

The Reactions of Lignin during Sulphate Pulping

Part XIII.* Reactions of Episulphide Structures with Alkali and with White Liquor** under Pulping Conditions

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Episulphide I, an intermediate in the cleavage of phenolic β -aryl ether structures by white liquor, was subjected to the conditions of alkali and sulphate pulping. Plausible formation pathways have been outlined for the low-molecular reaction products which were separated and identified (see Schemes 1 and 2). Experimental support for the validity of the schemes was provided by treating several of the proposed intermediates in a similar way and isolating identical reaction products. The reactions of compound I are illustrative of the final degradation steps of β -aryl ether structures leading to monomeric and polymeric phenolic products with concomitant partial elimination of sulphur.

On treatment with white liquor, milled wood lignin afforded the same monomeric phenolic degradation products as did episulphide I. This result lends further support for the presence of β -aryl ether structures in lignin and their mode of reaction during sulphate pulping as suggested in previous communications of this series.

In previous communications of this series^{1,2} the mechanism of cleavage of β -aryl ether linkages in phenolic phenylpropane units of lignin during sulphate pulping has been described. It has been shown by model experiments that the reaction proceeds *via* methylene quinone, benzylthiol, and episulphide structures and yields mixtures of phenolic degradation products which have not yet been characterised. The sulphur incorporated during the initial step

* Part XII, see Gierer, J., Pettersson, I. and Smedman, L.-Å. *Acta Chem. Scand.* **26** (1972) 3366.

** The term "white liquor" refers to a solution of NaOH (3.5 g) and Na₂S·9H₂O (3.1 g) in water (100 ml).

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of the reaction sequence (formation of benzylthiol structures) is to a large extent eliminated subsequent to episulphide formation.¹⁻³

When model compounds representing episulphide structures (*e.g.* I, see Scheme 1), or their precursors, benzylthiol structures, are treated with 2 N alkali at temperatures between 20 and 100°, *p*-dithianes (*e.g.* III) are formed as final products.^{1,2} It is probable that the episulphide ring is opened between the α -carbon atom and the sulphur atom, giving rise to β -mercaptomethylene quinone structures (*e.g.* II) which spontaneously dimerise.^{1,2} *p*-Dithianes are also obtained in good yields, when model compounds of the α -hydroxy- β -thiol type (*e.g.* XIX, see Scheme 2) are treated in the same manner.¹ However, if the treatment with alkali or white liquor is carried out at higher temperatures (about 140° or above), the episulphide, as well as the hydroxythiol and dithiane structures, are converted into mixtures of phenolic products with loss of most of the sulphur.¹⁻³

During sulphate pulping "uncondensed"⁴ phenolic units of the β -aryl ether type^{5,6} should form episulphide I as an intermediate.^{1,3} Therefore, this compound (in the form of its diacetate) was chosen as starting material in the present study for an investigation of the reactions involving the elimination of sulphur and the subsequent fragmentation to lower molecular weight products. Treatment of this compound with 2 N sodium hydroxide or white liquor at 180° for 2 h gave mixtures of phenolic products which were acetylated or methylated and separated by thin-layer, column and/or gas chromatographic methods. The main components of the monomeric fraction were identified by comparison with authentic samples (chromatographic behaviour, and mass spectral fragmentation patterns). The degradation products from both milled wood lignin and from some of the proposed intermediates (designated by asterisks in Schemes 1 and 2) were separated and identified in essentially the same manner.

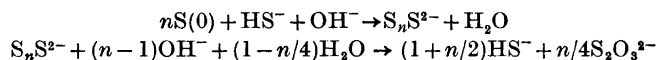
RESULTS AND DISCUSSION

In Schemes 1 and 2 the low-molecular weight products formed from compound I are summarised and plausible routes of their formation are tentatively outlined. As is the case for the dimerisation² of episulphide I, the processes of sulphur elimination and fragmentation should be preceded by an alkali-promoted opening of the thiirane ring giving rise to the reactive intermediate II, a β -mercaptomethylene quinone.³ At pulping temperature (180°), the latter may undergo two types of elimination as depicted in Schemes 1 and 2, both yielding conjugated intermediates (styrene derivatives).

In the *first type* of these eliminations (see Scheme 1) elemental sulphur is split off³ from episulphide (I) giving rise to coniferyl alcohol (IV). The predominant formation of coniferyl alcohol has been demonstrated (TLC) by mild alkaline treatment of the episulphide at 90°. Extensive desulphurisation of episulphide I in the form of the diacetate was also achieved in the absence of alkali or any other solvent by simply heating a sample to 90° for 4 h. In this instance the diacetate of coniferyl alcohol formed was isolated in a high yield and identified. The fact that aromatic derivatives of thiiranes readily

part with their sulphur to yield the corresponding substituted styrenes is well documented both in early and recent literature.^{7,8} The loss of sulphur was also observed during the preparation and purification of epithio compounds described in Part X of this series.²

The facile elimination of sulphur from the episulphide or from the β -mercaptomethylene quinone II may be regarded as a disproportionation, where the organic part is reduced to the olefin, and the inorganic part, sulphur, is oxidised from the $-II$ to the O -oxidation state. An attempt was therefore made to establish the elimination of elemental sulphur by heating appropriate model compounds with alkali or white liquor in the presence of metallic copper with exclusion of air. Activated copper and other activated metals (iron, zinc, nickel) are known to trap elemental sulphur.^{9,10} and, thus, the sulphur is prevented from reacting according to the scheme



with the formation of sulphide and thiosulphate ions.¹¹ The cupric sulphide formed was decomposed with hydrochloric acid and the liberated hydrogen sulphide estimated titrimetrically.¹² In separate runs it was established by GLC and TLC analyses of the resulting reaction mixtures that the presence of copper in the samples did not influence the process of sulphur elimination and the subsequent fragmentations (see below) to any noticeable degree.

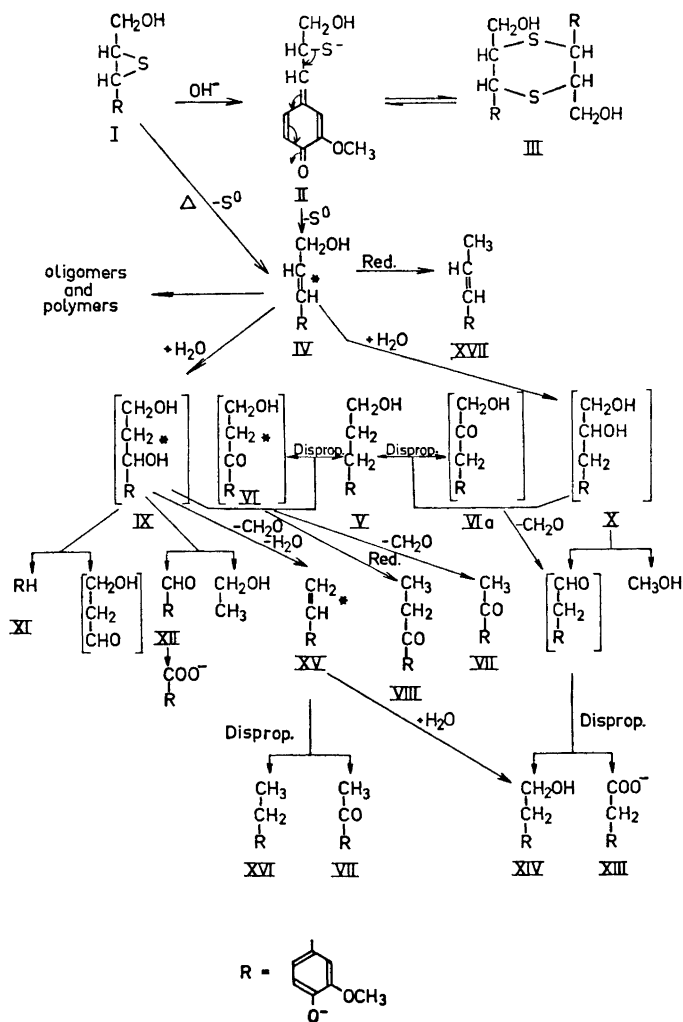
Table 1.

Compound	Yield S ⁰ (%)
α -Thioglycerol	13
α, β -Dithioglycerol	1 ^a
α, γ -Dithioglycerol	17
Tetraacetate of dithiane (III)	80
Diacetate of dithiane (III, CH ₃ replacing CH ₂ OH)	88
Triacetate of hydroxythiol XIX	87
Diacetate of episulphide I	99 ^a

^a Determined with the improved method (see experimental section).

In Table 1 the yields of elemental sulphur eliminated from several appropriate model and reference compounds are given. The figures are mean values from at least two different runs with either 2 N sodium hydroxide or white liquor. Corresponding blanks were run with the respective cooking liquor omitting the model compound. Due to incomplete exclusion of oxygen which causes the formation of copper sulphide from S($-II$), the reproducibility of the results was poor. However, much better values were obtained when the reaction was performed at lower temperature and in the presence of pyrogallol to absorb the small amount of oxygen present. From the values in Table 1 it may be concluded that the majority of the sulphur present in intermediate I, as well as in the dimerisation products (dithianes), is eliminated in elemental form, whereas the reference compounds only loose quantities hardly exceeding the limits of error of the determination methods.

Recently, evidence for the elimination of elemental sulphur from intermediates of the β -thiol^{13,14} and benzyl thiol¹⁵ types during treatment with alkali has been provided. The desulphurisation was followed indirectly by measuring the changes in thiol and sulphide concentrations by potentiometric titration.¹⁴ The reaction has been interpreted¹³⁻¹⁵ in terms of an intramolecular redox reaction of the previously^{1,2} suggested methylene quinone intermediates. In the present work another type of model compound (episulphide) and a direct method of determination of eliminated elemental sulphur was used. In spite of these differences, the results obtained in this study concerning sulphur elimination are in good agreement with those recently published.



Scheme 1.

After the removal of sulphur from episulphide I, the resulting coniferyl alcohol exhibits various reactions under the strongly alkaline conditions of alkali and sulphate pulping which are tentatively interpreted as follows (see Scheme 1): About two thirds of this intermediate polymerise and the remaining third adds the elements of water giving rise to the α,γ - and β,γ -diols IX and X, respectively. Parts of these diols undergo disproportionation, diol IX yielding dihydroconiferylalcohol (V) and hydroxyconiferylalcohol (β -ketol) VI and diol X affording V and the α -ketol VIa. Other parts of the diols IX and X undergo alkaline cleavage of carbon-carbon bonds^{16,17} yielding phenolic fragments of the C₆, C₆-C₁ and C₆-C₂ types. These include guaiacol (XI), vanillin (XII) and vanillic acid, vinylguaiacol (XV) and its disproportionation products 4-ethylguaiacol (XVI) and acetoguaiacone (VII), and the disproportionation products of homovanillin, homovanillic acid (XIII) and 2-(4-hydroxy-3-methoxyphenyl)-ethanol (XIV). Acetoguaiacone (VII) and homovanillin may also arise by elimination of formaldehyde from the ketols VI and VIa, respectively. In the presence of sulphide ions small amounts of ketol VI and of coniferylalcohol (IV) are reduced to propioguaiacone (VIII) and isoeugenol (XVII), respectively.

In addition to the previously mentioned phenolic reaction products the aliphatic fragments methanol and ethanol were obtained after treatment of episulphide I with alkali or white liquor at 180°.

Compounds V, VII, VIII and XI-XVII, as well as methanol and ethanol, were also obtained after appropriate treatment of coniferyl alcohol (IV). This result, together with the formation of IV after mild alkali or heat treatment of episulphide I, strongly strengthens the view that structures of the coniferyl alcohol type constitute important intermediates in the conversion of episulphide structures into low- and high-molecular sulphur-free products during sulphate pulping (see Scheme 1) (*cf.* also Ref. 15).

Further experimental support for the validity of Scheme 1 was provided by subjecting authentic samples of other proposed intermediates (VI, IX, and XV) to the conditions of alkali and sulphate pulping and by demonstrating the formation of the expected reaction products (compounds VII and VIII from VI, compounds V, VII, XI, XII, XIV-XVI, and ethanol from IX and compounds VII, XIV, and XVI from XV) (see Table 2).

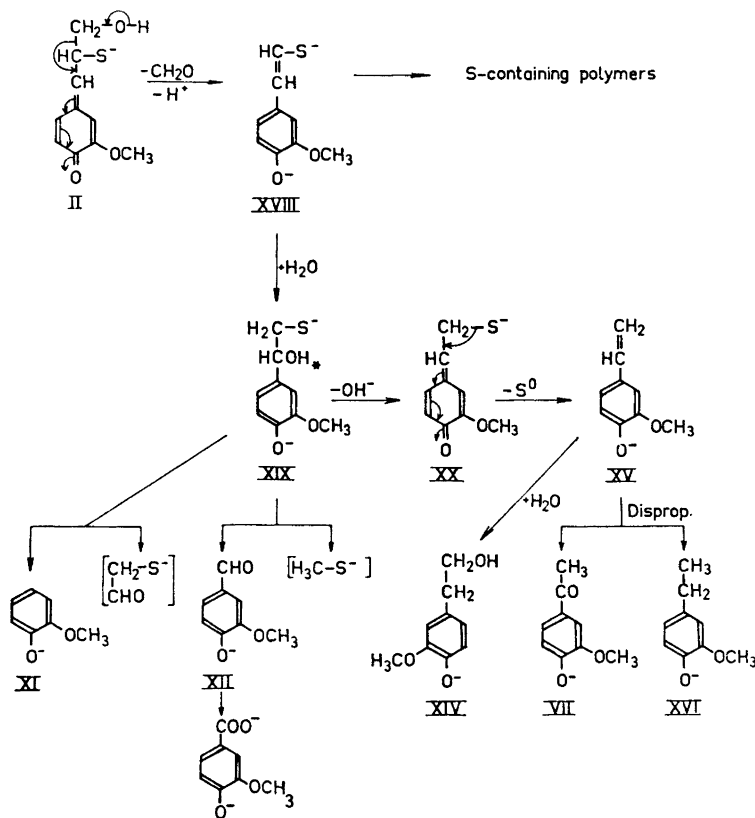
Treatment of the α,γ -diol IX with alkali gave, in addition to high molecular weight fractions and the compounds mentioned above, 1,1-bis-(4-hydroxy-3-methoxyphenyl)ethane, most likely arising by addition of guaiacol (XI) to vinylguaiacol (XV). This reaction between a conjugated compound and a reactive site in a phenol indicates a possible mode of repolymerisation of lignin degradation products formed during alkali and sulphate pulping.

The remaining compounds in Scheme 1 (depicted within parentheses) (VI, VIa, IX, X, β -hydroxypropionaldehyde and homovanillin) are likely to be intermediates but have not been identified. Compounds VII and VIII have been previously obtained from sulphate spent liquors and have been suggested to originate from β -aryl ether structures in lignin.¹⁸

The fragmentation reactions of coniferyl alcohol outlined in Scheme 1 are in many respects analogous to those reported previously for other conjugated intermediates, *e.g.* a stilbene^{19,20} and a 1,4-diarylbutadiene.²¹

Of the aliphatic fragmentation products, methanol may be liberated by alkaline cleavage of methyl aryl ether bonds and by cleavage of $C_\beta-C_\gamma$ -bonds. However, ethanol which is formed in appreciable amounts from episulphide I and from the intermediates IV and IX can only arise by cleavage of $C_\alpha-C_\beta$ -bonds in a reaction which also affords vanillin (XII) (see Scheme 1). The presence of ethanol in sulphate spent liquors has been considered to be due to microbial degradation of carbohydrate constituents *prior* to the pulping process.²² The present study provides a plausible explanation for its formation also *during* the process by alkaline fragmentation of coniferyl alcohol type intermediates formed in lignins. The fact that ethanol, present in kraft spent liquors, originates from lignin was confirmed by treating milled wood lignin with white liquor under pulping conditions and demonstrating the formation of considerable amounts of ethanol. After a similar treatment, holocellulose gave only traces of ethanol and cotton gave no ethanol at all.

A third aliphatic cleavage product, formaldehyde, should originate from terminal hydroxymethyl groups in intermediary methylene quinone structures. This elimination reaction, resulting in the cleavage of $C_\beta-C_\gamma$ -bonds is common to methylene quinone intermediates and is particularly pronounced with those



Scheme 2.

carrying an electron-attracting substituent, such as an aroxyl²³, an aryl^{24,25} or a thiol group (see Scheme 2) in the β -position. However, in spite of the general character of this elimination reaction, only traces of formaldehyde were occasionally detected in the sulphate spent liquors from model compounds. This is probably due to the immediate consumption of formaldehyde in various condensation reactions, particularly with phenolic nuclei³ ("Lederer-Manasse reactions"), self-condensation²⁶ and disproportionation (Cannizzaro) reactions.²⁶

The *second type* of elimination reaction exhibited by intermediate II also leads to the liberation of formaldehyde (see Scheme 2). The resulting styrene- β -thiol (XVIII) may in part polymerise yielding a sulphur-containing high molecular weight polymer. The other part may add the elements of water to give the α -hydroxy- β -thiol XIX. The latter intermediate can be expected to undergo analogous types of fragmentation as intermediate IX yielding guaiacol, vanillin and the appropriate aliphatic fragments (thiols). Another possible reaction path leads *via* methylene quinone XX to 4-vinylguaiacol (XV), in analogy to the desulphurisation of II (see Scheme 1). 4-Vinylguaiacol may add the elements of water to give XIV or disproportionate to yield VII and XVI in analogy to the corresponding reactions of coniferyl alcohol (IV). Thus, compounds VII, XI, XII, XIV–XVI and vanillic acid may have been formed *via* routes outlined in both Schemes 1 and 2.

Further support for the validity of Scheme 2 was obtained by treating an authentic sample of the proposed intermediate XIX with 2 N sodium hydroxide at 180° for 2 h and identifying the expected compounds (VII, XI, XII, XIV–XVI and vanillic acid) (see Table 2).

The reliability of the above results was verified by treating milled wood lignin with white liquor or 2 N sodium hydroxide under pulping conditions. The resulting mixtures of degradation products contained essentially the same monomeric and aliphatic compounds as were obtained from episulphide I and from coniferyl alcohol (IV) (see Table 2).²⁷ This result further confirms the validity of Schemes 1 and 2 and previous suppositions in this series on the mechanism of lignin degradation during sulphate pulping. The fact that the same phenolic and aliphatic products are formed on treatment of milled wood lignin with white liquor and with sodium hydroxide indicates that the degradation with the latter cooking liquor may also proceed to a certain extent *via* intermediates of the coniferyl alcohol type.

The secondary condensation and polymerisation reactions of the intermediary conjugated structures of the types IV and XV during alkali and sulphate pulping are currently being studied.

EXPERIMENTAL

Melting points are corrected. Evaporations were carried out under reduced pressure. *Thin-layer (TLC) and column chromatography.* For thin-layer chromatography silica gel HF₂₅₄ (E. Merck A.G., Darmstadt) was used as adsorbant and mixtures of petroleum ether-ethyl acetate in suitable ratios as solvent systems. The spots were developed by spraying with a 1 % solution of vanillin in conc. sulphuric acid and heating at 120° for about 10 min. The preparative separations were carried out by column chromatography using silicic acid (SilicAR CG-7 100–200 mesh, Mallinckrodt) as adsorbant and mixtures

Table 2. Products separated by column and/or gas chromatography and identified by mass spectrometry.

Starting compound (cooking liquor)	Guaiacol (XI)	Vanillin (XII)	Aceto- guaiacone (VII)	Propio- guaiacone (VIII)	Dihydro- coniferyl alcohol (V)	4-Ethyl- guaiacol (XVI)	4-Vinyl- guaiacol (XV)	4-(2-Hy- droxy- ethyl)- guaiacol (XIV)	Iso- eugenol (XVII)	Metha- nol	Etha- nol
Episulphide I (NaOH)	+	+	+	+	+	+	+	+		+	+
Coniferylalcohol (NaOH)	+	+	+		+	+	+	+		+	+
Coniferylalcohol (white liquor)	+	+	+	+	+	+	+	+	+	+	+
β -Hydroxy-propio- guaiacone (VI) (NaOH)			+	+							
4-(1,3-Dihydroxy- propyl)-guaiacol (IX) (NaOH)	+	+	+		+	+	+	+		+	+
4-Vinyl-guaiacol (XV) (NaOH)			+			+	+	+		+	+
4-(1-Hydroxy-2-mer- capto-ethyl)-guaia- col (XIX)	+	+	+			+	+	+		+	+
Milled wood lignin (NaOH)	+	+	+	+	+	+	+	+		+	+
Milled wood lignin (white liquor)	+	+	+	+	+	+	+	+	+	+	+

of ethyl acetate-petroleum ether in appropriate ratios as solvents. The elutions were followed by TLC.

Gas chromatography and mass spectrometry. The gas chromatographic separations were carried out with a Perkin-Elmer model 270 instrument (combination with a mass spectrometer). Column dimensions: 150 × 0.1 cm i.d. Column: 3 % silicon OV-1 Gaschrom. Q. washed with conc. hydrochloric acid and treated with dimethyldichlorosilane. Injection temperature: 180°. Detector: flame ionisation, 280°. Carrier gas: N₂ 20 ml/min. The mass spectra were recorded at 70 eV.

Model and reference compounds. The compounds used in this study were prepared as previously described (I,² III,² IV,²⁸ V,²⁹ VI,³⁰ VIII,³¹ IX,³² XIII,³³ XIV,³⁴ XV,^{29,35} XVI³⁴). Compound XIX was synthesised as follows:

α-Thioacetoxy-4-acetoxy-3-methoxy-acetophenone. 4-Acetoxy-3-methoxy- α -bromo-acetophenone³⁶ (9.34 g) was treated with potassium thioacetate (7.43 g) in dimethylformamide (100 ml) at room temperature for 5 h. The reaction mixture was poured into water and extracted with chloroform. The chloroform extract was washed with water (10 times) and dried with sodium sulphate. Evaporation of the solvent gave a slightly yellowish oil (8.75 g, 95.7 %) which crystallised in the refrigerator after some days. Recrystallisation from chloroform-hexane or from isopropyl ether (twice) yielded colourless crystals (4.0 g, 43.5 %), m.p. 70.5–71.5°. (Found: C 55.83; H 5.28; O 28.07; S 12.07. C₁₃H₁₄O₅S requires: C 55.30; H 5.00; O 28.34; S 11.36).

1-Hydroxy-1-(4-hydroxy-3-methoxy-phenyl)-ethane-2-thiol (XIX). α -Thioacetoxy-4-acetoxy-3-methoxy-acetophenone (3.50 g) was dissolved in dry ethyl ether (150 ml). The solution was added dropwise to a solution of lithium aluminium hydride (0.80 g) in the same solvent (100 ml). The reaction mixture was kept in an ice-bath until all starting material had been added and then at room temperature for another 2 h. The usual working-up procedure gave a yellowish oil (2.65 g, 98.4 %) which was purified by preparative thin-layer chromatography on silica gel HF₂₅₄ using chloroform as solvent. The pure compound XIX, a colourless oil, turned yellowish on standing at room temperature. (Found: S 15.05. C₉H₁₂O₃S requires: S 16.01.) It was identified by NMR and IR spectra and by conversion into its triacetate.

1-Acetoxy-1-(4-acetoxy-3-methoxy-phenyl)-2-thioacetyl-ethane (triacetate of XIX) was obtained by acetylation of XIX with acetic anhydride-pyridine. The compound was identified by NMR and mass spectra.

The remaining reference compounds were commercially available.

Cooking liquors. Sodium hydroxide (2 N) and "white liquor" were used as cooking liquors.

Treatment of model compounds with cooking liquors and working-up procedure

The treatment of the model compounds (0.1–1.0 g) with the cooking liquors was carried out at 180° for 2 h in an atmosphere of nitrogen. The resulting reaction mixtures were worked up in the following way:

After neutralisation with dry ice the mixture was extracted with ethyl acetate. The ethyl acetate layer was washed with water, dried (Na₂SO₄) and evaporated, and the residue was acetylated with acetic anhydride-pyridine.

The acetates were separated into several fractions by column and/or preparative thin-layer chromatography and the fractions were analysed by gas liquid chromatography combined with mass spectroscopy. The identifications were based on the retention times and on the mass spectral fragmentation patterns (comparison with the corresponding data of authentic samples). Fractions containing unsatisfactorily separated mixtures of acetylated degradation products were subjected to further separation(s) by column or thin-layer chromatography until the main components of the fractions obtained could be unambiguously identified using the above mentioned method.

Thus, many of the degradation products given in the general part (see Schemes 1 and 2) were found in several fractions. In this work no attempt was made to determine the proportions of the various monomeric reaction products. Their total amount varied between about 33 and 38 % calculated on the amount of starting material.

The formation of methanol and ethanol was demonstrated in separate runs. The sample (250 or 500 mg) was treated with cooking liquor (10 or 20 ml) in the usual way. Before opening, the autoclave was cooled first in a freeze box and then in powdered dry ice. The uppermost layer of the resulting solid mass was transferred into a 2 ml volumetric flask which was closed with a membrane. After heating the flask at 70° for about 30 min a sample of the gaseous content was withdrawn with a syringe and injected into the gas chromatograph. The chromatographic separation was performed using a Porapak Q column at 130°. The alcohols were identified by comparison of their retention times with those of authentic samples and of mixtures with authentic samples.

The formation of vanillic acid and homovanillic acid was demonstrated separately using an ion pair methylation method.³⁷ An aliquot of the reaction mixture was withdrawn and concentrated until a humid solid mass was obtained. Methylene chloride (2 ml) and tetrabutylammonium hydrogen sulphate (> 1.1 equiv.) were added and the mixture was triturated with ether (3 times) with ultrasonic agitation. After 20 min methyl iodide (1 ml > 4 equiv.) was added, the shaking was continued for another 10 min and then the mixture was refluxed for 1 h on a steam bath. Careful evaporation of the bulk of methylene chloride gave a residue which was exhaustively extracted with ether. Filtration through a small column (4 × 10 mm) of alumina yielded a solution of the mixture of methylated compounds which was investigated by GLC using an OV-1 column. In addition to the methyl esters of vanillic acid and homovanillic acid the presence of several other methylation products was indicated²⁷ but these products have not been included in the schemes.

Treatment of milled wood lignin with cooking liquors and working-up procedure

Milled wood lignin³⁸ (500 mg) was similarly treated with white liquor and sodium hydroxide. The resulting mixtures were worked up in the same way and the mixtures of acetates and methylation products obtained were analysed as mentioned above. The results are given in Table 2.

Demonstration of the formation of coniferyl alcohol (IV)

(a) *By mild alkaline treatment of episulphide I.* A mixture of dioxan (3 ml) and 0.01 N sodium hydroxide (3 ml) was saturated with nitrogen at 90°. Episulphide I in the form of its diacetate (60 mg) was added at the same temperature and allowed to react for 4 h. The resulting mixture was acetylated and investigated by TLC [benzene (75 %)-ethyl-acetate (15 %), run three times]. The diacetate of IV was shown to be the main component in the mixture which also contained some diacetate of the starting material (I).

(b) *By simple heat treatment of the diacetate of episulphide I.* The elimination of sulphur from the diacetate of episulphide I was brought about by heating a sample (60 mg) without any solvent to 90° for 4 h. The diacetate of IV was isolated by column chromatography as a colourless oil (yield 70 %) and identified by TLC and NMR (comparison with authentic diacetate of IV).

Determination of S⁰

Granulated copper was treated with boiling conc. hydrochloric acid, carefully washed with water, activated with conc. nitric acid (vigorous stirring) and again washed with water. The activated copper was immediately transferred to a glove-box filled with argon (careful exclusion of air). Glass ampoules were charged with the compound (50–100 mg), copper (25 g), and cooking liquor (5 ml) and temporarily closed by stoppers. During the sealing argon was passed into the ampoules. The latter were then treated as described in Refs. 11 and 12. After cooling, the ampoules were opened and their content was added to water. The CuS-containing copper was treated with conc. hydrochloric acid (200 ml) at 90° until all hydrogen sulphide had been released. The latter was passed into a receiver

and reacted with a solution (30 ml) of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (89.25 g $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) in conc. ammonia (650 ml, diluted with water 1:1). When the evolution of hydrogen sulphide had ceased, nitrogen was passed through the apparatus to assure complete removal of hydrogen sulphide from the reaction vessel and absorption in the receiver. Conc. hydrochloric acid (45 ml) and 0.1 N iodine solution (25 ml) were added to the suspension in the receiver to dissolve the precipitate. The resulting solution was titrated with 0.1 N sodium thio-sulphate.

The determination of elemental sulphur eliminated from episulphide I under milder conditions was carried out using an improved method: The diacetate of compound I (170 mg), together with pyrogallol (200 mg) and purified copper (50 g), was treated with 1 N sodium hydroxide (20 ml) at 100° for 1 h in a nitrogen atmosphere using a three-necked, round-bottomed flask, equipped with a reflux condenser and nitrogen inlet and outlet tubes. The liberation of hydrogen sulphide from the CuS -containing copper and the iodometric titration were carried out as described above (Found: elemental sulphur eliminated 18.30 mg (99.5 % of the theoretical yield.) A sample of 2,3-dimercaptopropanol (200 mg), when treated in a similar way gave off only 1.0 mg elemental sulphur (1.0 % of the theoretical yield).

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REFERENCES

1. Gierer, J. and Smedman, L.-Å. *Acta Chem. Scand.* **19** (1965) 1103.
2. Gierer, J. and Smedman, L.-Å. *Acta Chem. Scand.* **20** (1966) 1769.
3. Gierer, J. *Svensk Papperstidn.* **71** (1970) 571.
4. Leopold, B. *Acta Chem. Scand.* **6** (1952) 38; *Svensk Kem. Tidskr.* **64** (1952) 18.
5. Freudenberg, K. In Freudenberg, K. and Neish, A. C. *Constitution and Biosynthesis of Lignin*, Springer Verlag, Berlin-Heidelberg-New York 1968, p. 45.
6. Adler, E. *Svensk Kem. Tidskr.* **80** (1968) 279.
7. Staudinger, H. and Siegwart, J. *Helv. chim. Acta* **3** (1920) 840.
- 8a. Reid, E. E. *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing Co, New York 1960, Vol. 3, p. 19, 167.
- b. Schönberg, A. and v. Vargha, L. *Ber.* **64** (1931) 1390.
- c. Campaigne, E. In Patai, S. *The Chemistry of the Carbonyl Group*, Interscience, London-New York-Sydney 1966, p. 938.
9. Ref. 8a., p. 116.
10. Schönberg, A. and Nickel, S. *Ber.* **64** (1931) 2323.
11. Teder, A. *Svensk Papperstidn.* **70** (1969) 294.
12. Ahlgren, P. and Hartler, N. *Svensk Kem. Tidskr.* **78** (1966) 404.
13. Brunow, G. and Miksche, G. E. *Acta Chem. Scand.* **23** (1969) 1444.
14. Brunow, G., Ilus, T. and Miksche, G. E. *Acta Chem. Scand.* **26** (1972) 1117.
15. Brunow, G. and Miksche, G. E. *Acta Chem. Scand.* **26** (1972) 1123.
16. Shemyakin, M. M. and Shehukina, L. A. *Quart. Rev. Chem. Soc.* **10** (1956) 261.
17. Salomaa, P. In Patai, S. *The Chemistry of the Carbonyl Group*, Interscience, London - New York - Sydney 1966, p. 197.
18. Enkvist, T., Ashorn, T. and Hästbacka, K. *Paper and Timber* (Finland) **44** (1962) 395.
19. Turunen, J. *Comment. Phys. Math.* **28** (1963) No. 9; Enkvist, T. and Turunen, J. *Chim. Biochem. Lignin, Cellulose, Hemicellulose*, Grenoble 1964, p. 177.
20. Gierer, J. Pettersson, I. and Smedman, L.-Å. *Acta Chem. Scand.* **26** (1972). 3366.
21. Gierer, J. and Opara, A. E. *Unpublished work.*
22. Wilson, D. F. and Hrutford, B. F. *Tappi* **54** (1971) 1094.
23. Gierer, J. and Norén, I. *Acta Chem. Scand.* **16** (1962) 1713.
24. Adler, E., Marton, J. and Falkehag, S. I. *Acta Chem. Scand.* **18** (1964) 1311.
25. Nimz, H. *Chem. Ber.* **98** (1965) 3160.
26. Marton, J., Marton, T., Falkehag, S. I., and Adler, E. *Advan. Chem. Ser.* **59** (1966) 125.
27. Gierer, J. and Pettersson, I. *Unpublished work.*
28. Freudenberg, K. and Hübner, H. H. *Chem. Ber.* **85** (1952) 1181.

29. Coscia, C. J., Schubert, W. J. and Nord, F. F. *J. Org. Chem.* **26** (1961) 5085.
30. Fisher, H. E. and Hibbert, H. *J. Am. Chem. Soc.* **69** (1947) 1208.
31. Belg. Pat. 614,525 Aug. 28, 1962, U.S. Appl., March 1, 1961, Mead Johnson and Co., *Chem. Abstr.* **59** (1963) 512d.
32. Kratzl, K. and Miksche, G. E. *Monatsh.* **94** (1963) 530.
33. Muszynski, E. *Acta Pol. Pharm.* **18** (1961) 471; *Chem. Abstr.* **58** (1963) 3334h.
34. Arlt, H. G., Gross, S. K. and Schuerch, C. *Tappi* **41** (1958) 64.
35. Hachihama, Y. and Shono, T. *Chem. Abstr.* **56** (1962) 10380 f.
36. Erdtman, H. and Leopold, B. *Acta Chem. Scand.* **3** (1949) 1358.
37. Strömberg, S. *Personal communication*.
38. Björkman, A. *Svensk Papperstidn.* **59** (1956) 477.

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