

Formation of low molecular weight phenols from »milled wood lignin» during sulphate and soda cooking

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SUMMARY: The formation of low molecular weight phenols during sulphate and soda cooking of "milled wood lignin" has been studied. According to analytical gel filtration experiments considerably greater amounts of such materials are formed in cookings with birch lignin than in the corresponding experiments with spruce lignin. From both spruce and birch lignin somewhat larger amounts of low molecular weight products were formed during sulphate cooking than during soda cooking.

By the use of gel filtration, low molecular weight fractions were separated from reaction mixtures obtained on cookings with spruce lignin. Chromatography on silica gel columns, followed by further investigations, resulted in the identification of a number of phenols. With the exception of the fact that more catechol compounds were obtained during sulphate cooking, the composition of fractions from sulphate cooking and soda cooking showed striking similarities. Almost all the identified compounds have previously been detected in cooking liquors from wood.

Reaction mixtures obtained during soda cooking (spruce lignin) were also examined using a different work-up procedure which was developed with special attention to hydrophilic compounds. Minor amounts of guaiacylglycerol and 3-(4-hydroxy-3-methoxyphenyl)-1,2-propanediol were obtained.

The origin of most of the identified products is discussed.

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The formation of low molecular weight phenols under the conditions used in sulphate and soda cooking of wood has been studied by several workers (1). Although the formation of phenols on alkaline treatment of carbohydrates has been demonstrated (2), there is no doubt that the major part of the phenols originates from the lignin portion of the wood. In the present investigation¹

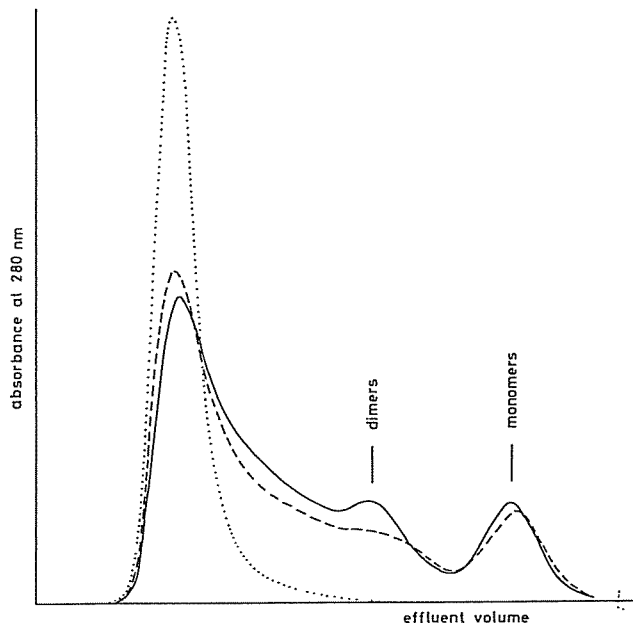


Fig. 1. Gel filtration [Sephadex G-25, eluent: dioxan — water (1:1)] of "milled wood lignin" from spruce (····) and reaction mixtures obtained during sulphate cooking (—) and soda cooking (— — —) of this material.

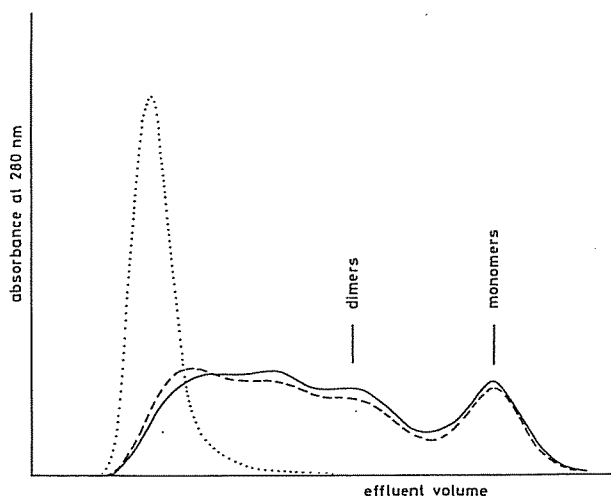


Fig. 2. Gel filtration [Sephadex G-25, eluent: dioxan — water (1:1)] of "milled wood lignin" from birch (····) and reaction mixtures obtained during sulphate (—) and soda cooking (— — —) of this material.

the formation of such phenolic materials in cooks of "milled wood lignin" (3), MWL, has been studied. The liberation of low molecular weight compounds (monomers and dimers) can readily be demonstrated in gel filtration experiments. Fig. 1 and 2 show the absorbance at 280 nm versus elution volume on gel filtration of cooking mixtures and nontreated lignin. Calibration of the column was made on the basis of experiments with lignin model compounds (4). Since it is likely that the specific absorbance at 280 nm varies with molecular weight, the curves shown in fig. 1 and 2 probably do not give an entirely correct picture of the amounts of low molecular weight materials formed.

The degradation of lignin during sulphate and soda cooking can essentially be attributed to cleavage of alkyl aryl ether linkages (5, 6). Comparison of the results obtained with spruce and birch lignins shows that greater amounts of monomers and dimers are formed from birch lignin; this is in all likelihood a consequence of the relatively large number of syringyl units (3) and ether bonds susceptible to alkaline cleavage (7) in birch lignin.

Experimental

Paper chromatography (PC).

As a detecting agent, diazotized sulphanilic acid in 2% aqueous Na_2CO_3 was used. Examinations for the presence of compounds VII (R_f 0.05, red-violet), VI (R_f 0.10, red-violet), and I (R_f 0.73, red-orange) were made using the solvent system ligroin-water-chloroform-methanol (7:5:2:1) (8). The solvent system butanol-water (1:1) was

¹A preliminary report was given at "Organikerdagarna", Uppsala, June 16—18, 1969 [Kemisk Tidskrift 82(1970)32].

used (descending, upper layer moving phase) for the detection of compounds XIV (R_f 0.55, orange) and XVII (R_f 0.74, red-violet).

Thin layer chromatography (TLC).

Plates coated with a 0.3 mm thick layer of silica gel (Merck HF₂₅₄) were used. Eluting agents were benzene-ethyl acetate (1:1) (R_f values: XVII, 0.03; XVIII, 0.22; III, 0.38; guaiacol, 0.50), benzene-dioxan-acetic acid (90:25:4), (9), (R_f values: VIII, 0.20; IX, 0.22; V, 0.25), and chloroform (R_f value for guaiacol: 0.30). As detecting agent, iodine vapour was used (brown spots). Guaiacol was also made visible by spraying with an ethanolic solution of 2,6-dibromo-N-chloroquinonimine followed by dilute aqueous NaOH [blue spot, cf. (10)]. In preparative experiments the zones containing the materials of interest, detected by UV light, were scratched off and the compounds eluted with acetone.

Gas chromatography.

A Perkin-Elmer Model 900 instrument was used. Column dimensions: 200×0.3 cm o.d. stainless steel tubing. Column packing: 3 % SE-30 (ultraphase) on Chromosorb W (Pierce). Temperatures: Injection 260°, column 195°, and manifold 240°C. Carrier gas: N₂, 30 ml/min. Detector: FID. Tricosane was used as internal standard. Identification of components was made by relative retention times and mass spectra, which were taken using an LKB 9000 gas chromatograph-mass spectrometer unit.

Preparation of 3-(4-hydroxy-3-methoxyphenyl)-1,2-propanediol (XVII) and its triacetate.

Compound XVII was prepared according to (11). Compound XVII was acetylated by treatment with equal amounts of acetic anhydride and pyridine for 24h. The gas chromatogram of the reaction mixture showed only one peak. The NMR spectrum was consistent with the triacetate of XVII.

Preparation of 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (XVIII).

Compound XVIII was prepared by catalytic hydrogenation of 1-(4-benzyloxy-3-methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone (12). A 1.0 g sample of the latter compound was hydrogenated in 50 ml dioxan-water (9:1) using 0.6 g of Pd/C as catalyst. A small amount of 2-molar HCl was added to the reaction mixture to accelerate the reaction rate. After 18 h the calculated amount of hydrogen had been consumed. The catalyst was filtered off and, after dilution with water, the reaction mixture was extracted with chloroform. The extract was dried over Na₂SO₄ and the solvent removed by film evaporation. According to TLC the residue contained compound XVIII. Separation of XVIII was accomplished by chromatography on a silica gel column (50 g SiO₂). As eluent benzene-ethyl acetate (1:1) was used. From the column a fraction consisting of XVIII, weighing 0.31 g, was obtained. Purification was made by distillation (175–180 °C/3 Pa). The product was identified as 3-(4-hydroxy-3-methoxyphenoxy)-2-(2-methoxyphenoxy)-1-propanol (13) (XVIII) by IR and TLC.

Analytical gel filtration experiments.

A solution of 65–85 mg of lignin in 10 ml of 1-molar NaOH or a "white liquor" (0.87-molar NaOH which was 0.13-molar in respect to Na₂S) was heated at 170 °C for 4 h in a 10 ml stainless steel autoclave. After cooling, a 0.75 ml sample was acidified with 0.75 ml of hydrochloric acid (1.1-molar in experiments with 1-molar NaOH and 1.2-molar in experiments with "white liquor") whereupon 1.5 ml of dioxan was added. Samples of nontreated lignin were prepared by dissolving 3–5 mg lignin in 3 ml dioxan-water (1:1).

The samples were examined by gel filtration on Sephadex G-25 (medium) with dioxan-water (1:1) as eluent according to the procedure described in (14).

Investigation of low molecular weight phenols formed upon sulphate cooking of spruce lignin.

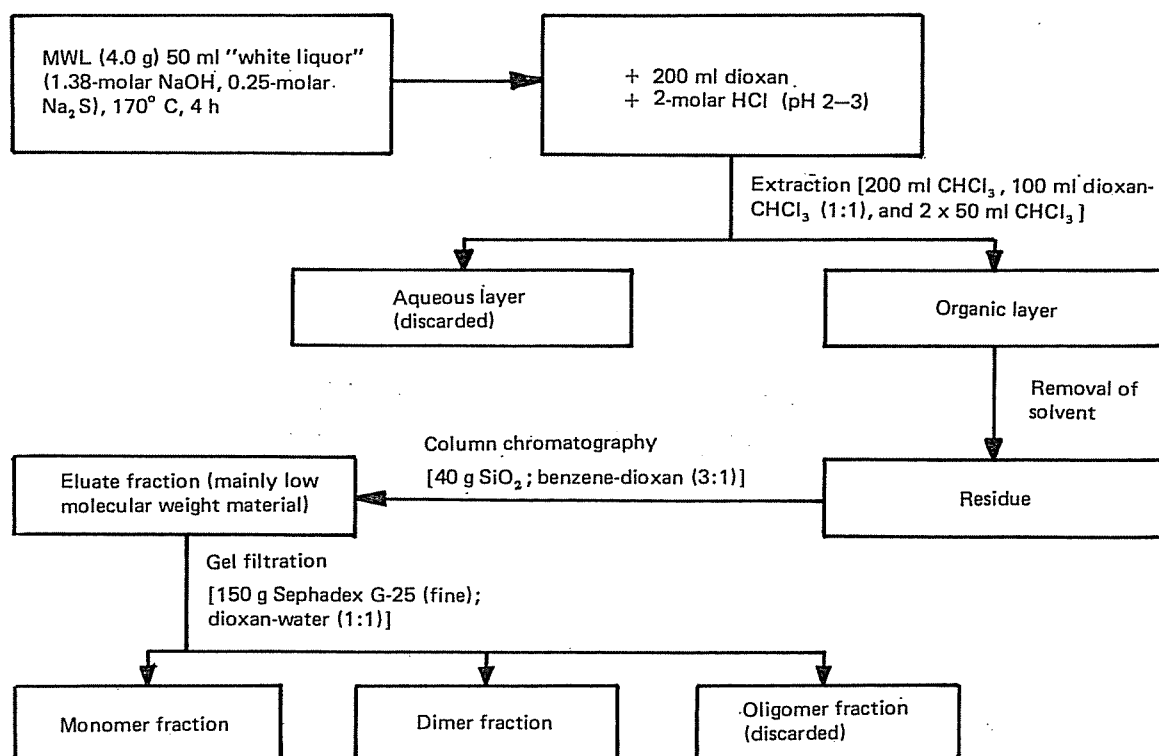
Cooking conditions and work-up procedures [cf. (15)] are shown in *scheme 1*. Yields of fractions are given in *table 1*.

The monomer fraction and the dimer fraction were each divided into sub-fractions by column chromatography on silica gel according to the standard procedure described in (15). In the latter work, the division into sub-fractions was made on the basis of an examination of the eluate from the silica gel column by TLC using benzene-ethyl acetate (1:1) as eluent. In the present study, and additional examination was made using benzene-dioxan-acetic acid (90:25:4) as eluent. Sub-fractions obtained were examined to identify individual components. Crystalline compounds were identified by m.p., mixed m.p., and comparison of their IR spectra with those of the authentic compounds. The results are summarized in *table 2*.

Investigation of low molecular weight phenols formed during soda cooking of spruce lignin.

Procedure A. As cooking liquor 1.5-molar NaOH was used. Otherwise the experimental conditions were the same as in the above described sulphate cooking experiment. Yields of fractions are given in *table 1*. Results from examinations of the monomer and dimer fractions are summarized in *table 2*.

Procedure B. Solutions of nontreated or borohydride reduced MWL (0.75 g) from spruce in 60 ml of 2-molar NaOH were prepared in a stainless steel autoclave lined with teflon. Air was replaced by nitrogen and the autoclave was kept at 170 °C for 2h (or 4h in some of the experiments with nontreated lignin). After cooling, the content was dropped into 60 ml 2-molar HCl under stirring with a magnetic stirrer. The pH was adjusted to 2 with hydrochloric acid and aqueous NaOH. The precipitate was filtered off and washed with 2×15 ml of 1-molar NaCl. The solution and the washings were extracted with 3×150 ml of chloroform. The pH of the aqueous layer was then adjusted to 4 and the solvent removed by freeze-drying. The remaining solid, mainly



Scheme 1. Cooking conditions and work-up procedures

consisting of NaCl, was soaked with acetone (3×100 ml). The acetone was removed by film evaporation and the residue was weighed after being dried *in vacuo*. The weight of the residue obtained in different experiments were of the order of 1 % of the original lignin. Examination by paper chromatography indicated the presence of guaiacylglycerol (XIV) and, probably, 3-(4-hydroxy-3-methoxy-phenyl)-1,2-propanediol (XVII). To obtain further proof of the presence of these compounds, the residues were acetylated [treated with acetic anhydride-pyridine (1:1) for 24h] and the reaction mixtures examined by gas chromatography. The presence of the *erythro* and *threo* forms of the tetraacetate of XIV (16) and the triacetate of XVII was demonstrated. The results were confirmed by gas chromatography-mass spectrometry. Although the amounts of acetates of XIV and XVII were small (according to gas chromatographic estimation) the peaks due to these products dominated the chromatogram. Yields of XVII given in this paper have been corrected for losses in the extraction step (see below).

Soda cooking of 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (XVII).

A solution of 124 mg of XVII in 10 ml of 2-molar NaOH was heated in a stainless steel autoclave for 4h at 170 °C. The reaction mixture was transferred to a separatory funnel, acidified to pH 2 with 10 ml of 2-molar HCl, and extracted three times with 20 ml of chloroform. In a separate experiment it was found that

upon extraction under these conditions 78 % of XVII remains in the aqueous layer. The chloroform layer was dried over Na₂SO₄ and the solvent was removed by film evaporation. The pH of the aqueous layer was adjusted to 5.4 and the water was removed by freeze-drying.

The residue obtained from the chloroform layer, weighing 71 mg, was subjected to chromatography on a silica gel column (50 g SiO₂; 2.5×18 cm). The flow rate was 25 ml/h. Initially, benzene-ethyl acetate (1:1) was used as eluent. From the eluate 80–110 ml, 30 mg of guaiacol was obtained and from the eluate 130–240 ml, 16 mg of starting material was obtained. When the effluent volume was 300 ml, elution was continued with ethyl acetate as eluent. From the eluate 1100–

Table 1. Yields (in per cent of the original lignin) of fractions obtained from spruce lignin during sulphate and soda cooking.

	Sulphate cooking (%)	Soda cooking (%)
Essentially low molecular weight fraction (incl. monomers and dimers)	37	27
Monomers	6.8	5.8
Dimers	11.0	7.5

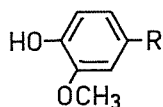
Table 2. Low molecular weight phenols formed upon sulphate and soda cooking of "milled wood lignin" from spruce (4.0 g). M refers to the monomer fraction and D to the dimer fraction isolated after gel filtration.

Fraction number	Recovered amount, mg		Compounds detected	Comments on identification
	sulphate	soda		
M 11—12	—	3	unknown	guaiacol absent (TLC)
M 13—17	15—19	7	unknown	PC
M 18—23	20—26	7	propiovanillone (I)	m.p. 78—79 °C (lit. 80 °C)
M 24—27	27—30	68	vanillin (II)	m.p. 105 °C (lit. 115 °C) after purification by prep. TLC
M 28—30	31—34	21	acetovanillone (III)	m.p. 200 °C (lit. 210 °C) after soaking with CH ₂ Cl ₂
M 31—36	35—40	45	vanillic acid (IV)	cryst. V (m.p. 120 °C, lit. 142—143 °C) and VIII (m.p. 146 °C, lit. 153 °C) from fractions obtained by prep. TLC
M 37—42	41—46	18	homovanillic acid (V) (sulphate and soda), 3,4-dihydroxybenzaldehyde (VIII) (sulphate)	(sulphate), cryst. V (m.p. 138—140 °C) from CH ₂ Cl ₂ -benzene (soda)
M 43—48	47—59	11	3',4'-dihydroxyacetophenone (IX)	m.p. 113 °C (lit. 116 °C) after cryst. from CH ₂ Cl ₂ -benzene (sulphate), traces detected by TLC (soda)
M 49—67	60—66	39	dihydroconiferyl alcohol (VI) (sulphate and soda), 2-(4-hydroxy-3-methoxyphenyl)-ethanol (VII)? (sulphate)	PC
D 18—24	22—25	46	4,4'-dihydroxy-3,3'-dimethoxystilbene (XI)	m.p. 210 °C (lit. 212—213 °C) after cryst. from ethanol

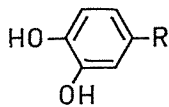
1440 ml, 7 mg of XVII was obtained. The products were identified by TLC and IR. The residue obtained from the aqueous layer mainly consisting of NaCl was soaked with 3×20 ml acetone. The acetone extract was dried over Na₂SO₄ and the solvent evaporated. A residue weighing 31 mg was obtained. The product was identified by PC and IR as XVII. The total yield of XVII was 46 %.

Sulphate cooks

Yields of the low molecular weight fractions obtained are given in table 1. Results from the fractionation of the monomer fraction and the dimer fraction are shown in table 2.



- I R = COCH₂CH₃
 II R = CHO
 III R = COCH₃
 IV R = COOH
 V R = CH₂COOH
 VI R = CH₂CH₂CH₂OH
 VII R = CH₂CH₂OH



- VIII R = CHO
 IX R = COCH₃

From the monomer fraction, vanillin (II) was found to be the most abundant monomer (1.7 % of the original lignin). Other compounds isolated were vanillic acid (IV), acetovanillone (III), 3,4-dihydroxybenzaldehyde (VIII), 3',4'-dihydroxyacetophenone (IX), and homovanillic acid (V). The fraction of the latter compound had a relatively low m.p. and was apparently contaminated. The presence of propiovanillone (I), and, possibly, dihydroconiferyl alcohol (VI) was indicated by paper chromatography.

4,4'-Dihydroxy-3,3'-dimethoxystilbene (XI) was a prominent constituent of the dimer fraction and could be obtained in a crystalline state.

Additional support for the formation of VI during sulphate cooking was obtained in a separate cooking experiment (the cooking conditions were those used in the analytical experiments, but with about ten times higher lignin concentration) in which a monomeric fraction (5 % of the original lignin) was separated from the reaction mixture and examined by gas chromatography (using trimethylsilyl derivatives) according to procedures described in (14). Major peaks in the gas chromatogram corresponded in retention times to the derivatives of II, III, and IV; only a few minor peaks due to unidentified products appeared. According to the results obtained in both the gas chromatographic examination and the paper chromatographic examination in the above-described experiment, 2-(4-hydroxy-3-methoxyphenyl)-ethanol (VII) may also have been formed. Essentially all the compounds mentioned above, have previously been detected in black liquor (1d).

Soda cooks

The yields of the low molecular weight fractions obtained are given in table 1. Results from the fractionation of the monomer and the dimer fractions are given in table 2.

The major component of the monomer fraction (2 % of the original lignin) was vanillin (II). Other compounds isolated were vanillic acid (IV), acetovanillone (III), and homovanillic acid (V). Paper chromatography indicated the presence of propiovanillone (I) and dihydroconiferyl alcohol (VI). The presence of a trace of 3',4'-dihydroxyacetophenone (IX) was indicated by TLC.

A prominent component of the dimer fraction was 4,4'-dihydroxy-3,3'-dimethoxystilbene (XI), which could be separated in a crystalline state.

Hydrophilic compounds are easily lost in the fractionation procedures used in the above described experiment. To study the prevalence of such products in soda cooking mixtures (heating with 2-molar sodium hydroxide at 170 °C for 2h), a different fractionation method was used (*Procedure B*, see Experimental). An examination of the individual components showed the presence of guaiacylglycerol (XIV) (*erythro* and *threo* forms) and 3-(4-hydroxy-3-methoxyphenyl)-1,2-propanediol (XVII). According to a gas chromatographic estimation, the yields of compounds XIV and XVII were about 0.05 % and 0.01 % of the original lignin, respectively. Compound XVII was obtained in about the same yield in experiments with a 4h cooking time.

Discussion

The conditions used during the sulphate and soda cooking experiments with MWL made in the present study differ in certain respects from those prevailing during commercial pulping (17). The relevance of such differences has not been considered in the following.

The elution curves obtained in analytical gel filtration experiments, see fig. 1 and 2, indicate that both spruce and birch lignin, under otherwise similar conditions, are more thoroughly degraded on sulphate cooking than on soda cooking. [Concerning the degradation of lignin on alkaline pulping, see (5) and (6).] The results obtained with spruce lignin are in accord with other analytical gel filtration studies of the fragmentation during alkaline cooking (18). The fact that more low molecular weight material was obtained in preparative experiments with spruce lignin by sulphate cooking than by soda cooking (table 1) is consistent with the analytical gel filtration experiments. However, according to preparative as well as analytical experiments, the differences in the formation of very low molecular weight material (monomers and dimers) are not very pronounced.

Examination of monomer fractions separated from the reaction mixtures obtained on sulphate and soda cooking of spruce lignin revealed the presence of guaiacol compounds I—VI; in both cases vanillin (II) was the most abundant constituent. In addition, catechol com-

pounds VIII and IX were separated from the monomer fraction obtained in the sulphate cooking experiment. The presence of compound IX (in trace amounts) also in the monomer fraction obtained during soda cooking was indicated. The difference in the occurrence of catechol compounds can be explained by the fact that the relatively strong nucleophiles (sulphide and hydro-sulphide ions) present in the sulphate cooking reagent cause demethylation (5, 6). Stilbene XI was a prominent constituent of the dimer fraction obtained in both the soda and sulphate cooking experiments. With the exception of compound IX, all the compounds obtained on sulphate cooking of "milled wood lignin" are present among the products detected by Enkvist and co-workers (1d) in black liquor. Among the products obtained during soda cooking, compounds II, III, IV and XI have been shown to be formed upon soda cooking of wood by Tanaka and Kondo (1a). Guaiacol, which has been found in soda (1a) and sulphate (1d) waste liquor from wood, has not been detected in the present studies with isolated lignin; possibly the guaiacol formed is consumed in condensation reactions (5).

According to the results obtained from hydrosulphide cooking studies, acetovanillone (III) and propiovanillone (I) formed from wood during this treatment originate from guaiacylglycerol- β -aryl ether structures in the lignin (19). It therefore seems reasonable to assume that compounds I and III obtained under the cooking conditions used in the present study also arise from such structures. Homovanillic acid (V) may also originate from this type of structure; thus the formation of considerable amounts of V upon sulphate cooking of a model compound of the β -aryl ether type, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol, has been reported (20). However, in other studies with this model compound the formation of V could not be confirmed (21). Stilbene XI can be assumed to arise from structural elements of type X (fig. 3), since the model compound 1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol has been shown to give stilbene XI on alkaline treatment (22). It is in this connection noteworthy that the occurrence of minor amounts of p,p'-dihydroxystilbene structures in the polymeric fraction of

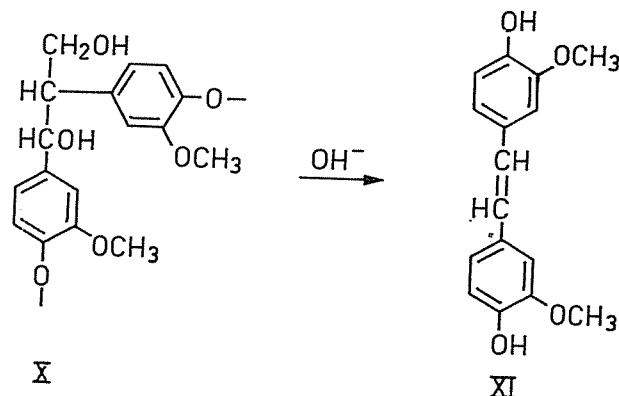


Fig. 3. Formation of stilbene XI from lignin structures of type X during sulphate and soda cooking.

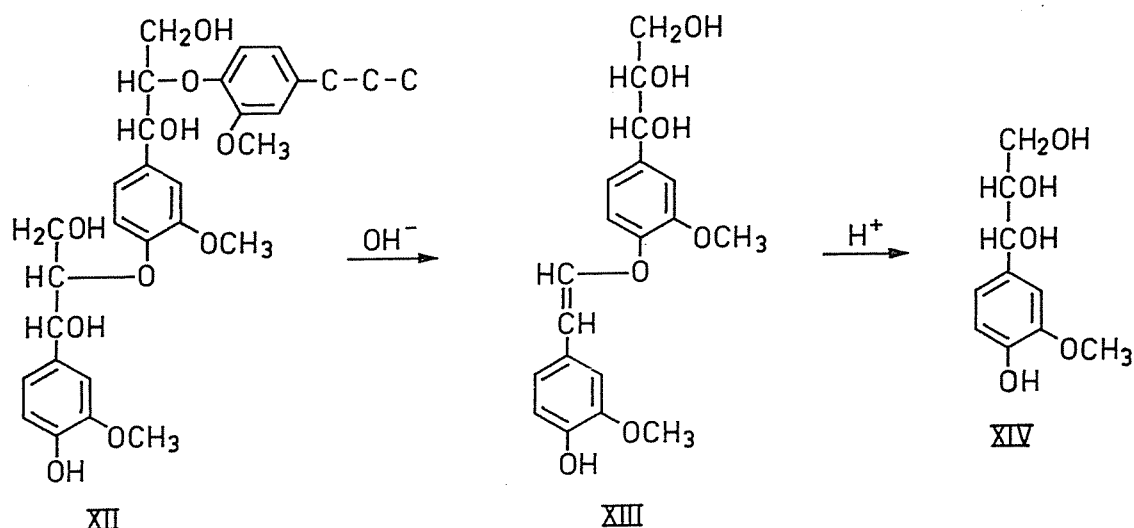


Fig. 4. Suggested reaction route for the formation of guaiacylglycerol (XIV) from lignin structures of type XII in soda cooking experiments according to procedure B.

"milled wood lignin" subjected to sulphate cooking has been demonstrated (23).

Components of a decidedly hydrophilic nature can be expected to be lost in the work-up procedures used in the above discussed studies of the formation of low molecular weight phenols. From reaction mixtures obtained during soda cooking, fractions of hydrophilic materials were separated in yields of the order of 1 % using a different fractionation method. Examination of the individual components showed the presence of guaiacylglycerol (XIV) (*erythro* and *threo* forms) and 3-(4-hydroxy-3-methoxyphenyl)-1,2-propanediol (XVII). The yield of XIV was about 0.05 % of the original lignin. According to Gierer and co-workers (24, 5) units with glycerol side chains can be expected to be formed upon soda cooking of lignin. However, guaiacylglycerol per se is rapidly destroyed during soda cooking (21) and it was therefore surprising to find this compound among the degradation products. One explanation could be that

XIV is not liberated during the soda cooking but during an acidic treatment involved in the work-up procedure (see Experimental).

According to this view, guaiacylglycerol would originate from sequences of three units as in structure XII. Thus, upon soda cooking, structure XII should give rise to enol ether structure XIII (25), and in a subsequent acidic treatment the enol ether can be expected to be hydrolysed (25, 26), giving guaiacylglycerol (fig. 4). It is of interest to note that a tetrameric compound containing a sequence of units of the type present in structure XII has been obtained on mild hydrolysis of spruce wood (27).

The yield of 3-(4-hydroxy-3-methoxyphenyl)-1,2-propanediol (XVII) was of the order of 0.01 % of the original lignin. One explanation of the formation of XVII could be that structures of type XVI are present in lignin and that the glycol ether bond is cleaved during soda cooking (5) resulting in a liberation of XVII (cf.

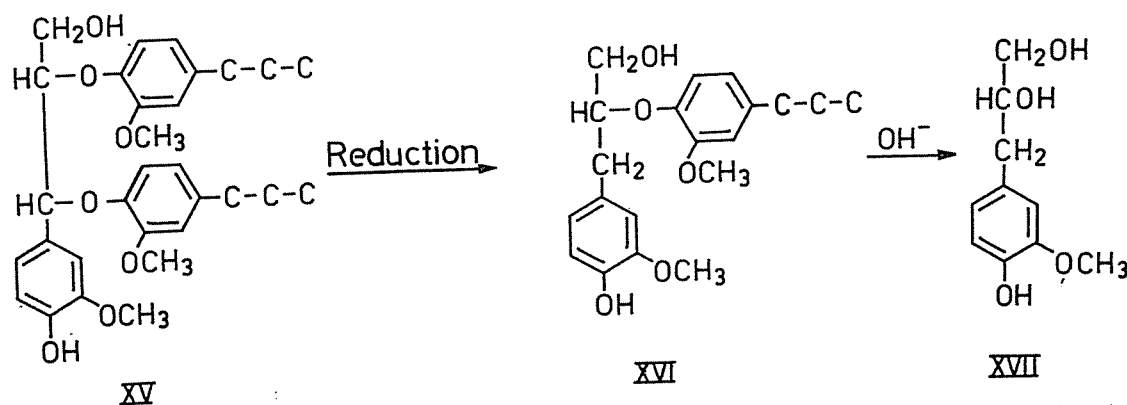


Fig. 5. a. Formation of XVII from lignin structures of type XV on reduction with sodium borohydride followed by soda cooking.

b. Suggested reaction route for the formation of XVII from lignin structures of type XV during soda cooking.

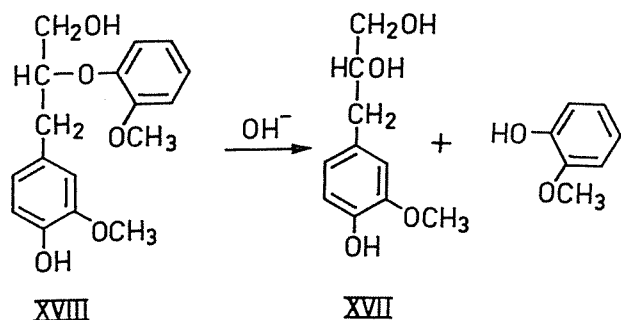


Fig. 6. Formation of 3-(4-hydroxy-3-methoxyphenyl)-1,2-propanediol (XVII) and guaiacol from 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (XVIII) during soda cooking.

fig. 5). Thus a model compound representative of structure XVI, viz. 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (XVIII), gave XVII and guaiacol upon soda cooking (fig. 6). The assumption that structures of type XVI are present in lignin finds some justification in the fact that, in recent lignin degradation studies, compounds of 3,4-dibenzyltetrahydrofuran type have been obtained (15, 28); such compounds may arise from lignin structures which, like structures of type XVI, contain units carrying a methylene group in the α -position. However, since the yield is very small and other possibilities for its formation during the drastic conditions of soda cooking (e.g. from benzyl aryl ether structures, see below) are conceivable, the detection of XVII can hardly be taken as proof for the occurrence of structures of type XVI in lignin.

It is known that model compounds of type XV undergo a reduction on treatment with sodium borohydride in alkaline solution resulting in products with a methylene group in the α -position (13). Lignin structures of type XV can thus be expected to be converted to structures of type XVI on borohydride treatment (29). That borohydride treated lignin was found to give a yield of XVII five times higher than nontreated lignin upon soda cooking suggests that structures of type XVI are actually formed on borohydride reduction of lignin (fig. 5a). This constitutes additional proof for the occurrence of benzyl aryl ether structures of type XV in lignin. Earlier evidence for the presence of such structures comes from studies of the liberation of phenol groups on hydrolysis (30). Possibly XVII obtained from nontreated lignin also is formed from benzyl aryl ether structures of type XV (or such structures formed during the soda cooking from the corresponding type of structure with etherified phenolic group) via reduction and subsequent cleavage of the β -aryl ether bond (fig. 5b).

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