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The Reactions of Lignin during Neutral Sulphite Cooking

Part I. The Behaviour of β-Arylether Structures

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The behaviour of structural elements of the β-arylether type towards neutral sulphite solutions under the conditions of neutral sulphite cooking has been studied using appropriate model compounds. It has been found that the main reactions involved are:

1) Cleavage of the β-arylether bond in phenolic phenylpropane units with formation of the corresponding styrene-ω-sulphonic acid structures and
2) Cleavage of methylether bonds in phenolic and non-phenolic phenylpropane units with formation of methane sulphonic acid.

In comparative experiments using acidic sulphite solutions no appreciable arylether cleavage reactions have been observed, sulphonation in the α-position being the dominant reaction.

The results are discussed with reference to known features of neutral sulphite pulping.

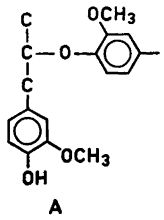
During the past two to three decades neutral sulphite cooking has become an important pulping process. Its main feature is a limited delignification leading to high-yield pulps of varying brightness. The observed discolorations, characteristic of neutral sulphite pulps, are mainly attributed to specific chromophoric systems formed in the lignin by the action of neutral sulphite. Successful removal of these chromophores by lignin-removing or lignin-retaining bleaching requires a detailed knowledge of their chemical nature and their mode of formation. Furthermore, accurate information concerning the reactions involved in the partial delignification may be of great importance for process control.

The present series of papers concerns investigations into the reactions of lignin during neutral sulphite cooking with particular reference to those which form chromophoric systems. Part I deals with the structural changes which may occur in β-arylether structures under process conditions. Model compounds representing β-arylether moieties in lignin were treated with neutral sulphite solutions (pH 7) at 180° for 3 h. The resulting mixtures were

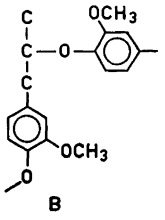
separated into water-soluble and chloroform-soluble fractions, the main components of which were isolated and identified. Concurrently, some of the model compounds were treated with acidic sulphite solutions (pH 1.5) at 135° for 7 h and the results compared with those from the corresponding treatments with neutral sulphite solutions.

RESULTS

Structural elements of the β-arylether type may be present both in phenolic (A) and non-phenolic (B) lignin units. As model compounds representing these lignin structures the β-guaiacylethers of α-(4-hydroxy-3-methoxyphenyl)-glycerol (I)[1,2] and of α-(3,4-dimethoxyphenyl)-glycerol (II)[3] were chosen.



A



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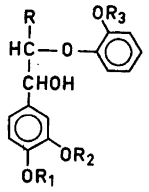


I	$R=CH_2OH$, $R_1=H$, $R_2=R_3=CH_3$
II	$R=CH_2OH$, $R_1=R_2=R_3=CH_3$
III	$R=R_1=H$, $R_2=R_3=CH_3$
IV	$R=H$, $R_1=R_2=R_3=CH_3$
V	$R=H$, $R_1=R_2=CH_3$, $R_3=H$
VI	$R=H$, $R_1=CH_3$, $R_2=H$, $R_3=CH_3$
VII	$R=CH_2OH$, $R_1=R_2=CH_3$, $R_3=H$
VIII	$R=CH_2OH$, $R_1=CH_3$, $R_2=H$, $R_3=CH_3$
IX	$R=CH_2OH$, $R_1=CH_3$, $R_2=R_3=H$

Since the hydroxymethyl group in type A was, to a large extent, split off (see below), the behaviour of the phenolic structural variant (A) was also studied using compound III.[4] In order to elucidate the influence of the *p*-hydroxyphenyl and *p*-methoxyphenyl substituents on the cleavage of the guaiacylether bond, the neutral sulphite treatment was also carried out with the guaiacyl-glycerylethers XII and XIV[5] as reference compounds. The results of these model studies are summarised in Table 1.

Table 1. Products after treatments with neutral and acidic sulphite solutions.

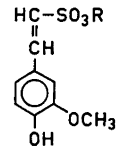
Compound	Products after treatment with *neutral* sulphite solution		Approximate degree of splitting of the guaiacylether bond by neutral sulphite solution	Products after treatment with *acidic* sulphite solution	
	chloroform-soluble fraction	water-soluble fraction		chloroform-soluble fraction	water-soluble fraction
a) phenolic					
I	guaiacol, pyrocatechol, demethylation products of I (traces)	methane sulphonic acid styrene sulphonic acid (X) unidentified sulphonic acid (small amount)	80 % [a]	guaiacol (traces) polymeric material	α-sulphonic acid
III	guaiacol, pyrocatechol, demethylation products of III (traces)	methane sulphonic acid styrene sulphonic acid (X)	80 % [a]	guaiacol (traces) polymeric material	α-sulphonic acid (30 %)
b) non-phenolic					
II	guaiacol, pyrocatechol, VII, VIII, IX, starting material	methane sulphonic acid, styrene sulphonic acid (X),[c] and unidentified sulphonic acid (small amounts)	13 % [b]	guaiacol (traces) starting material unidentified compound (traces)	α-sulphonic acid
IV	guaiacol, pyrocatechol, V, VI, starting material	methane sulphonic acid, styrene sulphonic acid (X) [c], (small amount)	13 % [b]	guaiacol (traces) starting material unidentified compound (traces)	α-sulphonic acid (42 %)
XII	guaiacol, pyrocatechol (traces), XIII, starting material	methane sulphonic acid	6 % [b]	guaiacol (traces) starting material	starting material
XIV	guaiacol, pyrocatechol (traces), XV, starting material	methane sulphonic acid	6 % [b]		

[a] calc. from the amount of crude Ba-salt of styrene sulphonic acid X. [b] calc. from the amount of isolated guaiacol and pyrocatechol. [c] identified only by paper- and thin-layer chromatography.

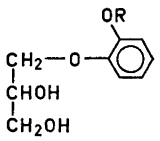
Treatment with neutral sulphite

a) *Phenolic β-arylethers (A).* Treatment of compound I or III with neutral sulphite under the conditions mentioned above resulted in extensive cleavage of the β-arylether bond. The chloroform-soluble fractions of the reaction products contained guaiacol, pyrocatechol, and small amounts of further phenolic components, probably demethylation products of the starting materials (*cf.* the behaviour of compounds II and IV, see below).

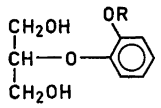
The main reaction product, *trans*-4-hydroxy-3-methoxy-styrene-ω-sulphonic acid (X), was obtained from the water-soluble fractions and isolated as its methylester (XI). The structure and configuration of the ester were assigned on the basis of elemental analysis and NMR spectrum (see experimental section). In addition to the styrene sulphonic acid X, the water-soluble fractions from the neutral sulphite treatments of the compounds I and III contained methane sulphonic acid as a major component. This acid was isolated and characterised as its *p*-bromophenacylester by analysis, melting point and NMR spectrum.* Furthermore, compound I yielded a small amount of an unidentified sulphonic acid.



X R = H
XI R = CH3



XII R = CH3
XIII R = H



XIV R = CH3
XV R = H

b) *Non-phenolic β-arylethers (B).* The chloroform-soluble fractions of the products from neutral sulphite treatment of the non-phenolic model compounds II, IV, XII, and XIV contained guaiacol, small amounts of pyrocatechol, and the respective demethylation products V—IX, XIII, and XV. The latter were characterised as their acetates by analyses, NMR spectra, and alkaline cleavage.

The water-soluble fractions contained considerable amounts of methane sulphonic acid. In addition to methane sulphonic acid, compounds II and IV afforded small amounts of the styrene sulphonic acid X. Compound II also yielded traces of a further unidentified acid. No appreciable amounts of 3,4-dimethoxy-styrene-ω-sulphonic acid (X, OCH_3 instead of OH) could be detected.

Obviously, styrene-ω-sulphonic acid X is only formed from phenolic β-arylether structures represented by the compounds I and III. The small amounts obtained from the compounds II and IV probably arise through partial demethylation of the methoxyl groups *para* to the side chains (conversion of non-phenolic into phenolic β-arylether structures). This limitation

* Methane sulphonic acid had been isolated previously after treatment of methyl β-D-glucopyranoside with neutral sulphite but was erroneously considered to be propane-2,2-disulphonic acid.[5] A reinvestigation revealed, however, that it was identical with our sulphonation product.[6]

indicates that the free phenolic hydroxyl groups (*e.g.* in I and III) play an important role in the cleavage of the β-arylether bond to form styrene-ω-sulphonic acid structures (*e.g.* X).

Treatment with acidic sulphite

For the sake of comparison, compounds I—IV were also treated with acidic sulphite solutions of pH 1.5 at 135° for 7 h. Under these conditions the dominant reaction was found to be sulphonation in α-position to yield the corresponding benzyl sulphonic acids in agreement with the results of previously reported model studies.[3,8] Two of these benzyl sulphonic acids (from compounds III and IV) were isolated and characterised as their methylesters by elemental analyses and from NMR spectra (see experimental section). In addition to α-sulphonation, the phenolic β-arylethers I and III underwent extensive condensation reactions yielding high molecular weight materials. No styrene-ω-sulphonic acids were formed and the cleavage of β-arylether bonds was found to be negligible. Furthermore, no splitting of the methylether bonds to form methane sulphonic acid was observed.

DISCUSSION

The results of the present model studies show that at least two types of arylether cleavage reactions may take place, when lignin is treated with neutral sulphite solutions.

The first type is the extensive cleavage of β-arylether linkages with the formation of styrene-ω-sulphonic acid structures. It may be assumed that this cleavage starts at originally present phenolic phenylpropane units and continues as long as the unit containing the liberated phenolic hydroxyl group, in its turn, carries a β-arylether bond. Thus, under the conditions of neutral sulphite pulping, a comprehensive degradation of lignin should occur, which is contrary to what is observed in practice. However, this discrepancy can be accounted for by the supposition that the degradation of lignin due to the cleavage of β arylether linkages is counterbalanced, at least partly, by the immediate polymerisation of the resulting styrene-ω-sulphonic acid structures. As a net result, the number of aryl-alkylether bonds in lignin, after treatment with neutral sulphite solutions, should be lower, and the number of carbon-carbon linkages higher, than before the treatment, rendering the lignin more resistant to the conditions of continued neutral sulphite pulping. This could explain the fact that delignification during neutral sulphite cooking only proceeds to a certain stage (about 50—60 %), provided the pH-value of the cooking liquor is kept constant.[9]

The second type of arylether splitting reaction concerns the cleavage of methylether linkages (*cf.* Ref. 10) with the formation of methane sulphonic acid. This type is operative both in phenolic and non-phenolic phenylpropane units.

As a consequence of these splitting reactions a considerable increase in phenolic hydroxyl groups in the resulting lignin may be expected. If both types of ether splitting reactions attack one and the same aromatic nucleus

in lignin, pyrocatechol groupings will be formed. It is known that these groupings are susceptible to oxidation giving rise to *o*-quinoid structures and their polymerisation products. The latter may constitute important chromophoric components in high-yield pulps.[10] In particular, *o*-quinoid groups in styrene structures, formed by demethylation of 4-hydroxy-3-methoxystyrene-ω-sulphonic acid structures (*cf.* compound X) followed by oxidation, as well as their various possible Diels-Alder adducts and polymerisation products could be considered as potential chromophoric systems.

A comparison between the behaviour of β-arylether structures towards neutral and acidic sulphite solutions reveals that the cleavage of β-arylether bonds with the formation of styrene-ω-sulphonic acid structures, and the splitting of methylether bonds yielding methane sulphonic acid, constitute characteristic features of *neutral* sulphite cooking.

Work on the elucidation of the mechanisms of these ether cleavage reactions is in progress. The possible role of styrene structures as a source of chromophoric systems in high-yield pulps will be the subject of further studies.

EXPERIMENTAL

All melting points are corrected. Evaporations were carried out under reduced pressure.

Paper chromatography. The composition of the aqueous solutions of sulphonic acids was investigated by paper chromatography using Whatman No. 3 paper, a mixture of ethanol-conc. ammonia-water (12:1:3) as solvent and bromophenol blue as spray reagent.

Thin-layer chromatography. Sulphonic acid esters and other chloroform-soluble compounds were separated on both analytical and preparative scale by thin-layer chromatography using silica gel HF_{254} and chloroform or a mixture of chloroform and ethanol (9:1) as solvent systems. Iodine vapour was used as developer unless otherwise stated.

NMR-spectroscopy. The NMR-spectra were obtained on a Varian A-60 spectrometer. Deutero-chloroform was used as solvent and tetramethylsilane as internal reference throughout.

Model compounds. All model compounds were prepared and purified as previously described.[1-5]

Cooking liquors. Neutral sulphite solution: $Na_2S_2O_5$ (0.25 moles) in distilled water (1 l) adjusted to pH 7 with 2 N NaOH. *Acidic sulphite solution:* SO_2 in distilled water (total SO_2 content 6.23 %) adjusted to pH 1.5 with 2 N NaOH.

Cooking conditions

Neutral sulphite treatments. The model compound (2 g) dissolved or suspended in the neutral sulphite solution (80 ml) was heated in an autoclave of stainless steel at 180° for 3 h. To improve solubility, non-phenolic model compounds were treated with a solution of $NaHSO_3$ in water containing 15 % dioxane.

Acidic sulphite treatments. The model compound (2 g) was treated with acidic sulphite solution (80 ml) at 135° for 7 h.

Working-up procedure

After evaporation of the dioxane, if present, the solutions were extracted with chloroform to remove phenolic products of the cleavage reactions and, in some cases, the unreacted portion of the starting material. The components of the chloroform extract were separated by preparative thin-layer chromatography and identified, in some instances after acetylation, by elemental analyses and NMR-spectra.

The aqueous solutions were passed through a column of Dowex 50W—X8 cation exchange resin (in the H^+ form) and concentrated to about 100 ml. After saturation with nitrogen (to remove SO_2), the solutions were first investigated by paper chromatography and then neutralised with barium hydroxide. The precipitates of barium sulphate were filtered off and the filtrates evaporated to dryness. The residues consisted of barium sulphonates and small amounts of water-soluble phenols, (particularly pyrocatechol and guaiacol). The latter were removed by extraction with chloroform. The sulphonic acids were liberated by cation exchange and neutralised with an excess of silver oxide. After filtration, the aqueous solutions were evaporated and the residues dried *in vacuo*. Portions of these crude mixtures of silver sulphonates were then converted into methyl esters by treatment with an excess of methyl iodide in acetonitrile at room temperature for 24 h.[11] Further samples of the silver sulphonate mixtures were heated with *p*-bromophenacylbromide on a steam bath for 2 h in order to isolate and characterise the methane sulphonic acid formed as its *p*-bromo-phenacylester.

The reaction mixtures from the acidic sulphite treatments of compounds I—IV and XII were worked up as described previously.[3,8]

The results of the treatments with neutral and acidic sulphite solutions are summarised in Table 1.

Products from neutral sulphite treatments

Methane sulphonic acid-p-*bromo-phenacylester* was obtained from the water-soluble fractions after treatment of the compounds I—IV, XII, and XIV as described above and recrystallised from ethanol; m.p. 124—125° (lit. 118—119°).[12] (Found: C 36.87; H 3.12; O 21.66; S 10.75; Br 27.50. Calc. for $C_9H_9O_4SBr$: C 36.88; H 3.07; O 21.84; S 10.94; Br 27.27). The NMR spectrum shows a singlet (3H) at 3.28 ppm, another singlet (2H) at 5.50 ppm and an unresolved doublet (4H) at 7.79 ppm. These signals are attributable to the methyl-, methylene- and aromatic protons, respectively.

trans-*4-Hydroxy-3-methoxy-styrene-ω-sulphonic acid methylester* (*XI*) was isolated after treatment of compounds I and III as described above. (Found: C 49.20; H 5.20; O 32.47; S 12.95; OCH_3 26.09. $C_{10}H_{12}O_5S$ requires: C 49.19; H 4.92; O 32.76; S 13.13; OCH_3 25.40). In the NMR spectrum the olefinic protons exhibit two doublets ($J_{trans}=15$ cps) centered on 7.53 and 6.55 ppm. The aromatic protons give an unresolved multiplet (3H) around 6.98 ppm, the protons of the sulphonic ester methoxyl and the ether methoxyl show resonance at 3.96 ppm (3H) and at 3.85 ppm (3H), respectively.

The small amounts of compound XI obtained from the compounds II and IV were identified by comparison of thin-layer chromatograms of the sulphonic acid methylester mixtures with the chromatogram of compound XI isolated from the reaction mixture obtained by neutral sulphite treatment of compound III.

1-O-(*2-Hydroxyphenyl*)-*glycerol* (*XIII*) and 2-O-(*2-hydroxyphenyl*)-*glycerol* (*XV*) were isolated from the chloroform extracts of the products from the guaiacyl-glycerylethers XII and XIV, respectively, and purified by thin-layer chromatography. Compound XIII crystallised on standing and after recrystallisation from benzene yielded colourless needles melting at 82—84° (lit. 87—88°).[13] (Found: C 58.81; H 6.51; O 34.86. Calc. for $C_9H_{12}O_4$: C 58.71; H 6.52; O 34.77). Compound XV was acetylated with acetic anhydride in pyridine and identified as its triacetate by elemental analysis (Found: C 57.88; H 5.81; O 36.39. $C_{15}H_{18}O_7$ requires: C 58.08; H 5.80; O 36.11) and NMR spectrum (see Table 2).

1-(*3-Acetoxy-4-methoxy*)-*1*-O-*acetyl-2*-O-(*2-methoxyphenyl*)-*ethylene-glycol* (diacetate of V) and 2-O-(*2-Acetoxyphenyl*)-*1*-O-*acetyl-1*-(*3,4-dimethoxyphenyl*)-*ethyleneglycol* (diacetate of VI). The chloroform-soluble fraction of the products from compound IV contained two demethylated compounds which were separated from the other components (guaiacol, pyrocatechol, and starting material) by preparative thin-layer chromatography. Acetylation with acetic anhydride in pyridine gave a mixture of these two diacetates in a proportion of about 1:2. This mixture was characterised by elemental analysis (Found: C 63.87; H 6.01; O 30.12. $C_{20}H_{22}O_7$ requires: C 64.19; H 5.88; O 29.93), NMR-spectrum (see Table 2) and alkaline hydrolysis [14] yielding guaiacol and pyrocatechol in a proportion of roughly 1:2 (thin-layer chromatography).

2-O-(*2-Acetoxyphenyl*)*1,3-di*-O-*acetyl-1*-(*3,4-dimethoxyphenyl*)-*glycerol* (triacetate of VII), *1*-(*3-acetoxy-4-methoxyphenyl*)-*1,3-di*-O-*acetyl-2*-O-(*2-methoxyphenyl*)-*glycerol* (tri-

Table 2. Proton chemical shifts (δ-values in ppm) of isolated acetates.[a]

Compound	OAc				OMe			aliphatic H		
	aliphatic		aromatic							
	1-OAc	3-OAc	2-OAc	3-OAc	2-OMe	3-OMe	4-OMe	1-H	2-H	3-H
Triacetate of compound XV	2.05	2.05	2.27	—	—	—	—	4.80—4.00 ^{m}+		
Mixture of diacetates of compounds V and VI	2.07 2.13	— —	2.25	2.28	3.85	3.88	3.80	6.10	4.20	—
Triacetate of compound VII	2.12	2.00	2.18	—	—	3.87	3.87	6.00^{d}	4.85—4.00^{m}+	
Triacetate of compound VIII	2.07	2.02	—	2.30	3.80 3.82	—	3.80 3.82	6.00^{d}	4.80—3.95^{m}+	
Tetraacetate of compound IX	2.07	1.98	2.23	2.30	—	—	3.80	6.00^{d}	4.90—3.95^{m}+	

[a] The integrated curves were all in agreement with the number of protons exhibiting the respective signals. The aromatic protons gave unresolved multiplets at 7.20—6.60 ppm. d=doublet, m=multiplet, +=unresolved,

acetate of VIII), and *1-(3-acetoxy-4-methoxyphenyl)-2-O-(2-acetoxyphenyl)-1,3-di-O-acetylglycerol* (tetraacetate of IX). Similarly, these compounds were isolated from the chloroform-soluble fraction after neutral sulphite treatment of compound II, by means of preparative thin-layer chromatography (solvents: chloroform-acetone 9:1 and chloroform-ethanol 19:1) followed by acetylation and chromatographic separation of the resulting acetates (solvent: benzene-ethyl acetate 17:3, 3 times). The structural assignments are based on elemental analyses (see below), the NMR-spectra (see Table 2) and the results of the alkaline hydrolyses [14] which produced pyrocatechol from the acetates of compounds VII and IX and guaiacol from the triacetate of compound VIII.

Elemental analyses. Triacetate of VII: Found: C 62.26; H 5.90; O 31.75. $C_{23}H_{26}O_9$ requires: C 61.90; H 5.83; O 32.27. Triacetate of VIII: Found: C 61.99; H 5.83; O 31.88. $C_{23}H_{26}O_9$ requires: C 61.90; H 5.83; O 32.27. Tetraacetate of IX: Found: C 61.14; H 5.94; O 32.76. $C_{24}H_{26}O_{10}$ requires: C 60.78; H 5.48; O 33.74. The amount of compound IX available did not allow any further purification.

Products from acidic sulphite treatments

The barium salts of the α-sulphonic acids formed from the compounds III and IV on treatment with acidic sulphite were converted into the sulphonic acid methylesters as described for styrene-ω-sulphonic acid X (see above). The barium salt of the sulphonic acid from compound III was acetylated with acetic anhydride in pyridine before esterification.

1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxy-phenoxy)-ethane-1-sulphonic acid methylester crystallised as colourless needles from ethanol; m.p. 92–95°. (Found: C 55.87; H 5.64; O 31.01; S 7.78. $C_{19}H_{22}O_8S$ requires: C 55.62; H 5.38; O 31.20; S 7.81). The NMR spectrum shows three singlets at 2.27 ppm (3H), at 3.73 ppm (3H) and at 3.78 ppm (6H), probably attributable to the protons of the acetyl-, sulphonic ester methoxyl- and ether methoxyl groups, respectively. The aliphatic protons and the aromatic protons exhibit unresolved multiplets around 4.72 ppm (3H) and 6.97 ppm (7H), respectively.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-phenoxy)-ethane-1-sulphonic acid methylester, isolated as colourless needles and recrystallised from carbon tetrachloride-hexane, melted at 83–84°. (Found: C 56.41; H 5.77; O 29.29; S 8.24. $C_{18}H_{22}O_7S$ requires: C 56.55; H 5.75; O 29.31; S 8.39). The NMR spectrum is very similar to that of the sulphonic acid methylester acetate obtained from compound III (see above), except that the singlet produced by the acetyl protons is missing and an additional singlet appears in the region of 3.80 ppm (3H), due to the protons of the third aromatic methoxyl group.

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