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# Reactions of Lignin During Sulfate Pulping. Part XV.* The Behaviour of Intermediary Coniferyl Alcohol Structures

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Coniferyl alcohol (*1*), a suggested intermediate in the degradation of *p*-hydroxy-arylglycerol-*β*-aryl ether structures during sulfate pulping, was treated with alkali and white liquor under varying conditions. Three types of reaction, fragmentation, condensation and sulfidation, were observed. The relationships between these reactions and their dependence on alkalinity, sulfidity and substrate concentration are discussed on the basis of competition for the key intermediate, the extended quinone methide (*2*).

The results may help to explain two processes that occur during alkali and sulfate pulping: the formation of residual lignins and the degradation of lignins by cleavage of carbon–carbon bonds.

Some years ago, it was proposed that coniferyl alcohol and coniferyl alcohol–like structures are intermediates in the degradation of *p*-hydroxy-arylglycerol-*β*-aryl ether units, when lignins are treated with white liquor ** at 170–180 °C [1,2] ("sulfate pulping", *cf.* also Ref. 3). This view was based on the observation that model compounds representing such units are in part converted into coniferyl alcohol or related compounds, when treated under similar conditions.[1,2] Intermediates thought to be formed during this conversion were found to behave in the same way.[1,2] The role of coniferyl alcohol as an intermediate in the degradation of lignins by the action of white liquor was further supported by treating a suggested precursor, an episulfide, with this reagent. The monomeric compounds produced by this treatment were also formed when milled wood lignin was reacted with white liquor under similar conditions.[2]

However, alkaline *degradation* of coniferyl alcohol and of coniferyl alcohol-like structures accounts for only a minor part of the consumption of these structures during sulfate pulping. The main part is converted into high molecular weight material through conjugate addition reactions.[4–6] This type of *condensation* reaction probably contributes to the formation of residual lignins.

By analogy with sulfonation,[7] a third type of reaction, *sulfidation*, is likely to occur when coniferyl alcohol-like intermediates are treated with white liquor.

The present work is concerned with these three types of reaction, *i.e.* degradation, condensation and sulfidation, their dependence on the reaction conditions and their relative importance.

## RESULTS

*A. Treatment of coniferyl alcohol with aqueous sodium hydroxide. Trans*-coniferyl alcohol was chosen as the model substrate in this study. The reaction products were isolated and identified as the acetates.

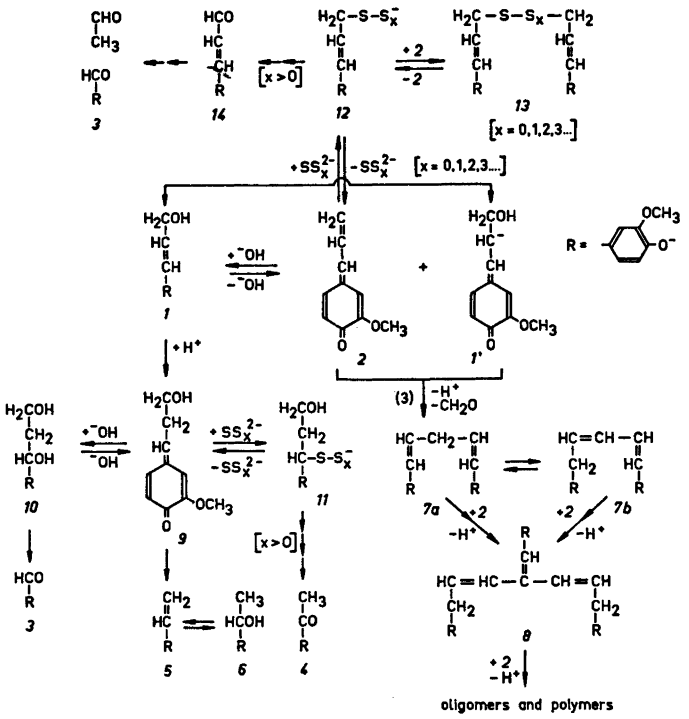
Table 1 (part A) summarizes the qualitative results from the treatment of coniferyl alcohol (*1*) with alkali at five alkali and three substrate concentrations. It can be noted that at high concentrations of alkali, degradation reactions (formation of products *3* and *5*) dominate, whereas low concentrations of alkali favour condensation reactions (formation of oligomers

* Part XIV, see Ref. 6.

** The term „white liquor" refers here and in the following to aqueous solutions of NaOH and $Na_2S.9H_2O$ in varying concentrations.

*Table 1.* Treatment of coniferyl alcohol (*1*) with sodium hydroxide (part A), and with white liquor (part B) at 140 °C for 1.5 and 4.0 h. Sulfidity [a] in all runs: 52 %. Analyses by HPLC. +, ++ and +++ refer to relative amounts of isolated products.

| Amount of *1*/mg | Concentrations | | | Isolated products | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | [*1*]/mM | [$HO^-$]/M | [$S^{2-}$]/M | *1* | *3* | *5* | *7a*+*7b*+*8* | Polymeric material | *12* [*x*=0] | *12* [*x*=1] | *13* |
| A | | | | | | | | | | | |
| 9.2 | 3.4 | 0.01 | – | – | – | – | | +++ | | | |
| 9.2 | 3.4 | 0.05 | – | + | + | + | | +++ | | | |
| 9.2 | 3.4 | 0.1 | – | + | + | + | +++ | +++ | | | |
| 9.2 | 3.4 | 0.5 | – | ++ | ++ | ++ | ++ | ++ | | | |
| 9.2 | 3.4 | 1.0 | – | +++ | +++ | +++ | + | + | | | |
| 150 | 56 | 0.1 | – | (+) | + | + | + | +++ | | | |
| 150 | 56 | 0.5 | – | + | ++ | ++ | +++ | ++ | | | |
| 150 | 56 | 1.0 | – | ++ | ++ | ++ | ++ | + | | | |
| 360 | 200 | 0.5 | – | (+) | + | + | ++ | +++ | | | |
| 360 | 200 | 1.0 | – | (+) | + | + | +++ | ++ | | | |
| B | | | | | | | | | | | |
| 9.2 | 3.4 | 0.1 | 0.035 | + | + | + | (+) | +++ | – | – | (+) |
| 9.2 | 3.4 | 0.5 | 0.18 | ++ | + | + | – | ++ | + | + | ++ |
| 9.2 | 3.4 | 1.0 | 0.35 | ++ | ++ | + | – | + | +++ | +++ | +++ |
| 150 | 56 | 0.1 | 0.035 | (+) | (+) | (+) | + | +++ | – | – | – |
| 150 | 56 | 0.5 | 0.18 | + | + | + | – | ++ | ++ | – | ++ |
| 150 | 56 | 1.0 | 0.35 | + | + | ++ | – | + | ++ | – | ++ |
| 360 | 200 | 0.5 | 0.18 | – | + | (+) | ++ | +++ | (+) | – | – |
| 360 | 200 | 1.0 | 0.35 | (+) | + | + | ++ | ++ | + | – | – |

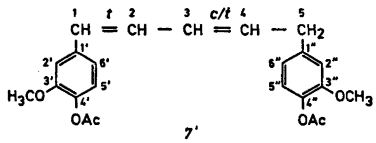



*Scheme 1* Reactions of coniferyl alcohol with alkali and white liquor The phenolic compounds are depicted as anions

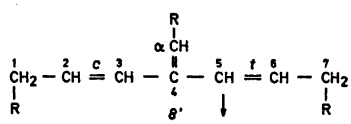
and polymers). These trends are observed at all three substrate concentrations used. Variation of the temperature between 120 and 171 °C at constant alkali (1 M) and substrate (56 mM) concentrations did not influence the qualitative composition of the reaction mixture but changed the proportions of the degradation and condensation products. For the study of the effect of the other variables, an intermediate temperature (140 °C) was chosen.

The degradation products *3*, *4* and *5* (Scheme 1) have been isolated previously after treatment of *1* with alkali and white liquor under different conditions; and their formation has been tentatively outlined.[2] The main pathways of formation of *3* and *4* during treatment of *1* with white liquor are now found to involve hydropolysulfides as intermediates, whereas *5* (and the hydration product *6*) are shown to arise mainly by direct alkaline degradation of *1*.

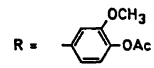
The dimer *7*, also reported previously,[6] is found, using HPLC and $^1$H NMR methods, to consist of three isomers. These isomers include the symmetrical *trans*, *trans-7a*; *trans*, *trans-7b* and *trans*, *cis-7b*. The latter two were isolated and purified. No products of 1,6-addition of *1'* to *2* were found. However, 1,6-additions were observed when the alkaline treatment of *1* was



*7'*
(diacetate of *7b*)



*8'*
(triacetate of *8*)

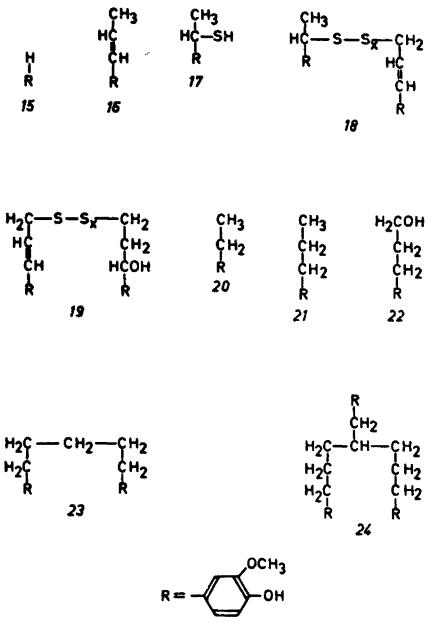


carried out in the presence of simple phenols (*e.g.* 2,6-xylenol) acting as carbanion source.[6]

In addition to the dimers, mixtures of isomeric forms of the trimer *8* and of polymers were obtained. The mixture of trimers gave six partially resolved peaks on HPLC. One of the components of the mixture (*cis, trans-8*) was isolated in pure form.

The $^{13}C$ NMR spectrum of the polymeric fractions contained sharp signals attributable to C 1′ and to C 6′ in 4-acetoxy-3-methoxyphenyl compounds having a conjugated double bond in the side chain (see formulae *7′* and *8′*) and showed features similar to those of the spectrum given by *trans, trans-7b*.

Catalytic hydrogenation of the reaction mixture from the alkaline treatment of *1* gave, among other products, the saturated dimer (*23*) and trimer (*24*), originating from *7* and *8*, respectively, as well as hydrogenated polymeric fractions. The $^{13}C$ NMR spectrum of the latter contained signals characteristic of 4-acetoxy-3-methoxyphenyl compounds having a methylene group in the position *para* to the acetoxy group, and showed striking similarities to the spectrum of hydrogenated *8*.




*B. Treatment of coniferyl alcohol with white liquor.* This treatment was performed at constant sulfidity [8] (52 %) using three different

*Table 2.* Yields of some reaction products from the treatments of *1* (9.2 mg) with sodium hydroxide (part A) and with white liquor (part B) at 140 °C. Concentration of *1*: 3,4 mM in all runs. Analyses by GC and HPLC.

| Conditions | | | Isolated products (Yields % of theoretical) | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[HO^-]$/M | $[S^{2-}]$/M | Reaction time/min | *1* | *3* | *4+16* | *5* | *6* | Sum |
| A | | | | | | | | |
| 0.11 | – | 20 | 25.6 | 2.6 | – | 2.6 | 0.7 | 31.5 |
| 0.54 | – | 20 | 61.8 | 3.2 | – | 6.3 | 3.6 | 74.9 |
| 1.06 | – | 20 | 67.6 | 3.0 | 0.4 | 5.8 | 3.1 | 79.9 |
| 0.11 | – | 40 | 21.5 | 4.1 | – | 4.7 | 1.9 | 32.2 |
| 0.54 | – | 40 | 46.9 | 3.7 | 0.4 | 9.3 | 7.2 | 67.5 |
| 1.06 | – | 40 | 56.3 | 3.5 | 0.4 | 9.6 | 7.1 | 76.9 |
| 0.11 | – | 80 | 9.7 | 6.0 | – | 4.9 | 2.1 | 22.7 |
| 0.54 | – | 80 | 27.4 | 6.4 | 0.4 | 12.6 | 10.6 | 57.4 |
| 1.06 | – | 80 | 32.2 | 7.5 | 0.9 | 12.9 | 11.6 | 65.1 |
| 0.11 | – | 240 | 1.8 | 5.5 | 0.4 | 4.9 | 4.5 | 17.1 |
| 0.54 | – | 240 | 4.5 | 7.7 | 1.1 | 14.7 | 12.5 | 40.5 |
| 1.06 | – | 240 | 9.7 | 10.1 | 1.2 | 18.5 | 17.6 | 57.1 |
| B | | | | | | | | |
| 0.79 | 0.35 | 20 | 39.6 | 3.1 | 1.4 | 3.8 | 1.7 | 49.6 |
| 0.79 | 0.35 | 40 | 16.5 | 8.6 | 2.3 | 5.3 | 3.8 | 36.5 |
| 0.79 | 0.35 | 80 | 5.9 | 16.6 | 4.1 | 5.1 | 4.8 | 36.5 |
| 0.79 | 0.35 | 240 | 3.7 | 24.1 | 5.5 | 4.7 | 5.2 | 43.2 |

*Table 3.* Treatment of compounds *1* and *13* [$x=0$] with sodium hydroxide and white liquor at 140 °C for 1.5 h on a preparative scale.

| Compound (g) | Concentrations | | | Total yields/g | | | Isolated products (mg, % of theoretical) |
|---|---|---|---|---|---|---|---|
| | [*1*]/mM | [$HO^-$]/M | [$S^{2-}$]/M | Before LC | After LC Mono- and oligomeric products | After LC Polymeric products | |
| *1* (2.00) | 56 | 1.0 | – | 2.40 | 0.968 | 0.957 | *1* (200, 8.3), *3* (132, 5.5), *5* (69, 2.9), *7a* (41, 1.7), *7b* tt (205, 8.5), *7b* tc (82, 3.4), *8* (120, 5.0) |
| *1* (1.00) | 56 | 0.5 | – | 0.964 [a] | 0.309 | 0.350 | *3* (1.5, 0.2), *6* (29, 3.0), *20* (33, 3.4), *21* (10, 1.1), *22* (92, 9.5), *23* (37, 3.8), *24* (48, 5.0) |
| *1* [b] (1.50) | 56 | 0.87 | 0.35 | 1.99 | 0.807 | 0.662 | *1* (158, 8.0), *3* (23, 1.2), *5* (16, 0.8), *6* (20, 1.0), *12* [$x=0$] (211, 10.6), *13* [$x=0$] (108, 5.4), *16* (3, 0.2), *17* (14, 0.7), *18* [$x=0$] (55, 2.8) |
| *1* (2.26) | 3.4 | 0.83 | 0.35 | 2.22 | 1.82 | 0.158 | *1* (272, 12.3), *3* (87, 3.9), *5* (64, 2.9), *6* (100, 4.5), *12* [$x=0$] (70, 3.2), *12* [$x=1$] (218, 9.8), *13* and *18* (mixture) (916, 41.0), *19* (56, 2.5) |
| *13* [$x=0$] (1.00) | 28 | 1.0 | – | 1.14 | 0.386 | 0.707 | *1* (61, 5.4), *3* (33, 2.8), *5* (14, 1.2), *6* (14, 1.2) *14* (7.0, 0.6) |
| *13* [$x=0$] (1.01) | 28 | 0.83 | 0.35 | 1.35 | 0.906 | 0.475 | *1* (31, 2.3), *3* (63, 4.7), *5* (0.6, 0.1), *6* (13, 0.9), *13* and *18* (mixture) (202, 15.0), *15* (1.5, 0.1), *16* (7.9, 0.6) |

[a] The mixture of acetylated products was hydrogenated in glacial acetic acid using Pd on charcoal as catalyst prior to the separation. [b] The treatment was carried out at 100 °C for 69 h.

substrate, alkali and sulfide concentrations. The results are summarized in part B of Table 1. In general, the dependence of the formation of degradation and condensation products on the alkali concentration was similar to that found for treatment with alkali alone (Table 1, part A). However, the treatment with white liquor yielded larger proportions of vanillin (*3*) and smaller proportions of 4-vinylguaiacol (*5*) and apocynol (*6*) (Table 2).

The reaction with white liquor afforded, in addition to degradation and condensation products, a variety of hydrosulfides and sulfides *e.g. 12* [$x=0$ or 1] and *13* [$x=0-4$] (see Table 1, part B). Under certain conditions, the total yield of hydrosulfides (*12*, $x=0$ and 1) and sulfides (*13*, *18* and *19*) amounted to 64 % of the starting material consumed. Compound *7* and *8* were not found in the reaction mixture. This is shown in Table 3 which for comparison also contains the results from two treatments of *1* with alkali and of *13* [$x=0$] with alkali and white liquor.

When diconiferyl sulfide (*13*, $x=0$) was treated with sodium hydroxide under the conditions given in Table 3, one third of the resulting reaction mixture consisted of monomeric and oligomeric compounds, the content of this fraction in monomeric components being similar to that obtained by alkaline treatment of *1*. The remaining two thirds of the reaction mixture was polymeric material (Table 3). Treatment of diconiferyl sulfide with white liquor gave the monomeric + oligomeric and the polymeric fractions in about the reverse proportions (Table 3). Again, the qualitative composition of the fraction containing the monomeric and oligomeric compounds resembled that obtained after a similar treatment of *1*. The ratio of sulfidation products to condensation products was found to increase with increasing excess of sulfide ions relative to the amount of *1* used (Table 1, part B). Furthermore, when the ratio of sulfide ion to *1* is increased, di- and oligothio compounds become more dominant over sulfidation products containing one sulfur atom (*cf.* yields of *12* $x=0$ and $x=1$ in Tables 1 and 3).

When *1* was treated with white liquor containing varying amounts of (added) elemental sulfur, simulating polysulfide cooking, vanillin (*3*) and acetoguaiacone (*4*) strongly dominated among the reaction products [9] (Table 4). It is noteworthy that the yield of vanillin first increased and then decreased with increasing sulfur content of the cooking liquor, while the yield of acetoquaiacone first decreased and then increased. Conversely, the yields of vinylguaiacol (*5*) and apocynol (*6*) steadily decreased with increasing amounts of added sulfur.

## DISCUSSION

The reactions of coniferyl alcohol (*1*) with aqueous sodium hydroxide and with white liquor are summarized in Scheme 1.

The alkaline degradation and condensation of *1* and the dependence of the reactions involved in these two processes on the alkali and coniferyl alcohol concentrations can be rationalized by assuming an equilibrium between the substrate (*1*) and the extended quinone methide (*2*).

*At low alkalinities* and/or high substrate concentrations, condensation by conjugate 1,8-addition of the carbanion from coniferyl

*Table 4.* Yields of some reaction products from treatment of *1* (9.2 mg) with polysulfide solutions at 140 °C for 4 h. Concentration of *1* in all runs: 3.4 mM. Analyses by GC and HPLC.

| Concentrations of reagents/M | | | Isolated products Yields/% of theoretical | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[HO^-]$ | $[S^{2-}]$ | $[S^0]$ | *1* | *3* | *4* | *5* | *6* | Sum |
| 0.17 | 0.87 | 0 | 1.3 | 12.1 | – | 1.7 | 2.1 | 17.2 |
| 0.20 | 1.0 | 0.01 | – | 15.8 | 11.3 | 1.5 | 1.9 | 30.5 |
| 0.20 | 1.0 | 0.05 | – | 68.1 | 6.5 | 1.3 | 1.6 | 77.5 |
| 0.17 | 0.87 | 0.1 | – | 55.6 | 11.8 | 0.8 | 0.6 | 68.8 |
| 0.17 | 0.87 | 0.5 | – | 39.9 | 16.6 | – | – | 56.5 |
| 0.17 | 0.87 | 1.0 | – | 29.4 | 19.8 | – | – | 49.2 |

alcohol (*1'*) to the extended quinone methide (*2*)[4–6] is the dominant reaction. This addition is followed by the elimination of a proton and formaldehyde giving rise to *7*.[6] Apparently, the mode of formation of the dimer (*7*) also applies to the formation of the trimer (*8*) (conjugate addition of the carbanion from *7* to *2*). The similarities between $^{13}C$ NMR data of the polymeric fractions and those of *trans,trans-7b* indicate that the further condensation follows the same course.

Instead of eliminating a proton and formaldehyde, the primary product of condensation of 1' and 2 could stabilize by addition of hydroxide ion to the quinone methide moiety, followed in part by ring closure to give a tetrahydropyran derivative.[5] However, under the conditions used in the present work, no such reaction was observed. Apparently, the elimination of a proton and formaldehyde from the primary condensation product successfully competes with the nucleophilic addition of a hydroxide ion (*cf.* also the behaviour of other quinone methide intermediates[10] and of *9*, see below).

The oligomeric and polymeric fractions contain highly unsaturated structures which have undergone an alkaline treatment at elevated temperature. It can be expected that the most stable forms, *i.e.* those having the most extended conjugation, will dominate (*cf.* ratio of *7b* to *7a*, Table 3).

Conversely, *at high alkalinities* and/or low substrate concentrations the formation of the extended quinone methide (*2*) and thus condensation, is suppressed. Instead, more extensive degradation to give mainly 4-vinylguaiacol (*5*) and apocynol (*6*), together with smaller amounts of vanillin (*3*), takes place (Table 2). Apparently, the formation of *5* (and *6*) proceeds by formaldehyde and proton elimination from quinone methide *9*, while *3* is likely to arise by hydroxide ion addition to *9*, followed by alkaline fragmentation of the resulting *10*. These fragmentation steps are supported by the observation that alkaline treatment of authentic *10* yields *3*, *5* and *6* (*cf.* also Ref. *2*).

In the case of treatment with white liquor, the condensation of *1* is outweighed by sulfidation reactions. This is due to a successful competition of sulfide (and polysulfide) ions with carbanion 1' for the extended quinone methide (*2*). Conjugate 1,8-addition of sulfide and disulfide ions to *2* gives coniferyl hydrosulfide (*12*, $x=0$) and coniferyl hydrodisulfide (*12*, $x=1$), respectively, while conjugate 1,8-addition of coniferyl hydrosulfide anions (*12*) to the same enone (*2*) affords diconiferyl sulfides (*13*). The formation of *12* and *13* with $x>0$ may be attributed to the presence in white liquor of small amounts of polysulfide ions. In spite of the low concentration of polysulfide ions and the high concentration of sulfide ions prevailing in white liquor, oligo- and polysulfur compounds are formed preferentially.

By analogy with hydroxide ions, sulfide (and polysulfide) ions may add to *2* in an equilibrium reaction yielding the corresponding coniferyl hydrosulfides (*12*) and sulfides (*13*). The intermediacy of *2* in the sulfidation of *1* is supported by the fact that the aromatic methyl ether of *1*, which cannot give *2*, reacts very slowly with sulfide ions. The small extent of reaction can probably be ascribed to a slow sulfidolytic demethylation to give *1*. Support for the reversibility of the sulfidation reactions was provided by treating *13* ($x=0$) with alkali and white liquor and by identifying essentially the same reaction products as were obtained by corresponding treatments of *1* (Table 3). The competition between sulfidation on the one hand, and condensation and fragmentation on the other, may be rationalized by considering the equilibria between sulfide ions and *2*, and coniferyl hydrosulfides or sulfides to be rapid at the temperature used. This allows ultimate conversion into the stable products (condensation and degradation products).

The preferential degradation of *1* with formation of *3* on treatment with white liquor or – more pronounced – with solutions of polysulfides (see Table 4) may be interpreted[9,5] in terms of a 1,8-addition of polysulfide ions ($SS_x^{2-}$, $x>0$) to *2*, followed by proton abstraction with internal disproportionation, alkaline conversion of thioconiferaldehyde into *14* and alkaline degradation of *14*. Formation of *3* by alkaline degradation of *11* [$x=0$], analogous to the reaction of *10* (see above), appears less likely, since treatment of *11* [$x=0$] or *10* with white liquor for 4 h at 140 °C afforded only about 3–5 % of *3* as compared to 24 % obtained from *1* (Table 2). The dominant alkaline deg-

*Table 5.* Yields of some reaction products from the treatment of *10* (10.1 mg) and *11* [$x=0$] (10.9 mg) with sodium hydroxide and white liquor at 140 °C for 40 min. Concentration of *10* and *11* [$x=0$] in all runs: 3.4 mM. Analyses by GC and HPLC.

| Compound | Concentrations/M | | Isolated products (Yields/% of theoretical) | | | | |
|---|---|---|---|---|---|---|---|
| | $[HO^-]$ | $[S^{2-}]$ | *1* | *3* | *5* | *6* | Sum |
| *10* | 1.0 | – | 8.1 | 3.2 | 22.9 | 23.6 | 57.8 |
| *10* | 0.83 | 0.35 | 2.4 | 1.8 | 23.1 | 23.0 | 50.3 |
| *11* | 0.83 | 0.35 | 1.7 | 0.9 | 21.0 | 20.8 | 44.4 |

radation of *10* and *11* [$x=0$] proceeding *via* the common intermediate *9* leads to *5* and *6* (see Table 5).

The formation of acetoguaiacone (*4*) may be explained by a reaction sequence similar to that proposed for the formation of *3 via 14*.[9,5] This sequence involves 1,6-addition of polysulfide ions to *9* (formation of *11*), followed by proton abstraction, disproportionation, conversion of the thio ketone into the ketone and alkaline degradation of the latter.

In the presence of an excess of polysulfide ions, the degradations to give *3* and *4* (Table 4) following the routes described above appear to compete successfully with the alkaline degradation, affording *5* and *6* as main products, and also with the alkaline condensation, which leads to *7*, *8*, oligomers and polymers. Although no hydropolysulfides (*11* and *12*, $x>0$) or polysulfides (*13*, $x>0$) were found in the mixture, such compounds should be intermediates in the formation of *3* and *4* (*cf.* formation of *3* on treatment of divanillyl disulfide with alkali or white liquor[11]).

## CONCLUSIONS

Coniferyl alcohol and coniferyl alcohol-like intermediates, arising from *p*-hydroxy-arylglycerol-*β*-aryl ether structures in lignins during sulfate pulping, undergo three types of conversion:

(a) alkali-promoted degradation,
(b) alkali-induced condensation and
(c) sulfidation.

The relationships between these reactions and their dependence on the conditions used can be rationalized in terms of competition of hydroxide, sulfide, polysulfide and carbanions for extended quinone methide structures (*e.g.* 2) which are the key intermediates. The additions of hydroxide, sulfide or polysulfide ions to these intermediates are reversible processes, whereas the addition of carbanions (condensation) and the degradation are irreversible. This interpretation explains the effect of high alkalinity which favours degradation at the expense of condensation and of high sulfidity which retards condensation.

The behaviour of extended quinone methides (*e.g.* 2) is thus analogous to that of other intermediates of the quinone methide type arising from phenolic lignin structures during treatment with alkali or white liquor.[3,12–16] Also in these cases, high alkalinity favours degradation and sulfidation constitutes only a temporary protection against condensation and degradation.

## EXPERIMENTAL

*Materials.* Compounds *1*,[17] *1*-arom. Me ether,[17] *5*,[18] *6*,[19] *14*,[20] *20*,[21] *21*[22] and *22*[23] were prepared as previously described. The remaining compounds used in this study were synthesized (*10–13*),[24] or were commercially available (*3*, *4*, *16*).

*Treatments and work-up procedure.* A typical treatment on the *analytical* scale was carried out in the following way: The model compound was dissolved in the cooking liquor which was continuously saturated with nitrogen. An aliquot of the solution (15.0 ml) was transferred into a stainless steel autoclave having a volume of 20 ml. The air was replaced by nitrogen and the autoclave was sealed with a stainless steel cap having a teflon gasket. The autoclave was put into an oil bath at the reaction temperature. After a measured period of time, the reaction was stopped by putting the autoclave into ice-water. An aliquot (10.0 ml) was transferred into a 150 ml beaker, chloroform (10.0 ml) containing internal standard (anthracene) was added and the aqueous solution was neutralized

to pH 6–7 (pH-paper) with 10 % phosphoric acid and extracted. The extraction was repeated twice. The combined chloroform extracts were dried with sodium sulfate, filtered on a Büchner funnel and evaporated under reduced pressure. The residue was acetylated with a mixture of acetic anhydride and pyridine (1:1) (2 ml) by keeping the solution at room temperature overnight. The reaction mixture was then evaporated azeotropically under reduced pressure first with 2 × 20 ml of toluene, and then with 10 ml of chloroform. The residue was dissolved in chloroform to a concentration of about 10 mg/ml. Quantitative analyses were performed in duplicate with an estimated error of ± 5 %.

The treatments on the *preparative* scale were carried out in the same way, except that larger autoclaves (110 ml and 2500 ml) and larger amounts of model compounds, cooking liquor and solvent were used.

Reaction conditions and results are summarized in Tables 1, 2, 4 and 5 for the treatments on the analytical scale and in Table 3 for those on the preparative scale.

*Chromatographic methods.* All solvents were freshly distilled. *Analytical HPLC* was carried out using a Water's ALC/GPC 502/401 chromatograph equipped with an extra pump and a gradient programmer. A UV-detector (280 nm) with an 8 μl cell was used. The samples were separated with ethyl acetate in light petroleum (60–71 °C) on a 4.1 × 150 mm stainless steel column, packed with Partisil 5 μm silica gel, using a concave gradient from 3 % to 43 % with respect to ethyl acetate. The run time of the gradient was 40 min and the total flow 2.0 ml/min. After each run the column was regenerated by washing with pure ethyl acetate and the initial solvent ratio was restored by an appropriate continuous change of the composition of the eluent (about 10 %/min to ensure minimum variation in retention times).

The fractions from preparative separations were analyzed under isocratic conditions with ethyl acetate and light petroleum (60–71 °C) in suitable ratios.

Fractions, eluted with more then 43 % ethyl acetate in light petroleum, were arbitrarily regarded as polymeric. A pentamer, isolated after alkaline condensation of 4-vinylguaiacol [6] was eluted at this solvent strength.

*Preparative LC.* Preparative separations were performed on a Merck Lobar column size B using the Waters chromatograph with suitable gradients of ethyl acetate in light petroleum (60–71 °C) determined in the analytical runs. Typical flow rates were 4.5 and 6.0 ml/min. The fractions were collected during 2 min using an LKB Ultrorac fraction collector. The separations were followed by an LKB Uvicord II UV-detector at 280 nm. The fractions were combined according to the preparative and analytical chromatograms.

Both the analytical and preparative separations were carried out with a run volume of the gradient of about 40 times the void volume. This value was increased as the separations became more difficult.

To obtain pure compounds, the combined fractions from the initial separations were further separated on a Merck Lobar column size A or by recycling on an Altex column 10 × 250 mm packed with LiChrosorb 5 μm using the same solvent system as described above.

*Gas chromatography.* Analytical separations were carried out with a Perkin-Elmer (F-17) gas chromatograph. A 6 mm × 2 m stainless steel column packed with 3 % SE-30 on Chromosorb HP 80–110 mesh was used. A suitable temperature program was found to be 175–280 °C, 7.5 °C/min. Determination of the yields of acetylated phenols was achieved using a Philips DP 88 integrator and anthracene as internal standard.

*Spectroscopy.* $^1$H NMR spectra were run on either a Perkin-Elmer R 12 60 MHz-instrument or a Varian HA-100 100 MHz-instrument. If necessary, coupling between protons was confirmed by decoupling experiments.

The *cis*- and *trans*-configurations of compounds *7b* and *8* were assigned on the basis of the coupling constants observed. Compounds *7b* (*trans-trans* and *trans-cis*) exhibited spectra of the ABCDX$_2$ type and compounds *8*, *12*, *13*, *18* and *19* spectra of the ABX$_2$ type. Some of the yields of the oligomeric products (*e.g. 7*, *13* and *18*) were determined from the $^1$H NMR spectra of mixtures in the following way: A part of the mixture was separated and the $^1$H NMR spectra of the isolated components were determined. The spectra showed methylene signals having characteristic chemical shifts. On the basis of these spectra the methylene signals in the spectrum of the original mixture were assigned to individual compounds and the yields could then be calculated.[55]

$^{13}$C NMR spectra were run on a Varian CFT-20 spectrometer.

Mass spectra were run on a Finnigan 3200 F instrument with data system 6000 or an LKB 9000 instrument. Samples were introduced to the mass spectrometer by a direct inlet system or a GC equipped with a SE-30 glass capillary column purchased from LKB. The spectra were taken using an ion energy of 20 or 70 eV.

## Product identification

trans,trans-*1,5-Bis(4-acetoxy-3-methoxyphenyl)-1,3-pentadiene (diacetate of* 7b*)*, amorphous, MS *m/e* (rel. int.): 396 (M, 2.5), 354 (M–42, 1.5), 312 (M–84, 0.8), 180 (57), 175 (36), 150 (68), 138 (100), 137 (65), 123 (37). $^1$H NMR: $\delta$ 2.28 [s, 6 H, 2 × $\phi$ OAc], 3.45 [H-5; d, 2 H, $J_{4,5}$ 6 Hz], 3.79 [s, 6 H, 2 × $OCH_3$],

~5.94 [H-4; dt, 1 H, ol, $J_{3,4}$ 15 Hz, $J_{4,5}$ 6 Hz], ~6.23 [H-3; dd, 1 H, ol, $J_{2,3}$ 9 Hz, $J_{3,4}$ 15 Hz], ~6.45 [H-1; d, 1 H, ol, $J_{1,2}$ 15 Hz], ~6.71 [H-2; dd, 1 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 9 Hz], 6,67–7.15 [m, 6 H, ar]. $^{13}$C NMR: $\delta$ 20.6 ($CH_3$ in acetate), 40.0 (C 5), 55.9 ($OCH_3$), 110.0 (C 2′), 112.7 (C 2″), 119.0 (C 6′), 120.7 (C 6″), 122.7 and 122.9 (C 5″, C 5′), 129.0 (C 4), 130.4 (C 3), 131.6 (C 1), 133.3 (C 2), 136,4 (C 1′), 138.1 (C 1″), 138.8 and 139.0 (C 4′, C 4″), 151.1 and 151.2 (C 3′, C 3″), 170.0 and 171.1 (C=O in acetate).

trans,cis-*1,5-Bis(4-acetoxy-3-methoxyphenyl)-1,3-pentadiene (diacetate of* 7b*)*, amorphous, MS *m/e* (rel. int.): 396 (M, 1.5), 354 (M−42, 0.2), 312 (M−84, 0.3), 180 (63), 175 (40),150 (31), 138 (100), 137 (65), 123 (27). $^1$H NMR: $\delta$ 2.29 [s, 6 H, 2×$\phi$ OAc], 3.63 [H-5; d, 2H, $J_{4,5}$ 7 Hz], 3.79 [s, 3 H, $OCH_3$], 3.84 [s, 3 H, $OCH_3$], ~5.68 [H-4; dt, 1 H, ol, $J_{3,4}$ 11 Hz, $J_{4,5}$ 7 Hz], ~6.30 [H-3; dd, 1 H, ol, $J_{2,3}$ 10 Hz, $J_{3,4}$ 11 Hz], ~6.57 [H-1; d, 1 H, ol, $J_{1,2}$ 15 Hz], ~7.05 [H-2; dd, 1 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 10 Hz], 6.68–7.00 [m, 6 H, ar].

cis,trans-*1,7-Bis(4-acetoxy-3-methoxyphenyl)-4-(4-acetoxy-3-methoxy-benzylidene)-2,5-heptadiene (triacetate of* 8*)*, amorphous, MS *m/e* (rel. int.): 600 (M, 1.5), 558 (M−42, 5), 516 (M−84, 2), 474 (M−126, 1), 223 (8), 195 (19), 181 (18), 177 (15), 161 (23), 150 (23), 137 (100). $^1$H NMR: $\delta$ 2.29 [s, 9 H, 3×$\phi$ OAc], 3.45 [H-7; d, 2 H, $J_{6,7}$ 6 Hz], 3.63 [H-1; d, 2 H, $J_{1,2}$ 7 Hz], 3.80 [s, 6 H, 2×$OCH_3$], 3.85 [s, 3 H, $OCH_3$], 5.68 [H-2; dt, 1 H, ol, $J_{1,2}$ 7 Hz, $J_{2,3}$ 11 Hz], 6.19 [H-6; dt, 1 H, ol, $J_{5,6}$ 14 Hz, $J_{6,7}$ 6 Hz], 6.35 [H-3; d, 1 H, ol, $J_{2,3}$ 11 Hz], 6.39 [H-5; d, 1 H, ol, $J_{5,6}$ 14 Hz], 6.55–7.13 [m, 10 H, ol, ar].

*Acetyl-*trans*-3-(4-acetoxy-3-methoxyphenyl)-2-propenyldisulfide (diacetate of* 12 [x=*1])*, m.p 101–102 °C; MS *m/e* (rel. int.): 312 (M, 0.15), 205 (20), 163 (48), 131 (100). $^1$H NMR: $\delta$ 2.27 [s, 3 H, $\phi$ OAc], 2.37 [s, 3 H, SAc], 3.48 [H-3; d, 2 H, $J_{2,3}$ 7 Hz], 3.82 [s, 3 H, $OCH_3$], 6.07 [H-2; dt, 1 H, ol, $J_{1,2}$ 15 Hz, $J_{,23}$ 7 Hz], 6.38 [H-1; d, 1 H, ol, $J_{1,2}$ 15 Hz], 6.92 [s, 3 H, ar].

trans, trans-*Bis[3-(4-acetoxy-3-methoxyphenyl)-2-propenyl] disulfide (diacetate of* 13 [x=*1])*, amorphous, MS *m/e* (rel. int.): 474 (M, 0.07), 205 (31), 195 (6), 163 (81), 131 (100). $^1$H NMR: $\delta$ 2.28 [s, 6 H, 2×$\phi$ OAc], 3.47 [H-3; d, 4 H, $J_{2,3}$ 7 Hz], 3.82 [s, 6 H, 2×$OCH_3$], 6.13 [H-2; dt, 2 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 7 Hz], 6.43 [H-1; d, 2 H, ol, $J_{1,2}$ 15 Hz], 6.93 [s, 6 H, ar]. $^{13}$C NMR: $\delta$ 20.6 ($CH_3$ in acetate), 42.4 (C 3), 55.9 ($OCH_3$), 110.4 (C 2′), 119.1 (C 6′), 123.0 (C 5′), 124.9 (C 2), 133.2 (C 1), 135.8 (C 1′), 139.7 (C 4′), 151.4 (C 3), 168.8 (C=O in acetate).

trans, trans-*Bis-[3-(4-acetoxy-3-methoxyphenyl)-2-propenyl] oligosulfides (diacetates of* 13 [x=*2,3,4])*, amorphous, MS *m/e* (rel. int.): 570 (M, $0.5\times10^{-2}$), 538 (M, $1\times10^{-2}$), 506 (M, $1.5\times10^{-2}$), 205 (21), 195 (7), 163 (100), 131 (98). $^1$H NMR: $\delta$ 2.29 [s, 6 H, 2×$\phi$ OAc], 3.60–3.77 [H-3; d, d, d, 4 H, $J_{2,3}$ 7 Hz], 3.82 [s, 6 H, 2×$OCH_3$], 6.17 and 6.18 [H-2; dt, 2 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 7 Hz], 6.50 and 6.53 [H-1; d, 2 H, ol, $J_{1,2}$ 15 Hz], 6.94 [s, 6 H, ar]. $^{13}$C NMR: $\delta$ 20.4 ($CH_3$ in acetate), 41.3 and 42.1 (C 3), 55.7 ($OCH_3$), 110.2 (C 2′), 119.1 (C 6′), 122.7 (C 5′), 123.5 and 124.2 (C 2), 133.4 and 134.2 (C 1), 135.5 and 135.7 (C 1′), 139.5 (C 4′), 151.1 (C 3′), 168.7 (C=O in acetate).

cis,trans-*Bis[3-(4-acetoxy-3-methoxyphenyl)-2-propenyl] oligosulfides (diacetates of* 13 [x=*2,3* ]*)*, amorphous, MS *m/e* (rel. int.): 538 (M, 0.05), 506 (M, 0.05), 205 (25), 195 (13), 163 (98), 151 (11), 131 (100). $^1$H NMR: $\delta$ 2.29 [s, 6 H, 2×$\phi$ OAc], 3.58–3.78 [H-3, H-3′; m, 4 H], 3.82 [s, 6 H, 2×$OCH_3$], 5.83 [H-2′; dt, 1 H, ol, $J_{1',2'}$ 11 Hz, $J_{2',3'}$ 8 Hz], 6.16 [H-2; dt, 1 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 7 Hz], 6.50 [H-1; d, 1 H, ol, $J_{1,2}$ 15 Hz], 6.64 [H-1′; d, 1 H, ol, $J_{1',2'}$ 11 Hz], 6.95 [s, 6 H, ar].

*1-(4-Acetoxy-3-methoxyphenyl)-ethanethioacetate (diacetate of* 17*)*, amorphous, MS *m/e* (rel. int.): 268 (M, 2), 226 (M−42, 9), 151 (76), 150 (M−42−76, 100), 135 (60). $^1$H NMR: $\delta$ 1.66 [H-2; d, 3 H, $J_{1,2}$ 7 Hz], 2.29 [s, 3 H, $\phi$ OAc], 2.36 [s, 3 H, SAc], 3.81 [s, 3 H, $OCH_3$], 4.71 [H-1; q, 1 H, $J_{1,2}$ 7 Hz], 6.91 [s, 3 H, ar].

*1-(4-Acetoxy-3-methoxyphenyl)-ethyl-*trans*-3-(4-acetoxy-3-methoxyphenyl)-2-propenylsulfide (diacetate of* 18 [x=*0])*, amorphous, MS *m/e* (rel. int.): 430 (M, 3), 388 (M−42, 11), 205 (6), 195 (11), 183 (3), 163 (53), 151 (100), 131 (23). $^1$H NMR: $\delta$ 1.52 [H-2′; d, 3 H, $J_{1',2'}$ 7 Hz], 2.27 [s, 6 H, 2×$\phi$ OAc], 3.11 [H-3; d, 2 H, $J_{2,3}$ 6 Hz], 3.79 and 3.81 [2 s, 2×3 H, 2×$OCH_3$], 3.93 [H-1′; q, 1 H, $J_{1',2'}$ 6 Hz], 6.06 [H-2; dt, 1 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 6 Hz], 6.23 [H-1; d, 1 H, ol, $J_{1,2}$ 15 Hz], 6.91 [s, 6 H, ar].

*1-(4-Acetoxy-3-methoxyphenyl)-ethyl-*trans*-3-(4-acetoxy-3-methoxyphenyl)-2-propenyl oligosulfides(diacetates of* 18 [x>*0])*, amorphous, MS *m/e* (rel. int.): 205 (23), 195 (19), 163 (35), 150 (100), 137 (44), 135 (35), 123 (53). $^1$H NMR: $\delta$ 1.68 [H-2′; d, 3 H, $J_{1',2'}$ 7 Hz], 2.29 [s, 6 H, 2×$\phi$ OAc], 3.61 and 3.71 [H-3; d, 2 H, $J_{2,3}$ 7 Hz], 3.81 and 3.82 [s, 6 H, 2×$OCH_3$], 4.25 and 4.35 [H-1′; q, 1 H, $J_{1',2'}$ 7 Hz], 6.15 and 6.16 [H-2; dt, 1 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 7 Hz], 6.49 and 6.51 [H-1; d, 1 H, ol, $J_{1,2}$ 15 Hz], 6.92 and 6.95 [2 s, 2×3 H, ar].

*3-[1-Acetoxy-1-(4-acetoxy-3-methoxyphenyl)]-propyl-*trans*-3-(4-acetoxy-3-methoxyphenyl)-2-propenyl oligosulfides(triacetates of* 19 [x=*1,2,3])*, amorphous, MS *m/e* (rel. int.): 598 (M, $0.6\times10^{-2}$), 566 (M, $0.1\times10^{-2}$), 534 (M, $0.6\times10^{-2}$), 205 (23), 195 (22), 163 (84), 131 (100). $^1$H NMR: $\delta$ 2.07 [s, 3 H, ROAc], 2.29 [s, 6 H, 2×$\phi$ OAc], 2.14–2.46 [H-2′; m, 2 H], 2.85 and 2.91 [H-3′; t, 2 H, $J_{2',3'}$ 7 Hz], 3.59–3.86 [H-3; m, 2 H], 3.83 [s, 6 H, 2×$OCH_3$], 5.87 [H-1′; t, 1 H, $J_{1',2'}$ 7 Hz], 6.16 [H-2; dt, 1 H, ol, $J_{1,2}$ 15 Hz, $J_{2,3}$ 7 Hz], 6.52 [H-1; d, 1 H, ol, $J_{1,2}$ 15 Hz], 6.94 and

6.97 [s, 6 H, ar]. $^{13}C$ NMR: $\delta$ 20.7 ($CH_3$ in aromatic acetate), 21.2 ($CH_3$ in aliphatic acetate), 34.9, 35.4 and 35.7 (C 2′, C 3′), 41.3 and 41.8 (C 3), 55.9 ($OCH_3$), 74.0 (C 1′), 110.3 (C 2″), 110.9 (C 2‴), 118.8 (C 6‴), 119.3 (C 6″), 122.9 (C 5″, C 5‴), 124.0 (C 2), 133.8 (C 1‴), 134.1 (C 1), 135.7 (C 1″), 138.6 (C 4‴), 139.6 (C 4″), 151.2 (C 3″, C 3‴), 168.9 (C=O in aromatic acetate), 170.0 (C=O in aliphatic acetate).

*1,5-Bis(4-acetoxy-3-methoxyphenyl)-pentane (diacetate of 23)*, amorphous, MS *m/e* (rel. int.): 400 (M, 0.3), 358 (8), 316 (34), 151 (7), 137 (100). $^1H$ NMR: $\delta$ 1.13–1.86 [H-2, H-3, H-4; m, 6 H], 2.26 [s, 6 H, 2×$\phi$ OAc], 2.57 [H-1, H-5; t, 4 H, $J_{1,2}=J_{4,5}$ 7 Hz], 3.74 [s, 6 H, 2×$OCH_3$], 6.53–7.00 [m, 6 H, ar].

*1,7-Bis(4-acetoxy-3-methoxyphenyl)-4-(4-acetoxy-3-methoxybenzyl)-heptane (triacetate of 24)*, amorphous, MS *m/e* (rel. int.): 606 (M, 5), 564 (M−42, 100), 522 (M−84, 95), 480 (M−126, 73), 330 (18), 151 (55), 150 (20), 137 (31), 124 (16). $^1H$ NMR: $\delta$ 1.08–2.77 [m, 15 H], 2.26 [s, 9 H, 3×$\phi$ OAc], 3.78 [s, 9 H, 3×$OCH_3$], 6.56–7.08 [m, 9 H, ar].

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