diastereromers of **17** as shown in Figure 4. This compound was supplied by the Swedish authors for use in the present investigation.

To provide a model for the diphenyl-type structures, we sulfonated dehydrodivannillyl alcohol and prepared the corresponding acetylated methyl ester **18**.

Nuclear Magnetic Resonance Spectroscopy. The model compounds examined by nmr are listed in Figures 2, 3, and 4. The τ values and coupling constants of the compounds are compiled in Table II. The spectra of all compounds were recorded in deuteriochloroform. In general, the nmr spectra observed are found to be consistent with the spectra expected from the compounds synthesized. Certain generalizations may be made with respect to the different types of protons present in lignin.

Aromatic Protons. The location of signals arising from protons attached to aromatic rings of lignin-like sulfonates is in good agreement with those for unsulfonated model compounds. An unexpected difference however, was found for the three-carbon side-chain β-ethers **11–14** which exhibit a doublet at lower field than the aromatic protons. A similar effect has long been known for aromatic protons ortho to carbonyl groups.[16,18] The shift of one proton observed for the sulfonates contrasts with the deshielding of two protons caused by carbonyls (see Figure 5). No final explanation can be given as yet for this deshielding effect observed with some sulfonates. Formation of a hydrogen bond between the C_5-aromatic proton and the sulfonate group, however, might be suspected as a reason.

Another unusual shielding to high τ values was observed with the threo form of **17**. Nmr signals for all other aromatic protons are in accord with those reported by Ludwig *et al.*[16]

Aliphatic Protons. Whereas little interaction exists between aromatic and other protons present in lignin, the aliphatic protons of the side chain may be spread over nearly the total range of τ values. Depending on the substituents, α-methine protons have been observed as far downfield as τ = 3.75 ppm, and methyl protons have been reported to appear up to 9.35 ppm according to Ludwig.[18]

α-Methine Protons. The present results indicate that the locations of α-methine proton signals depend upon the neighboring substituents. Ether linkages and hydroxyl groups are the predominant substituents of the α-carbon atom in unaltered lignins. The sulfonation reaction attacks this position and substitutes ether and hydroxyl groups for a SO_3H group. This change of substituents

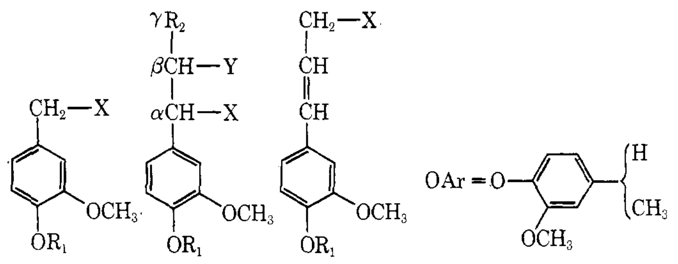
(29) K. V. Sarkanen and A. F. A. Wallis, private communication.

Table II
Chemical Shifts Observed in Lignin-like Sulfonates Investigated by Nuclear Magnetic Resonance–Spectroscopy (in τ Values)

Compound	Aromatic	$C_{\alpha}H$	$C_{\beta}H$	$C_{\gamma}H$	Ether OCH_3 3 position	Ether OCH_3 2 position	SO_2OCH_3	$C_{\alpha}H_3$	Phenolic Ac	Aliphatic Ac
1	2.94 (s)	5.65 (s)			6.14 (s)		6.20 (s)		7.69 (s)	
2	2.92 (s)	5.60 (q), $J = 14.7$	8.18 (d), $J = 7$		6.13 (s)		6.29 (s)		7.69 (s)	
3	2.82–3.11 (m)	5.86 (s)	7.58–7.77 (m)	9.09 (t), $J = 7$	6.16 (s)		6.38 (d), $J = 2$		7.70 (s)	
4	2.93 (s) + 2.96 (s)	5.85 (q), $J = 10.5, 5$	7.40–7.90 (m)	9.08 (t), $J = 7$	6.06 (s)		6.29 (s)			
5	2.92 (s)	5.10 (d), $J = 8$	3.36–3.96 m	4.38–4.67 (m)	6.14 (s)		6.23 (s)		7.69 (s)	
6	3.00 (s)	3.28 (d), $J = 16$	3.63–4.12 (m)	6.02 (d), $J = 7$	6.01 (s)		6.16 (s)		7.70 (s)	
7[a]	3.03 (m)	5.04–5.39 (m)	7.85–8.75 (m)	6.60–6.90 (m)	6.09 (s)		6.28 (s)			
8 A	3.05 (s)	5.59 (d), $J = 9$	4.27 (sext), $J = 16, 6, 6$	8.83 (d), $J = 6$	6.12 (s)		6.35 (s)			
					6.09 (s)		6.30 (s)			7.89 (s)
8 B (in mixture)	3.07 (m)	5.78 (d), $J = 12.5$	4.26 (sext), $J = 16, 6, 6$	8.73 (d), $J = 6$	6.11 (s)		6.31 (s)			7.96 (s)
9	3.02–3.37 (m)	5.37 (q), $J = 19, 3$	5.36 (d), $J = 3$		6.16 (s)	6.24 (s)	6.27 (s)	7.73 (s)		
10	2.87–3.30 (m)	5.35 (q), $J = 20, 2$	5.32 (d), $J = 4$		6.20 (s)	6.20 (s)	6.26 (s)	7.73 (s)	7.73 (s)	
11 A		5.63 (d), $J = 4$		8.72 (d), $J = 6$						
	2.90–3.25 (m) 2.47 (d), $J = 2$		4.53–4.92 (m)		6.08 (s)	6.23 (s)	6.33 (s)			
11 B		5.36 (d), $J = 7$		8.78 (d), $J = 6$	6.11 (s)			7.71 (s)		
12 A	2.93–3.09 (m)	5.61 (d), $J = 4$	4.60–4.85 (m)	8.66 (d), $J = 6$	6.15 (s)	6.22 (s)	6.35 (s)		7.69 (s)	
12 B	2.45 (d), $J = 2$	5.35 (d), $J = 7$		8.74 (d), $J = 6$		6.24 (s)				
13	2.94–3.30 (m), 2.51 (d), $J = 2$	5.42 (d), $J = 4$	4.56–4.93 (m)	5.68–6.03 (m)	6.09 (s)	6.23 (s)	6.35 (s)	7.70 (s)		7.99 (s)
14 A	2.93–3.31 (m), 2.43 (d), $J = 2$	5.39 (d), $J = 4$	4.69–4.88 (m)	5.65–6.06 (m)	6.17 (s)	6.25 (s)	6.37 (s)	7.71 (s)	7.70 (s)	8.00 (s)
14 B	2.93–3.31 (m), 2.43 (d), $J = 2$	5.17 (d), $J = 8$	4.69–4.88 (m)	5.65–6.06 (m)	6.21 (s)	6.24 (s)	6.38 (s)	7.71 (s)	7.70 (s)	8.06 (s)
15	2.17–2.47 (m), 3.05–3.30 (m)		4.05 (t), $J = 5$	6.05–6.2 (m)	6.06 (s), 6.12 (s), 6.13 (s)		6.26 (s)	7.73 (s)	7.73 (s)	
16 A	3.12–3.3 (m)	5.08 (d), $J = 3$	5.42 (sext), $J = 10, 2.5, 2.5$	6.95 (qu), $J = 152$ 6.45 (d), $J = 9$	6.13 (s)	6.16 (s)	6.23 (s)	7.66 (s)		
16 B	3.0–3.4 (m)	5.10 (d), $J = 5.5$	5.32 (qu), $J = 10.5, 5$	6.55 (d), $J = 5$	6.20 (s)	6.22 (s)	6.27 (s)	7.74 (s)		
17 Erythro	3.0–3.5 (m)	H: 5.43 (d), $J = 11$ H_2: 7.6–7.8 (m)	H: 5.8–6.2 (m) H_2: 8.4–8.8 (m)	A: 8.40 (d), $J = 6$ B: 9.18 (t), $J = 7$	6.23 (s)	6.28 (s)	6.42 (s)		7.65 (s) 7.77 (s)	
17 Threo	3.1–4.1 (m)	H: 5.57 (d), $J = 3$ H_2:	H: 5.6–6.1 (m) H_2:	A: 8.62 (d), $J = 7$ B: 9.17 (t), $J = 7$	6.20 (s)	6.23 (s)	6.38 (s)		7.58 (s) 7.72 (s)	
18	2.90–3.13 (m)	5.67 (s)			6.11 (s)		6.16 (s)		7.89 (s)	

[a] Concentration about 5% in deuteriochloroform.

Table III
Influence of Three Different Substituents on the Chemical Shifts of Adjacent Methine Protons in Nuclear Magnetic Resonance Spectroscopy



1 2-4 and 8-14 6

Compound	R_1[a]	R_2[b]	Y	Chemical Shifts for $C_\alpha H(C_\gamma H_2$ for 6) for X = OAc	OH	SO_2OCH_3
1	H-Ac			4.95 (s)	5.43 (s)	5.65 (s)
2	H-Ac	H	H	4.14 (q)	5.09–5.94 (m)	5.60 (q)
3	Ac	CH_3	H	4.34 (t)	5.53 (t)	5.86 (s)
4	CH_3	CH_3	H	4.41 (t)	5.55 (t)	5.85 (q)
6	CH_3			5.32 (d)	5.78 (d)	
	H-Ac			5.05 (d)[c]	5.69 (d)	6.02 (d)
8 A/B	CH_3	CH_3	OAc	4.10 (d)/4.21 (d)	5.37 (q)	5.59 (d)/5.78 (d)
9	CH_3	H	OAr	3.87 (q)	4.98 (q)	5.37 (q)
11 A	CH_3	CH_3	OAr	4.17 (d)	5.16 (d)	5.63 (d)
13 A	CH_3	CH_2OH-Ac	OAr	4.00 (q)	5.03 (m)	5.42 (d)
14 A	H-Ac	CH_2OH-Ac	OAr	3.89 (d)		5.39 (d)

[a] If R_1 = H-Ac, the compound with X = OH has R_1 = H, the compound with X = OAc or SO_3CH_3 has R_1 = Ac. [b] If R_2 = CH_2OH-Ac, the compound with X = OH has R_2 = CH_2OH, the compound with X = OAc or SO_3CH_3 has R_2 = CH_2OAc. [c] Acetylated coniferyl benzoate (1).

causes a significant change in chemical shifts of adjacent methine protons as is shown in Table III. The acetoxyl group is included in the table as a possible substituent since most nmr spectra of lignin preparations have been obtained from acetylated samples.[17,30] According to these data, the acetoxyl group has the strongest and the sulfonic acid ester group the weakest electron-withdrawing effect of the three groups.

The appearance of α-methine protons in nmr spectroscopy is of interest for the stereochemistry of α,β-disubstituted lignin model compounds. Although no general rule for the assignment of structures to stereoisomers on the basis of vicinal coupling constants (henceforth referred to as J and measured in hertz) exists, "the extremely common problem of differentiation between threo and erythro isomers can often be solved by consideration of the relative magnitudes of vicinal coupling constants."[31] A compilation of J_{vic} for a number of α,β-disubstituted lignin model compounds will therefore aid in the evaluation of the respective stereoisomeric forms (see Table IV). Since an assignment of the compound with the smaller J_{vic} to the erythro form seems not to be justified in general, an "A" form was assigned to those structures where the erythro form had a higher probability based on the method of synthesis, chromatographic behavior, and coupling constant.

The presence of a stable hydrogen bond between the α-hydroxyl hydrogen and the β-oxygen to form a five-membered ring in which the β-protons are nonequivalent was postulated on the basis of the fact that 1-(3,4-dimethoxyphenyl)-2-(2-methoxy-4-propylphenoxy)ethanol exhibited a quadruplet for its α-methine proton, whereas its acetate showed an almost normal triplet.[16] Since all three derivatives of 9 (alcohol, acetate, and sulfonate) show quadruplets as coupling pattern for the α-proton signal (see Table III), the nonequivalence of the β-protons must be due to factors other than hydrogen bonding. The possibility of free rotation about the C_α—C_β bond might be precluded by steric factors caused by the bulky X substituents.

Other Aliphatic Protons. Aliphatic protons appear over a wide range of τ values, as mentioned above. By restricting the presence of aliphatic protons to β-methine and γ-methylene groups, the aliphatic proton signals can be expected to appear in more limited areas. The γ-methylene group, which is generally connected to an oxygen or sulfur atom, seems to appear with, or very near, the methoxyl region whereas β-methine protons interfere with the region designed for the α-methine protons.

Methoxyl Protons. Methoxyl group signals usually appear over a small area of the nmr spectrum. The separation of ester from ether methoxyl group signals would be most valuable for structural analysis. The average location of these two types of methoxyl group signals, however, provides only slightly different τ values. Figure 6 suggests the distribution of methoxyl group signals of the compounds listed in Figures 2–4. The curves represent three major areas between τ 6.00 and 6.50 ppm. Methoxyl groups in 3 and 4 position of monomeric lignin-building units yield signals in the region of lowest τ values. The next higher τ values are associated with signals from methoxyl groups in the 2 position of phenoxy substituents of β-ethers. Ester methoxyl groups give signals with the highest τ values.

In general, methoxyl groups linked to sulfonic acid groups as esters yield signals at higher τ values than those attached to the molecules as ether groups. This was indicated by our observation that ethyl esters of 3 and 8 (obtained by reacting the sodium salts with ethyl iodide in-

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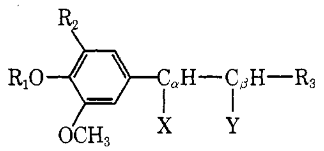
(30) B. L. Lenz, *Tappi*, 51, 511 (1968).
(31) S. Sternhell, *Quart. Rev., Chem. Soc.*, 23(2), 236 (1969).

Table IV
Coupling Constants in Nuclear Magnetic Resonance Spectroscopy of Benzylmethine Protons of Some Selected α,β-Disubstituted Lignin-like Structural Units



R_1	R_2	R_3	X	Y	J ("A" or Erythro), Hz	J ("B" or Threo), Hz	Author or Compound
CH_3	H	CH_3	SO_3CH_3	OAc	9	12.5	8
CH_3	H	CH_3	OH	OAr	3	8	Precursor of 11
CH_3	H	CH_3	OAc	OAr	4	7	Precursor of 11
CH_3	H	CH_3	SO_3CH_3	OAr	4	7	11
Ac	H	CH_3	SO_3CH_3	OAr	4	7	12
CH_3	H	CH_2OAc	SO_3CH_3	OAr	4	?	13
Ac	H	CH_2OAc	OAc	OAr	5	6	Precursor of 14
Ac	H	CH_2OAc	SO_3CH_3	OAr	4	8	14
CH_3	H	$CH_2SO_3CH_3$	OH	OAr	3	5.5	15
Ac	OCH_3	$CO_2C_2H_5$	OAc	OAc	7	4	Parrish (ref 8, 11)
H	OCH_3	CH_2OH	SO_3Na	OH	6	10	Parrish (ref 8, 11)
Ac	H	CH_2OAc	SO_3CH_3	OAr	4.1	7.9	Gierer (ref 15)
CH_3	H	CH_2OAc	SO_3CH_3	OAr	3.9	8.1	Gierer (ref 15)
a	*a*	*a*	OAc	OAr	4.9	6.1	Ludwig (ref 18)
a	*a*	*a*	OH	OAr	3.6	7.9	Ludwig (ref 18)

[a] Substituents not stated.

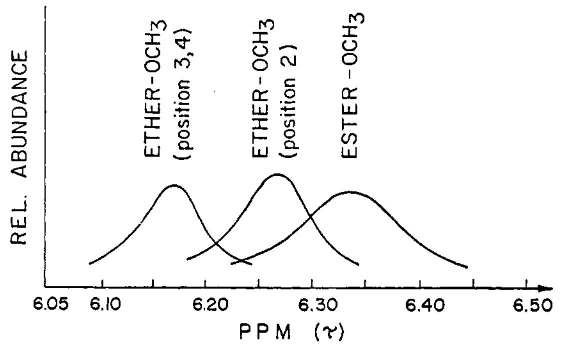


Figure 6. Distribution of signals reflecting methoxyl groups of compounds investigated.

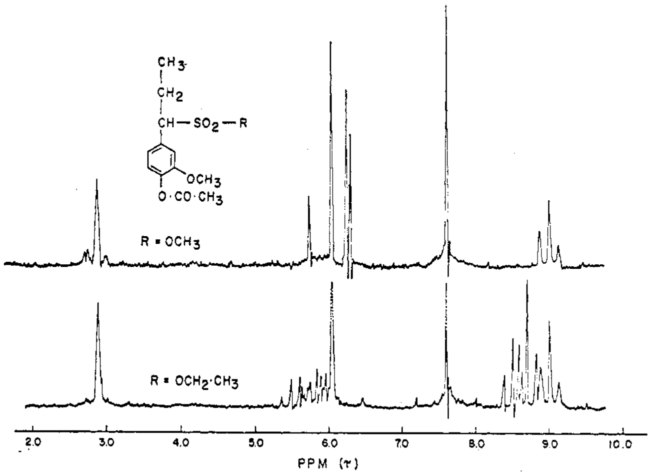


Figure 7. Nmr spectra of methyl *vs.* ethyl guaiacylpropanesulfonate.

stead of methyl iodide) raised methoxyl signals with lower τ values than the corresponding methyl esters (see Figure 7).

Acetoxyl Groups. Generally, the ranges now observed for τ values of acetoxyl groups in different positions of the C_9 unit compare well with the data reported earlier.[16-18] Acetyl groups of phenolic hydroxyls raise signals at lower τ values than those ot aliphatic hydroxyl groups. Phenolic acetyl groups ortho to biphenyl linkages, however, are shielded upfield and cannot be distinguished from their aliphatic counterparts. Weaker shielding is observed for compounds with aliphatic substituents ortho to the phenolic acetyl group as is demonstrated by **17**.

Since the signals of acetoxyl groups show little interference with other protons present in lignin preparations, they may serve as quantitative measures for hydroxyl groups originally present. Ludwig *et al.* and Lenz showed that the results of phenolic hydroxyl determinations by nmr spectroscopy are in good agreement with the results obtained by classical methods.[17,30]

Adjustment of Ranges of τ Values for Lignin Sulfonate Preparations. Ranges of τ values in the nmr spectra of lignin preparations were assigned to the various protons by Ludwig *et al.* These have been widely used in lignin chemistry[30,32,33] and were based upon proton signals observed for model compounds.

In this investigation, this type of data is being reported for sulfonated lignin model compounds in order to make the use of nmr spectroscopy applicable to lignin sulfonates and their derivatives. The results indicate that estimates can be made of the extent to which a number of different types of protons occur in lignin sulfonate preparations.

Generally the τ values associated with particular species protons in lignin-like sulfonates are the same or quite similar to those observed in the unsulfonated analogs, except in a few cases. Thus, aromatic protons in the 6 positions of α-sulfonated β-aryl ether compounds appear at

(32) D. E. Bland and S. Sternhell, *Aust. J. Chem.*, **18**, 401 (1965).
(33) B. F. Hrutfiord and J. L. McCarthy, *Advan. Chem. Ser.*, No. 59, 225 (1966).

Table V
Ranges of τ Values for Chemical Shifts of Signals in Nuclear Magnetic Resonance Spectroscopy from Protons Found in Model Compounds Adjusted for Lignin *vs.* Lignin Sulfonate Preparations

	Lignin			Lignin Sulfonates		
Types of Protons	Range	Models	Polymer	Models	Polymer	Range
Aromatic	2		2.00–3.72		2.00–3.72	2
Ortho to C_α=O		2.22–2.77		2.17–2.47	2.00–2.75	2a
Ortho to C_α—SO_3CH_3				2.43–2.51		
Others		2.73–3.65		2.87–4.1	2.75–3.72	2b
α-Vinyl		3.26–3.73		3.28		
β-Vinyl side chain	3	3.68–4.13	3.72–4.26	3.63–4.12	3.72–4.82	3–4
C_αH-R, R = OAc		3.75–4.33				
= OAr (cyclic)	4	4.42–4.53	4.26–4.82			
= SO_3CH_3				5.04–5.85		
C_βH—R; R = OAc, OAr	5		4.82–7.50	4.05–5.42	4.82–7.50	5
R = Ar		4.5–9.35		5.6–6.2		
$C\gamma H_2$—R; R = OAc, SO_3CH_3				5.65–6.95		
Other						
Methoxyl, ether		6.06–6.45		6.06–6.28		
ester				6.16–6.42		
Acetoxyl	6					6
Phenolic		7.66–7.82	7.50–7.81	7.58–7.73	7.50–7.81	
Ortho to "5-5"		5.90–7.93		7.89		
Ortho to "β-5"				7.77		
Aliphatic	7	7.89–8.20	7.81–8.42	7.89–8.06	7.81–8.42	7
Highly shielded	8		8.42–9.62		8.42–9.62	8

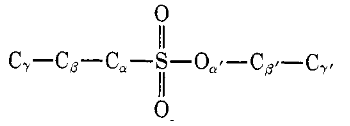
lower field, together with those aromatic protons adjacent to α-carbonyl groups.

Also, aliphatic protons of benzylic carbon atoms next to aryl (coumaran) or acetyl groups should be assigned to a range of τ values adjacent to the aromatic region. For sulfonated lignins, this type of proton is deshielded to a higher field (see Table III) with loss of a division between ranges 3 and 4. Other protons (vinyl groups, sidechain) are distributed over most of the spectrum, but do not influence the divisions used previously for lignin preparations. Table V lists the ranges of τ values found for model compounds and sets forth the ranges proposed for sulfonated and unsulfonated lignin samples.

Mass Spectroscopy. Organic sulfur compounds have been studied with respect to their mass spectral behavior.[34] Fragmentation pathways of several sulfonates have been proposed by Truce, Campbell, and Madding[35] and these propositions may be summarized and our findings may be presented and discussed in terms of a number of schemes which will now be set forth.

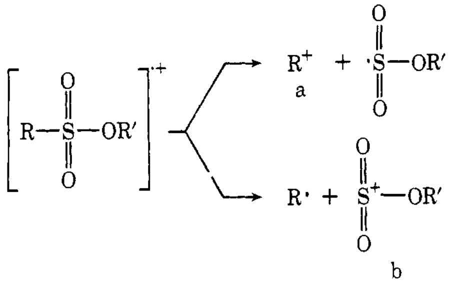
For alkanesulfonates, the parent peaks were found by Truce *et al.* to occur in about 1-3% abundance relative to the base (most abundant) peak. Scheme I has been used as a basis for consideration of various bonds undergoing cleavage where α cleavage means cleavage of the C—S bond, β cleavage refers to the C_α—C_β bond, etc. The most abundant ions in the spectra of alkyl alkanesulfonates have, in general, been attributed to fragments arising from the alkyl group (a) obtained upon α cleavage, as shown in Scheme II. The complementary fragment $(SO_2OR')^+$ (b) has been observed to a varying degree. The sulfonates were found to undergo several rearrangement processes in their mass spectroscopic fragmentation which depended mainly on the type of substitution present.

Scheme I

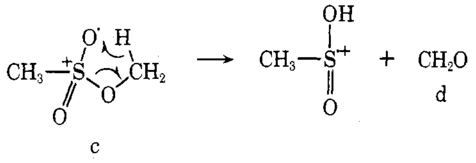


$C_\gamma—C_\beta—C_\alpha—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O_{\alpha'}—C_{\beta'}—C_{\gamma'}$

Scheme II



Scheme III



Methyl methanesulfonate (c) was found to yield formaldehyde (d) after rearranging according to Scheme III. Transfer of a γ-hydrogen occurred with methyl ethanesulfonate (e) (Scheme IV). A protonated methyl bisulfite ion (f) was recorded in the spectra of those compounds that contained β- and γ-hydrogens (Scheme V). Another rearrangement of compounds possessing γ-hydrogens involved a six-membered ring and led to β cleavage and formation of an olefin (g) (Scheme VI). The appearance of alkoxy ions (h) as fragments in the spectra of some sulfonates was explained as products of another rearrangement, shown in Scheme VII. After rearranging to a dialkyl sulfite (i), cleavage was observed to occur at two alternate

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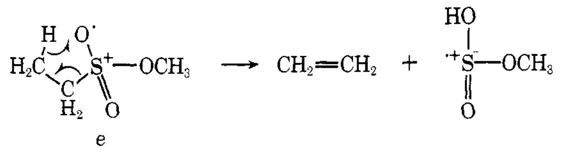
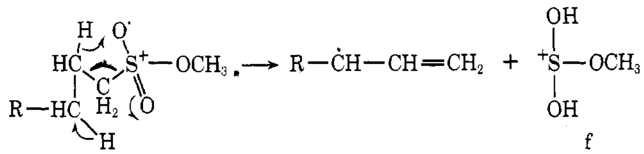
(34) H. Budzikiewicz. "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapter 19.

(35) W. E. Truce, R. W. Campbell, and G. D. Madding, *J. Org. Chem.*, 32, 308 (1967).

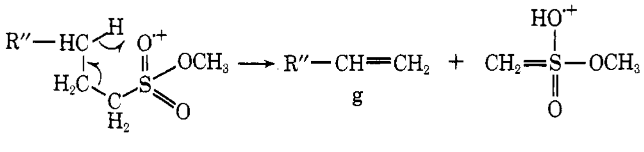
Scheme IV



Scheme V



Scheme VI



positions. The formation of such alkoxy ions (h) was in all cases accompanied by the formation of (R + CH_2O)$^+$ ions. Since an ion-molecule recombination reaction is unlikely, Truce, Campbell, and Madding explain this (R + CH_2O)$^+$ peak with "a three-centered rearrangement of sulfonate (k) to an ether (l) with the expulsion of sulfur dioxide" (Scheme VIII). Similar eliminations have been studied with sulfides, sulfoxides, and sulfones.[36]

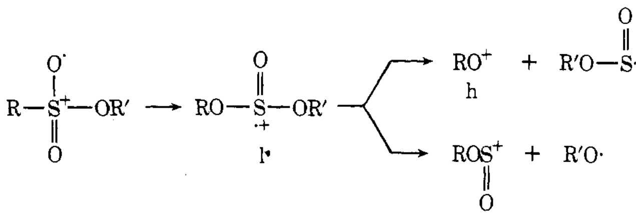
Lignin-like Sulfonates Studied. The lignin sulfonate model compounds studied are listed in Figures 2–4.

Most compounds showed molecule peaks of low abundance in agreement with the results obtained by Truce *et al.*[35] α cleavage, as indicated in Scheme II, and elimination of ketene or acetic acid from phenolic or aliphatic acetoxyl groups, were found to be major fragmentation paths of the molecules studied. All peaks exceeding 3% in relative abundance were accounted for and, in general, all mass spectra observed are consistent with those expected in consideration of the structures of the compounds studied. The presence of metastable compounds and corresponding peaks indicating a transition is marked by an asterisk.

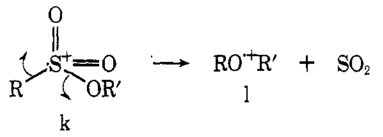
Monomers with Monosubstituted Side Chains. The monomers 1–6 exhibit similar fragmentation patterns. Only the relative abundances of the various fragments differ. α cleavage and ketene elimination predominate and give rise to the base peaks. The general fragmentation patterns are represented by Scheme IX. Neutral ketene molecules are eliminated from acetates of phenols and enols as was found earlier.[37] A rearrangement reaction has been proposed for this elimination.[38] The relative abundances of the molecule peaks and the fragments (M − CH_2CO)$^+$, (M − SO_3CH_3)$^+$, and (M − CH_2CO − SO_3CH_3)$^+$ for 1–6 are listed in Table VI.

Monomers with Disubstituted Side Chains. Aliphatic acetates and alcohols have a pronounced tendency to eliminate acetic acid or water.[38,39] This elimination may be either thermal or induced by electron impact. In the case of 1,2 elimination of acid or water, this question cannot be decided with certainty. It "may be visualized as a McLafferty rearrangement, except that the charge remains with the olefinic rather than the carbonyl-containing moiety."[39] Compound 8 eliminates acetic acid in such a rearrangement reaction (Scheme X). The ion (M − SO_3CH_3)$^+$, however does not follow this same mechanism, but rather eliminates ketene. This difference indicates the formation of a tropylium ion as intermediate, which in analogy to benzylium acetate eliminates ketene rather than acetic acid.[40] Further breakdown of this tropylium fragment (*m/e* 195), which signs as base peak, leads to a dehydrated and a demethylated derivative. The formation of the dehydrated ion at *m/e* 177 can also be explained with desulfonation of the (M − CH_3 − CO_2H)$^+$ ion in accordance with Scheme II.

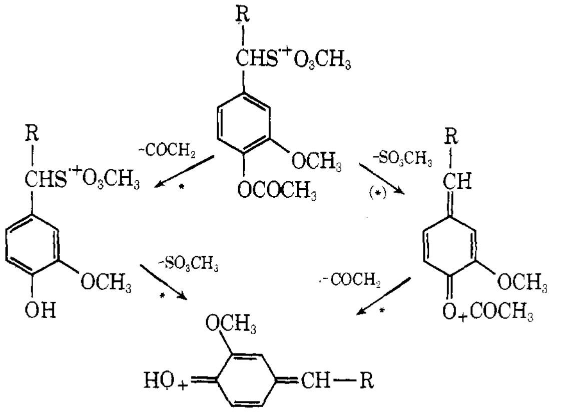
Scheme VII



Scheme VIII



Scheme IX



The disulfonate 7 exhibits a parent peak with less than 1% abundance. The fragment (M − $2SO_3CH_3$)$^+$ is recorded with 95% intensity. The base peak at *m/e* 221, however, cannot be interpreted using the usual fragmentation mechanisms. It originates from a *m/e* 316 fragment (*m/e* 221 + SO_3CH_3)$^+$ (22% abundance), as is substantiated by a metastable peak.

β-Ether Dimers. The principal fragmentation of alkyl aryl ethers is similar to alcohols and acetates. Cleavage occurs at the oxygen according to Scheme XI under formation of a phenol and an olefin, where the charge remains with the phenol,[41] or according to Scheme XII

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(36) J. Madsen, C. Nolde, S. Lawesson, G. Scholl, J. H. Bowie, and D. H. Williams, *Tetrahedron Lett.*, 4377 (1965).

(37) E. M. Emery, *Anal. Chem.*, 32, 1495 (1960).

(38) G. Spiteller, "Massenspektrometrische Strukturanalyse Organischer Verbindungen," Verlag Chemie, Weinheim/Bergstr., 1966, p 160.

(39) H. Budzikiewicz, ref 34, pp 468–471.

(40) M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, 31, 1557 (1959).

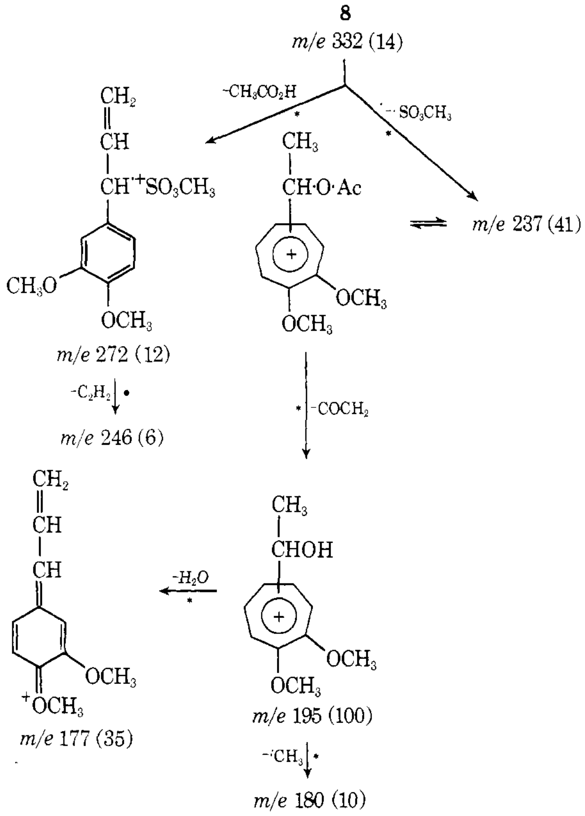
(41) H. Budzikiewicz, ref 34, p 241.

Table VI
Relative Abundances[a] in Mass Spectroscopy of Molecule Peaks and Some Typical Fragments of Lignin-like Sulfonate Monomers with Monosubstituted Side Chains

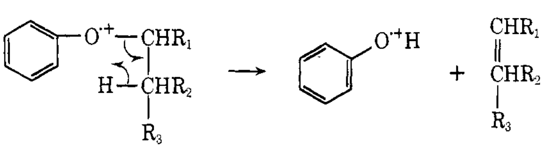
Compound	M^+	$(M-42)^+$ $(COCH_2)$	$(M-95)^+$ (SO_2OCH_3)	$(M-137)^+$ $(SO_3CH_3 + COCH_2)$
1	26	95*[b]	4	100*
2	2	3*	1	100*
3	9	12*	23	100*
4	10		100*	
5	8	6*	19*	100*
6	13	28*	3	100*

[a] In per cent of the base peak (100%). [b] An asterisk indicates the presence of a proper metastable peak for the transition.

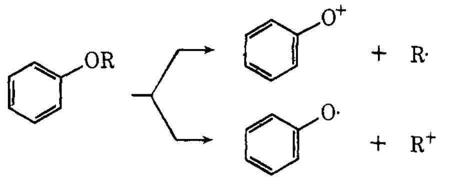
Scheme X



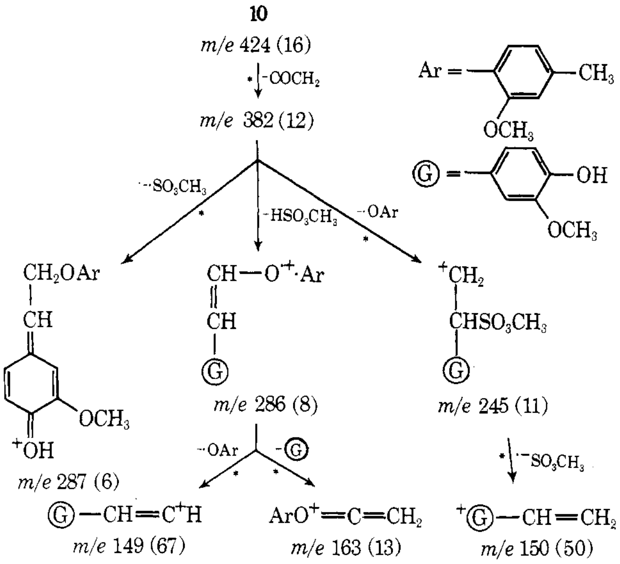
Scheme XI



Scheme XII



Scheme XIII



without hydrogen rearrangement under formation of a phenoxy ion or radical and an alkyl radical or ion. Fragments resulting from major fragmentation mechanisms of β-ethers are listed in Table VII.

Compounds **9** *and* **10**. Ketene elimination, α cleavage according to Scheme II or IV and ether bond rupture (Schemes XI or XII) are the dominant reactions occurring upon electron bombardment of the compounds of this series as outlined in Scheme XIII. The base peaks (*m/e* 138) of the spectra result from the aryl ether substituents in β position after rearranging according to Scheme XI. The second largest peaks (*m/e* 137) represent fragments originated in an ether-bond fission as outlined in Scheme XII. Fragmentation of the $(M - HSO_3CH_3 - CH_2CO)^+$ ion may proceed *via* side-chain elimination to a phenoxonium ion at *m/e* 163 as a minor alternative.

Compounds **11** *and* **12**. The methyl substituents in the β position of these compounds introduce two fragmentation pathways that occur in addition to the ones outlined in Scheme XIII for **9** and **10**. One of them is the pronounced cleavage of the C—C bond between α and β position of the sidechain, which gives rise to the base peaks at *m/e* 165 and 151 for **11** and **12**, respectively (*cf.* Scheme XIV). Sano and Sakakibara found a similar fragmentation for 1,2-bisguiacylpropane-1,3-diol.[42] The second pathway is an elimination of sulfur dioxide according to Scheme VIII, involving a three-centered rearrangement and the formation of a benzyl methyl ether. The low intensities of the respective peaks $(M - SO_2)^+$ signify the instability of the compounds formed toward electron bombardment. β-Aryl ether cleavage of these $(M - SO_2)^+$ ions helps to form oxonium ions with 21 and 15% relative abundance for **11** and **12**, respectively.

Another remarkable difference between the two groups of β-ethers (**9** and **10** *vs.* **11** and **12**) was noted in the nmr spectra of the compounds, which indicated that β-aryl ethers of phenylpropanes with sulfonate groups in α position (such as **11-14**) deshield one aromatic proton.

Compounds **13** *and* **14**. The spectra exhibited by these two compounds are very complex due to a variety of initial cleavage reactions, as outlined in Scheme XV for **13**. The common rupture of the C—S bond proceeds in accordance with Schemes II and IV and is in agreement with observations made with **9-12**. Also, elimination of SO_2 by a mechanism outlined in Scheme VIII was observed. β-

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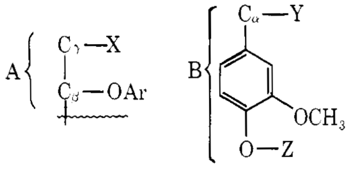
[42] Y. Sano and A. Sakakibara, *Mokuzai Gakkaishi*, **16**, 121 (1970).

Table VII
Major Fragmentation Mechanisms of β-Ethers in Mass Spectroscopy

	9	10	11	12	13	14	15	16
Acetyl elimination								
$(M - COCH_2)^+$		12*		2*	2			
$(M - CH_3CO_2H)^+$						10		
$(M - CH_3CO_2CH_3)^+$					3	7		
Sulfonate elimination								
$(M - SO_3CH_3)^+/(\sim - COCH_2)^+$	6/-	1/6*	6*/-	3*/4*	2/18	-/1	8*/-	1/-
$(M - HSO_3CH_3)^+/(\sim - COCH_2)^+$	17/-	1/8*	5*/-	1/2	-/-	-/-	-/-	5/-
$(M - SO_2)^+$			1	1	1			
Ether elimination								
$(M - OAr)^+/(\sim - COCH_2)^+$	1/-	/11*	12*/-	1/15*	18*/1	1/1	1/-	1/-
$(M - SO_3CH_3 - OAr)^+/(\sim - COCH_2)^{+a}$	15*/-	2*/67*	93*/-	3/37*	21/-	-1-	4/-	16/-
OAr	37	95	37	5	100	52	7	60
HOAr	100	100	39	25	63	29	28	20
C_α-C_β splitting[b]								
$A^b/(A-X)^+$	-/-		100*/-	100*/-	59*/16-20	1/100	1/67	6/57
$B^b/(B-Y)^+$	-/-	-/-	-/-	-/-	-/-	-/-	100*/-	100*/-
Base peak	$HOAr^+$	$HOAr^+$	Fragment A	Fragment A	^+OAr	Fragment (A-X)	Fragment B	Fragment B
Parent peak	2	16	33	31	46	1	8	64

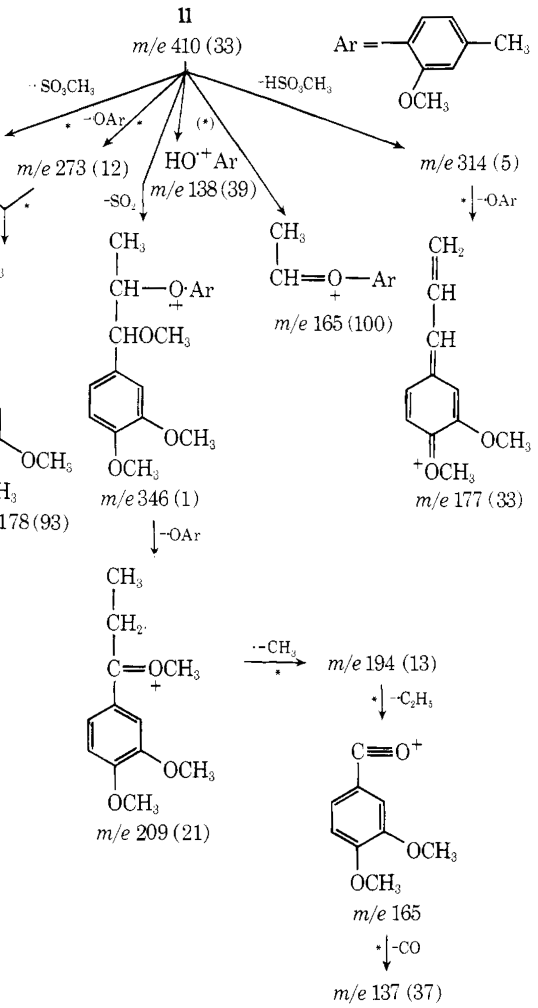
[a] With only the most abundant peak within m/e ±2 listed. [b] See adjoining column for structures A and B.



Ether cleavage follows the principles of Schemes XI and XII and raises the two most abundant peaks at m/e 137 and 138.

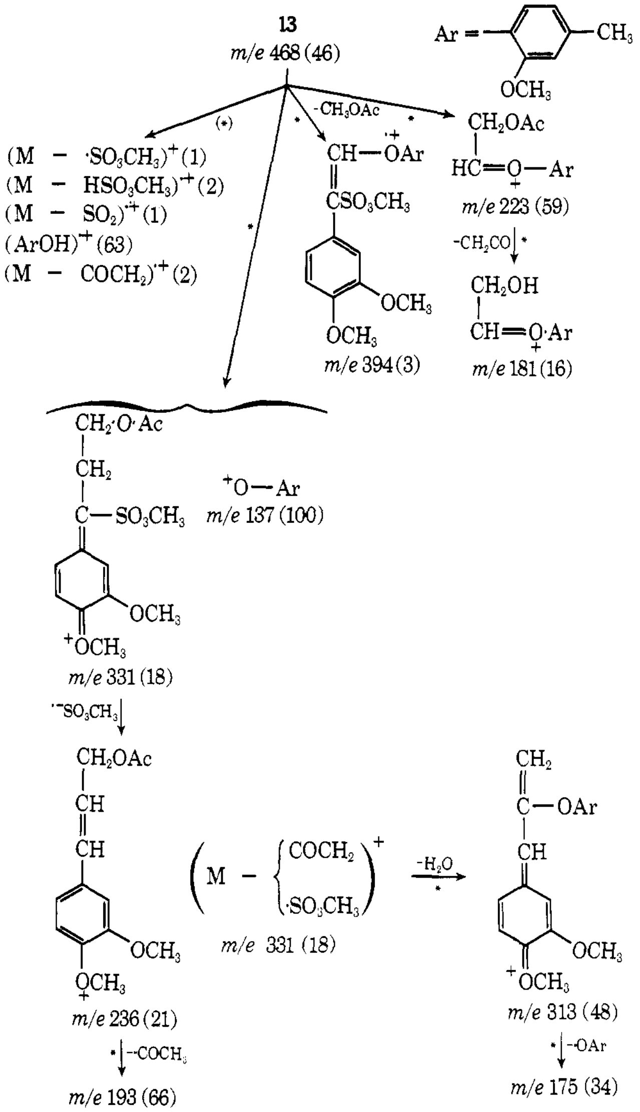
Rupture between α- and β-carbon atoms of the sidechains of compounds **13** and **14** is one of the most pronounced reactions following the electron impact in the mass spectrometer, as had already been found for **11** and **12**. This cleavage had not been observed with the phenyl ethanesulfonates **9** and **10**. Aliphatic acetoxy groups are being eliminated either as ketene, or as acetic acid (**14**), or as methyl acetate $(M - CH_3CO_2CH_3)^+$. Overall, the two compounds showed dissimilar fragmentation behavior possibly caused by a thermal instability of **14**, the spectrum of which varies with the time elapsed between injection into the ion source and recording of the spectrum.

Scheme XIV

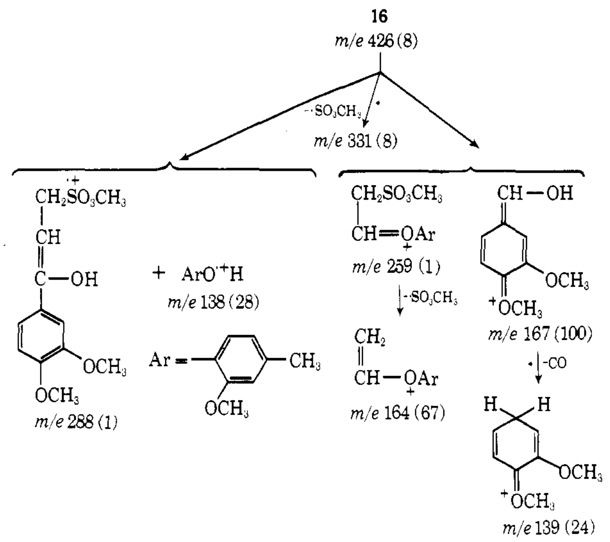


Compounds **15** *and* **16**. The spectra of these two compounds closely resemble their α-sulfonated counterparts. Like all other β-aryl ethers of phenylpropanes, fission of the C_α—C_β bond of the sidechain is relatively pronounced. In case of the γ-sulfonated models, however, the charge

Scheme XV



Scheme XVI



tends to stay with the oxygen-containing moiety (*cf.* Table VII).

The fragmentation pattern represented by **16** is indicated in Scheme XVI. It shows α cleavage and elimination of water or the β-aryl ether substituent according to Scheme XI. Most of the charge seems to remain with the eliminated β substituent which is represented by the peak at *m/e* 138. γ cleavage between α- and β-side-chain carbon atoms, which has been noted for all prior phenylpropane β-ethers gives rise to the base peak at *m/e* 165 and 167 for **15** and **16**, respectively, the corresponding fragments of which subsequently yield CO. Some charge remains with the rest of the molecules after γ cleavage, signified by the fragments at *m/e* 259. They then undergo α cleavage to form fragments at *m/e* 164.

Dimeric Model Compounds with C—C Linkages. Mass-spectroscopy of carbon—carbon linked dimeric lignin model compounds is of particular interest for structural studies of low molecular weight lignin degradation products. Dimer **17** which has been derived from sulfonation of dehydrodiisoeugenol (**14**) has the fragmentation pattern indicated in Scheme XVII.

Compound **17**. The conjugated system of the fragment $(M - HSO_3CH_3)^+$ may be the cause of predominance of elimination of the sulfonate group as a bisulfite radical after hydrogen rearrangement (Scheme IV) as compared with α cleavage (Scheme II). Elimination of two neutral ketene molecules and one bisulfite radical leads to a fragment which signs as base peak. Another ion, which yields a peak exceeding 10% relative abundance (*m/e* 193), originates from C_α—C_β bond rupture and loss of ketene from its phenolic acetoxy group. No fission between C_β and the phenyl group can be observed.

Compound **18**. Several peaks in the upper region of the spectrum are caused by fragments that have been formed from the molecular ion by losses of ketene and the sulfonate group with or without hydrogen rearrangement (Schemes II and IV) (see Scheme XVIII and Figure 8). The ion at *m/e* 367 indicates the presence of a fragment that has lost two ketene molecules and one sulfonate radical. Subsequently, the residual sulfonate group might be eliminated as bisulfite ion according to Scheme IV to form the diquinone methide ion (*m/e* 271) which appears as base peak, or as neutral fragment with 94 mass units (SO_3CH_2) which causes a peak at *m/e* 273. Both fragmentation concepts are supported by metastable peaks. The loss of the SO_3CH_2 mass unit has not yet been observed with sulfonates but can be explained with hydrogen rearrangement in a five-membered ring as indicated in Scheme XIX. Further breakdown of the ions at *m/e* 367 and 315 involves elimination of carbon monoxide, formaldehyde, and methyl radicals. A minor fragmentation pathway of the molecular ion starts with the elimination of carbon monoxide to yield an ion with 518 mass units. Similar fragmentations have been observed before with unsaturated esters.[43] Further breakdown of the $(M - CO)^+$ ion occurs in analogy to the $(M - COCH_2)^+$ ion. The spectra of both dehydrodieugenol and dehydrodivannillin reportedly show intense peaks accounting for $(m/2)^+$ ions.[23] The absence of similar fragments in the spectra of **17** and **18** is noteworthy, since arylaryl linkages and alkyl—aryl bonds seem stable against electron bombardment.

General. A number of generalizations may be suggested concerning the mass spectral elimination of acetyl, sulfo-

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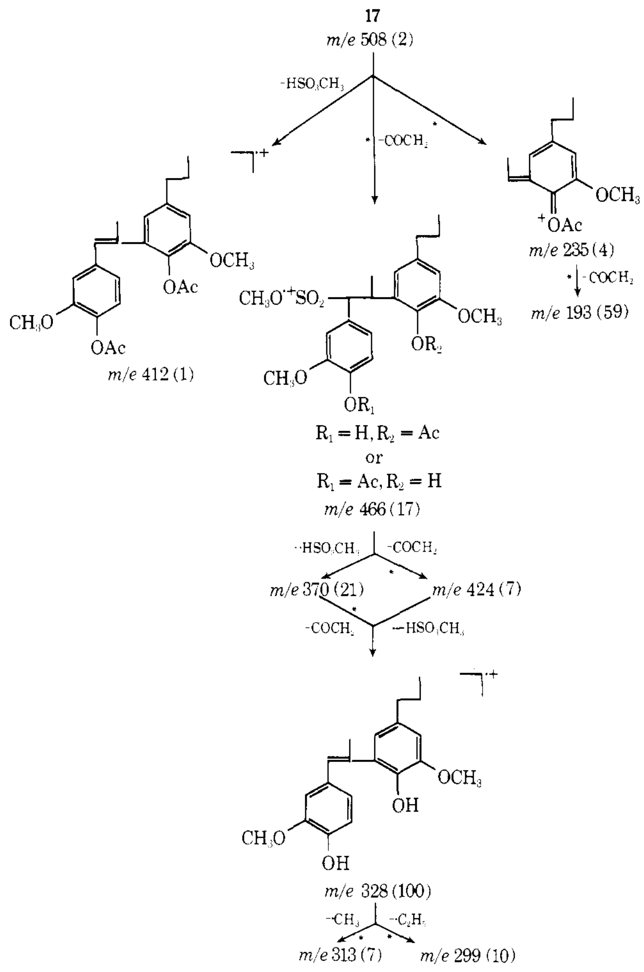
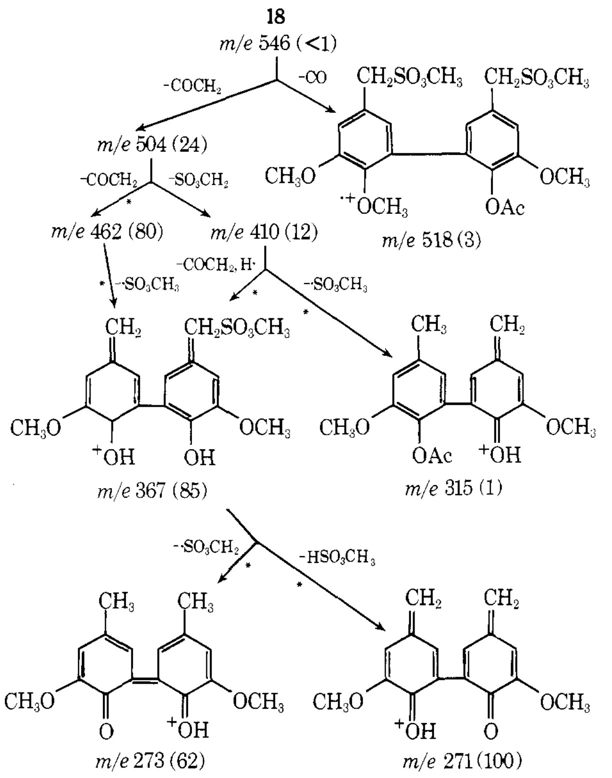
[43] J. H. Bowie, D. H. Williams, P. Madsen, G. Scholl, and S. O. Lawesson, *Tetrahedron*, **23**, 305 (1967).

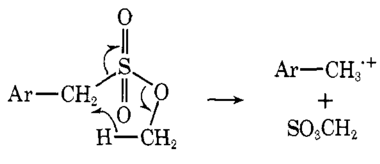
Scheme XVII



Scheme XVIII



Scheme XIX



nate, ether, and other prominent groups related to the structure and reactions of lignin sulfonates.

Monosubstituted monomers are characterized by cleavage of the C—S bond (α cleavage) and, if any phenolic acetoxy groups are present, by expulsion of ketene. Loss of both groups gives rise to the most abundant peaks in the spectra of six models studied in this category. Secondary aliphatic acetoxy groups are expelled either as acetic acid from the parent ion, or as ketene from the (M − $SO_3CH_3)^+$ ion. Primary aliphatic acetoxy groups from γ-methylol substituents of β-ethers are eliminated as ketene or methyl acetate molecules rather than as acetic acid. However, the main electron attack against β-ether compounds seems to be directed toward the aryl ether linkage. The phenol radical ion or the phenoxy ion might be liberated in such a cleavage reaction. A third possibility involves the formation of a fragment after cleavage of the α—β-carbon bond of the side chain where the charge remains partly with the aryl ether part. γ-Sulfonates like 15 and 16 might be recognized by means of this fragment. α-Cleavage and related fissions of the C—S bond seems to be widely suppressed by aryl ether eliminations. Expulsion of sulfur dioxide from the molecular ion could be observed only with 3-carbon side-chain β-ethers sulfonated in the α position. Carbon—carbon linked dimeric lignin sulfonate model compounds did not show any significant splitting into their monomeric partners. Loss of the sulfonate and acetyl groups gave rise to the most abundant peaks. Fission occurred between alkyl—alkyl bonds rather than between alkyl—aryl and aryl—aryl linkages.

It is anticipated that the results of these mass spectroscopy studies as well as the above-reported nmr spectroscopy studies, will be helpful in future studies of the structure and reactions of lignin sulfonate polymers.

Experimental Section

Detailed listings of syntheses and characterization of individual compounds has been deleted in favor of tabular compilations of their physical data and chemical shifts in spectroscopy, in Tables I and II, respectively. In Table I, yields are listed after sulfonation and after conversion of the sulfonates to acetylated and methylated derivatives. All melting points were taken on a Kofler micro-hot-plate apparatus and are uncorrected. Molecular weights were determined by mass spectroscopy (conditions as stated later). Elemental analyses were carried out by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany, where possible. In some instances, purification procedures yielded insufficient quantities for complete elemental analyses to be performed; in these cases, the elemental composition could not be obtained. Sulfonations were conducted following the standard procedure outlined later. Where this procedure was abandoned, modifications were stated in column 8 of Table I. In column 9 of the same table, reference is made to the syntheses of starting materials, as described in the literature.

Thin-Layer Chromatography. Sulfonic acid salts were separated by tlc using silica gel grade F_{254} and butanol-water (92:8) as developer. The acetylated and esterified sulfonates were separated using benzene-glacial acetic acid (5:1), benzene-ethyl acetate (1:1), or cyclohexane-ethyl acetate (1:1).

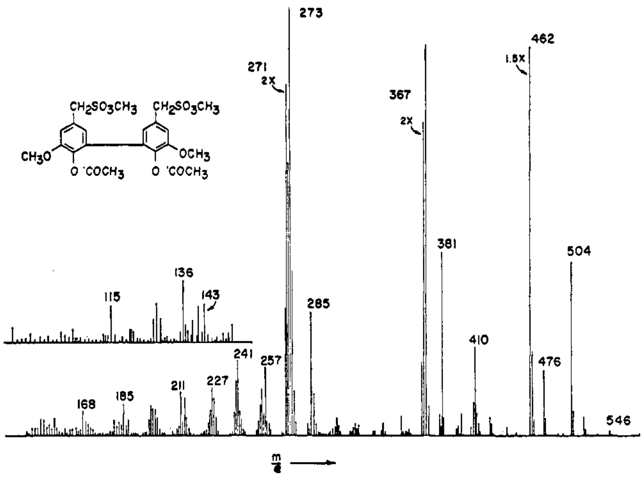


Figure 8. Mass spectrum of the dehydrodivanillylsulfonate (**18**).

Column Chromatography. Sulfonic acid esters of model compounds were separated on activated silica gel (Davison, grade 200 × 325) in benzene–ether (95:5).

Sulfonation Procedure. Unless otherwise stated, the cooking liquor was prepared by dissolving 10 g of $NaHSO_3$ in 100 ml of distilled water and adding 6 g of SO_2 to this solution. About 1.5 g of the model compound dissolved in 5–10 ml of dioxane was sealed in a 100-ml test tube together with 60 ml of cooking liquor. The mixture was kept at 105° overnight.

Working-Up Procedure. After sulfonation a stream of nitrogen was passed through the reaction mixture to remove the dissolved sulfur dioxide. Extraction with chloroform removed the unsulfonated starting material. The extracted aqueous solution was evaporated to dryness under reduced pressure and the residues were extracted with aqueous butanol (92%). The extracts were evaporated to dryness and acetylated with pyridine–acetic anhydride (1:1) (12 hr at room temperature) if OH groups were present. Then, the reaction mixture was evaporated to dryness, avoiding bath temperatures above 50°. The residues were dissolved in a few milliliters of absolute methanol, acetates were dissolved in water, eluted through a column of Dowex 50W-X8 (H^+) cation-exchange resin and neutralized with silver oxide. After filtration, these solutions were freeze-dried. The crude silver sulfonates were then methylated using an excess of methyl iodide in acetonitrile at room temperature for 24 hr. (All operations with silver lignin sulfonates present were performed in the dark.) The solutions were filtered and evaporated, and the remaining material was recrystallized.

Nuclear Magnetic Resonance Spectra. Spectra were obtained using a Varian A-60 nmr spectrometer. Samples were analyzed as 10–15% solutions in deuteriochloroform. Me_4Si was used as an internal standard.

Mass spectra were recorded on an AEI MS9 mass spectrometer with a direct inlet system, an ionization energy of 70 eV and a source temperature at 120 or 10° above the melting point of the compound studied.

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