

Lignin Chromophores. Part II.* The Behaviour of 2,4'- and 4,4'-Dihydroxystilbene Structures towards Oxygen—Alkali**

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The oxidation of 2,4'- and 4,4'-dihydroxystilbene structures, formed in lignins during alkaline delignification processes, has been studied by reacting appropriate model compounds with oxygen in alkaline media. The formation of the different reaction products is outlined in Scheme 1, which shows quinonemethide radicals as common intermediates, arising by a one-electron oxidation step. Quinonemethide radicals from 2,4'-dihydroxystilbenes (VIIIb) undergo ring closure to give 2-arylcoumaran-3-yl radicals (IX, XI) which dimerise (X) or are oxidised to 2-arylcoumarones (XII). Quinonemethide radicals from 4,4'-dihydroxystilbenes (XVb), however, undergo a further one-electron oxidation yielding 4,4'-stilbenequinones (XVI). The latter are subsequently oxidised to benzils (XIV). The significance of hydroxystilbene structures as potential chromophoric systems in alkali and sulfate lignins is briefly discussed.

In Part I of this series¹ the formation of 2,4'- and 4,4'-dihydroxystilbene structures in lignins during pulping has been summarised. Depending on the conditions employed, these stilbene groupings may constitute intermediate or final structures.²

Some years ago, it was reported that 2,4'-dihydroxystilbenes during alkaline pulping in the presence of oxygen are extensively converted into 2-arylcoumarones.² Recently,³

this conversion has been interpreted in terms of a two-stage oxidation, proceeding *via* radicals of the quinonemethide type (*cf.* also Ref. 4).

The aim of the present work was to elucidate the action of oxygen in alkali on 2,4'-dihydroxystilbene structures and on the 4,4'-dihydroxy isomers.

RESULTS AND DISCUSSION

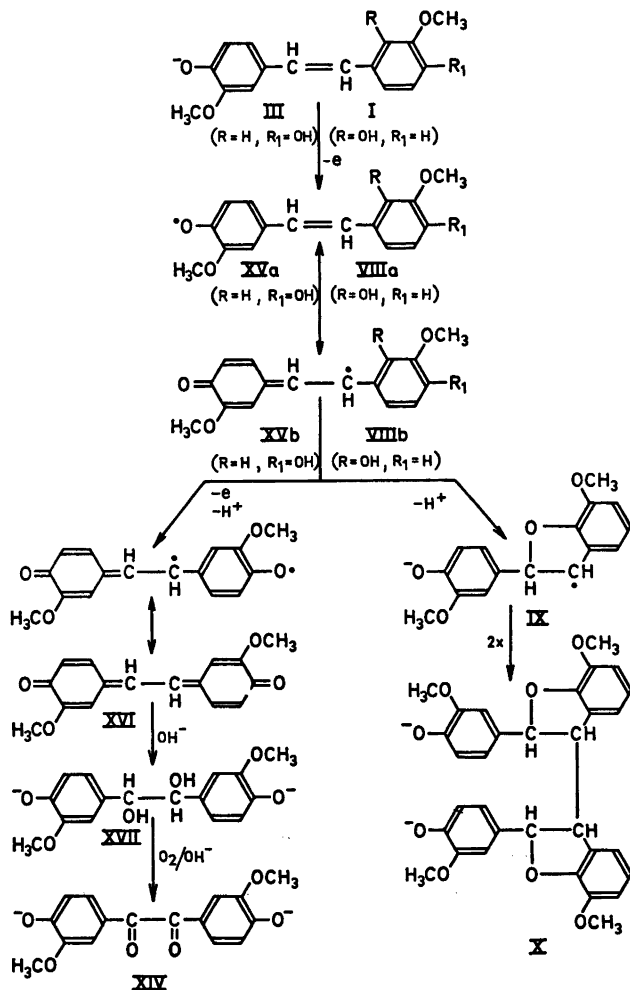
The suggested course of oxidation of the two types of dihydroxystilbenes is outlined in Scheme 1.

Oxidation of 2,4'-dihydroxy-3,3'-dimethoxystilbene. After treatment of the diacetate of stilbene I (II) with 2 M sodium hydroxide at 100 °C in the presence of oxygen for 3 h, acetylation of the resulting reaction mixture and separation of the components by column chromatography (see Experimental), the main reaction product was obtained in a crystalline state, m.p. 185–187 °C. The NMR-spectrum, the molecular ion (*m/e* 626) and the mass spectral fragmentation were in accordance with the data for the diacetate of the dimer X. It is suggested that compound X arises by the following route (see Scheme 1): Oxidation of I, formed from II by alkaline hydrolysis, gives the 4'-phenoxy radical (VIIIA). This radical, in its mesomeric quinonemethide form VIIIb, undergoes ring closure to give the 2-arylcoumaran-3-yl radical IX (*cf.* Ref. 3). The latter finally dimerises yielding compound X. Alternatively, the quinonemethide radical

* Part I, see Ref. 1.

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Scheme 1. Oxidation of 2,4'- and 4,4'-dihydroxystilbenes with oxygen in alkali.

VIIIb dimerises first to give a *bis*-quinone-methide which then by twofold ring closure yields compound X. The formation of *bis*-quinonemethides by oxidation of appropriate hydroxystilbenes (e.g. VII) with one-electron oxidants (e.g. dichloro-dicyanobenzoquinone, DDQ) has been reported earlier.⁵

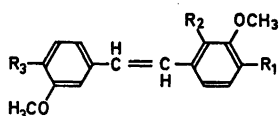
It is worthy of note that under similar conditions radical XI behaves differently from radical IX, the former being oxidised to an arylcoumarone derivative (XII).³ Dimerisation of XI appears to be excluded presumably owing to the steric hindrance caused by the *trans*-arrangement⁶ of the methyl and aryl sub-

stituents on the coumaran ring in XI.

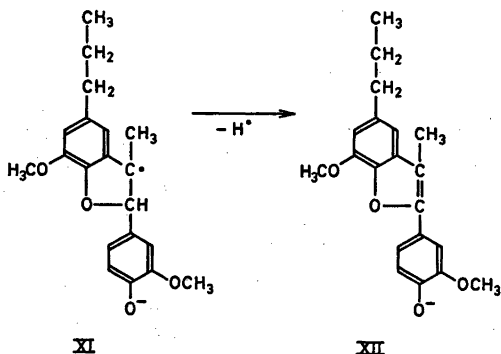
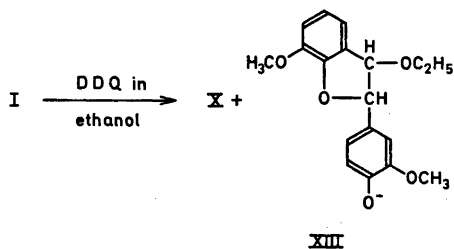
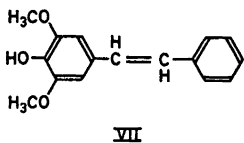
The reaction sequence proposed for the formation of compound X is based on the following experimental evidence:

The intermediacy of 4'-phenoxy radicals was supported by treating compound VI, in which formation of this type of radical is blocked by etherification of the 4'-hydroxyl group, under similar oxidative conditions. No dimeric product was formed and the starting material was recovered in almost quantitative yield in two stereoisomeric forms (TLC, NMR and mass spectra).

The intermediate formation of radical IX



- I $R_1 = H$, $R_2 = R_3 = OH$
 II $R_1 = H$, $R_2 = R_3 = OOCCH_3$
 III $R_1 = R_3 = OH$, $R_2 = H$
 IV $R_1 = R_3 = OOCCH_3$, $R_2 = H$
 V $R_1 = H$, $R_2 = OH$, $R_3 = OCH_3$
 VI $R_1 = H$, $R_2 = OOCCH_3$, $R_3 = OCH_3$



and/or VIIIb during oxidation was demonstrated as follows: The 2,4'-dihydroxystilbene derivative I, when oxidised with an equimolar amount of DDQ in ethanol for 30 min, gave, in addition to compound X, isolated as the di-

acetate (62 %), another major product (about 12 %) which was identified as the ethoxy-substituted arylcoumaran derivative XIII. It is, thus, concluded that formation of the latter, either by combination of radical IX or its quinonemethide precursor VIIIb with a solvent radical, or by addition of ethanol to the appropriate carbonium ion of the quinonemethide type, competes with dimerisation.

In addition to the dimer (X), small amounts of vanillin, guaiacol, and of three further (unidentified) compounds were detected in the form of their acetates by GLC-MS (*cf.* also Ref. 3).

Oxidation of 4,4'-dihydroxy-3,3'-dimethoxystilbene. Similar oxidative treatment of compound IV and working-up of the resulting reaction mixture gave the acetates of the following compounds: vanillil (XIV, main product), vanillin, guaiacol and acetoguaiacone, as well as a polymeric fraction. The acetates were identified by their melting points, NMR- and mass spectra.

It is suggested that the main product, vanillil (XIV), is formed as shown in Scheme 1.

In the first one-electron oxidation step, a stilbene semiquinone (phenoxy radical XVa and its mesomeric form, the quinonemethide radical XVb) is generated. This step is common to the oxidation of both types of dihydroxystilbenes investigated here. However, whereas the quinonemethide radical VIIIb derived from the 2,4'-dihydroxystilbene I cyclises (formation of IX) and dimerises (formation of X), the radical (XVb) derived from the 4,4'-dihydroxyisomer (III) undergoes a second one-electron oxidation, giving rise to the 4,4'-stilbenequinone XVI. Addition of hydroxyl ions to this *bis*-quinonemethide results in the formation of the anion of hydrovanilloin (XVII) which is then oxidised to vanillil (XIV).

The proposed intermediacy of stilbenequinone XVI and hydrovanilloin (XVII) in the formation of vanillil (XIV) was supported by the fact that XVI and XVII, when treated under similar conditions as used for the reaction of III, afforded XIV in high yields. Treatment of hydrovanilloin (XVII) with alkali in an atmosphere of nitrogen did not yield any XIV.

Vanillil (XIV) was found many years ago⁷ in the reaction mixture obtained after oxidation of liginosulfonates by cupric oxide. The

compound was considered to arise from $C_{\alpha}-C_{\alpha}$ linked lignin units by oxidative cleavage of the rest of the side chains.⁷⁻⁹ However, the 1,2-diarylpropane-1,3-dihydroxy structures, shown to be present in lignins,¹⁰⁻¹² constitute a more likely source of vanillil.¹³ Their conversion into 4,4'-dihydroxy-3,3'-dimethoxystilbene (III) by the action of alkali has been previously^{11,12} illustrated in model experiments and the oxidation of this stilbene with oxygen in alkali *via* the corresponding stilbenequinone to vanillil (*cf.* Ref. 14) has now been demonstrated. In contrast to its behaviour towards cupric oxide and alkali,⁷⁻⁹ vanillil when treated with oxygen-alkali under the aforementioned conditions does not undergo benzilic rearrangement and oxidative decarboxylation.

Vanillin, the other product formed in appreciable amounts (29 %) from compound IV on the oxidative treatment, presumably arises mainly by oxidative cleavage of the stilbene double bond.¹⁵ However, the formation of guaiacol and acetoguaiacol in minor amounts (3 and 4 %, respectively) indicates that alkaline (non-oxidative) fragmentation may also operate (*cf.* the behaviour of compound II and Ref. 3)

CONCLUSIONS

From the results of the model experiments reported in this work, it may be concluded that hydroxystilbene structures generated in lignins during various pulping processes^{2,3} are extensively oxidised by oxygen in alkaline media. Thus, 2,4'-dihydroxystilbene structures yield either arylcoumaran structures by coupling of the intermediate β -radicals with each other or with other radical species, or arylcoumarone structures by oxidation of the β -radical intermediates. 4,4'-Dihydroxystilbene structures are converted to benzil structures by oxidation of the β -radical and stilbenequinone intermediates.

These conversions of dihydroxystilbenes in alkaline media require the presence of oxygen. If air (oxygen) is replaced by nitrogen or if the treatment is carried out in aqueous alkali containing sulfide ions ("white liquor"),* the

unchanged dihydroxystilbene can be recovered in a high yield. The isolation of the arylcoumarone XII after treatment of dihydrodehydro-diisoeugenol with white liquor reported previously³ could only be reproduced if a sufficient amount of oxygen was present in the solution during the treatment.

The results imply that the oxidation of the hydroxystilbene structures formed in lignins during various pulping processes will be extensive during alkali pulping and, particularly, during oxygen-alkali pulping. During sulfate pulping, however, the cooking liquor usually does not contain sufficient oxygen (*cf.* also Refs. 16 and 17) to bring about extensive oxidation of hydroxystilbene structures. The latter may therefore be expected to survive this pulping treatment. Assuming phenoxy- and β -radicals are formed in the first oxidation step by the action of oxidants other than oxygen (*e.g.* quinonoid structures¹⁸), they would presumably be reduced to the initial hydroxystilbene structures by the reducing sulfur compounds present in the white liquor. In fact, spectrophotometric data indicating the presence of hydroxystilbene structures in lignins from sulfate spent liquors have been reported^{18,19} and stilbene III has recently²⁰ been isolated from a sulfate spent liquor.

The products of oxidation in alkaline media identified in the present work do not include stilbenequinones regarded as possible contributors to the color of sulfite pulps²¹ and bisulfite pulps.²² During the oxidation of 4,4'-dihydroxystilbenes in alkaline solution, stilbenequinone chromophores only appear as intermediates, whereas similar oxidation of 2,4'-dihydroxystilbenes does not even proceed *via* stilbenequinones (*cf.* also Ref. 4). For all these reasons it seems doubtful whether hydroxystilbene structures are converted to chromophoric systems of the stilbenequinone type during the sulfate cook. If such chromophoric systems actually are present in the residual lignins of sulfate pulps or in lignins obtained from sulfate spent liquors, they probably have been formed by autoxidation of the isolated products rather than by oxidation during the pulping process.

Sulfate pulps and sulfate lignins are light-yellow immediately after isolation from the pulping liquor. On exposure to air a rapid

* The term "white liquor" refers to a solution of NaOH (3.5 g) and $Na_2S \cdot 9H_2O$ (3.1 g) in water (100 ml).

discolouration takes place, the products assuming the well-known brown colour. Pulps and lignins produced by treatment of wood with oxygen-alkali are significantly lighter in colour than technical kraft pulps and lignins compared at the same degree of delignification. This difference in colour could be explained, at least partly, by the presence of dihydroxystilbene intermediates. Such structures would remain unaffected during sulfate pulping and afford stilbenequinone chromophores on subsequent exposure to air, whereas treatment with oxygen-alkali would remove them by oxidation to arylcoumaran, arylcoumarone and benzil structures.

These oxidation products, like the parent dihydroxystilbenes, do not constitute chromophoric systems *per se*. However, hydroxy-substituted stilbene, arylcoumarone and benzil structures could possibly explain part of the absorption of alkali and sulfate lignins in the near ultraviolet region (*cf.* Refs. 18 and 19). The conjugated double bond in the first two structures and the carbonyl groups in the last structures may function as efficient sensitising groups during the light-induced discoloration and degradation of pulps.^{23,24}

EXPERIMENTAL

Melting points are corrected. Evaporations were carried out under reduced pressure.

Thin-layer (TLC) and column chromatography. The reaction mixtures and the various fractions from the column chromatographic separations were investigated by thin-layer chromatography using silica gel HF₂₅₄ (E. Merck, Darmstadt) as adsorbant and light petroleum-ethyl acetate (2:1) as solvent system. Vanillin dissolved in conc. sulfuric acid served as developer. The preparative separations were carried out by column chromatography on silicic acid (Merck 60, 120-230 mesh) using the same solvent system.

NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer using deuteriochloroform as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts (δ values) are given in ppm downfield from TMS.

Mass spectra (MS) were run on a Perkin-Elmer 270 instrument at 20 eV using the direct inlet system or the combination with a gas-liquid chromatograph (GLC); column: silicon OV-1 (3%) on Gas Chrom Q washed with conc. hydrochloric acid and treated with dimethyl-

dichlorosilane. The temperature of the probe heater was between 110 and 230 °C; detector: 280 °C; injector: 180 °C.

UV spectra were recorded on a DK-2 Beckman spectrophotometer.

Model compounds

The hydroxystilbenes I, III, V and acetoxy-stilbenes II, IV, and VI used in this study were prepared as described in Part I¹ of this series. Stilbenequinone XVI was obtained by oxidation of stilbene III with DDQ⁵ (see below). Hydrovanilloin (XVII) was prepared by electrolytic reduction of vanillin according to Ref. 25.

Treatment of the model compounds with oxygen-alkali. The model compound in the form of the acetate (100-300 mg) was heated in 2 M sodium hydroxide (3-10 ml) in the presence of oxygen for 3 h at the temperatures given below. After neutralisation with carbon dioxide, the solution was repeatedly extracted with ethyl acetate. The combined extracts were dried (Na₂SO₄) and evaporated. The residue was acetylated with acetic anhydride-pyridine and the resulting mixture of acetylated compounds was separated into its components by preparative column chromatography and/or gas-liquid chromatography. The acetates were identified by their melting points, elemental analyses, NMR and mass spectra.

Compound II (300 mg, *trans*-form, m.p. 138-139 °C), in 2 M sodium hydroxide (10 ml), was heated at 100 °C (steam bath) for 3 h, a slow stream of oxygen passing through the solution. The reaction mixture was worked up and separated as described above. The following fractions were obtained from the column:

(1) Monomeric acetylated phenols (15 mg), consisting mainly of vanillin acetate and guaiacol acetate (GLC-MS).

(2) A crystalline fraction (183 mg, 61%) which after recrystallization from methanol was identified as *bis*-[2-(4'-acetoxy-3'-methoxyphenyl)-7-methoxycoumaran-3]-yl (diacetate of X), m.p. 185-187 °C. (Found: C 68.87; H 5.54; O 25.47. C₃₈H₃₄O₁₀ (626.36) requires: C 69.03; H 5.43; O 25.54). NMR: δ 7.00-6.10 (m, 12 H, arom. H), 5.45 (d, 2 H, 2 H_a), 4.30-3.65 (m, 2 H, 2 H _{β}), 3.89 (s, 6 H, 2 arom. OCH₃), 3.58 (s, 6 H, 2 arom. OCH₃), 2.20 (s, 6 H, 2 arom. OCCH₃). MS: 626 (10, M⁺), 584 (5), 313 (20), 271 (100), 243 (15).

(3) Mixture containing the diacetate of X and unknown reaction products (26 mg).

(4) Polymeric fraction (about 70 mg).

Compound VI (300 mg, *trans*-form, m.p. 103-104 °C) similarly treated gave a mixture of the two stereoisomers of the starting material, indicating isomerisation *via* the *o*-quinone-methide radical or the *o*-quinonemethide carbanion. One of the isomers was obtained in crystalline form. (Found: C 69.48; H 6.06;

O 24.42. $C_{19}H_{20}O_5$ (328.19) requires: C 69.53, H 6.09, O 24.38). The two forms exhibited almost identical mass spectra MS: 328 (24, M^+), 286 (100), 271 (20) but migrated at sufficiently different rates to allow separation of the mixture by TLC and preparative column chromatography. The crystalline isomer turns blue and the amorphous greyish-brown on spraying with vanillin-conc. sulfuric acid, followed by heating.

Investigation of the crude acetylated reaction mixture by GLC-MS revealed the presence of traces of the acetates of vanillin, acetoguaiacone and guaiacol.

Compound IV (300 mg, *trans*-form, m.p. 228–229 °C) in oxygen-saturated 2 M sodium hydroxide (10 ml) was heated in an autoclave at 180 °C. Column chromatography of the acetylated reaction mixture afforded in the order given: (1) guaiacol acetate (6.9 mg, 3 %); (2) vanillin acetate (67.3 mg, 29 %); (3) acetoguaiacone acetate (9.3 mg, 4 %); (4) *4,4'*-diacetoxy-3,3'-dimethoxybenzil (vanillil diacetate, diacetate of XIV); 116 mg, 50 %; m.p. 138–139 °C. NMR: δ 7.76–6.96 (m, 6 H, arom. H), 3.87 (s, 6 H, 2 arom. OCH_3), 2.28 (s, 6 H, 2 arom. $OCCH_3$); λ_{max} (methanol) 262 nm (ϵ , 25,700) and 318 nm (shoulder (ϵ , 15,700)); (5) Polymeric material (32.5 mg, 14 %).

After treatment of compound IV (150 mg) with white liquor (10 ml) at 180 °C and usual working-up, starting material (100 mg, m.p. 224–227 °C) was recovered. GLC-MS analysis of the acetylation mixture after removal of the starting material showed the presence of small amounts of catechol diacetate, guaiacol acetate and of an unknown compound (M^+ 306).

Compound II and the 2,4'-dihydroxystilbene derivative obtained from dihydro-dehydro-diisoeugenol²⁶ were likewise resistant to treatment with white liquor.

3,3'-Dimethoxy-4,4'-stilbenequinone (XVI) (50 mg) and *hydrovanilloin* (XVII) (50 mg) were similarly treated with oxygen-saturated 2 M sodium hydroxide (6 ml) at 180 °C. In both cases, usual working-up provided high yields (about 90 %) of the diacetate of vanillil (XVI), identical by m.p. (137–138 °C) as well as NMR and mass spectra with the product obtained from compound IV.

Treatment of XVII with nitrogen-saturated 2 M sodium hydroxide gave a mixture of phenolic substances which did not contain any detectable amount of compound XIV (TLC).

Oxidation of hydroxystilbenes with DDQ

Compound I^{1,4} (m.p. 133.5–134.5 °C) (100 mg) was dissolved in anhydrous ethanol (5 ml). An equimolar amount of DDQ (85.2 mg, 0.37

mmol) was added to the solution at room temperature with stirring. After 30 min, the solution was evaporated and the resulting oily residue (210 mg) was chromatographed on a column of silica gel. The first fraction gave an amorphous product which on the basis of its NMR- and mass spectra was identified as *2-(4'-hydroxy-3'-methoxyphenyl)-3-ethoxy-7-methoxycoumaran* (XIII) NMR: δ 6.92–6.70 (m, 6 H), 5.47 (d, 1 H), 4.98 (d, 1 H), 3.97–3.52 (q, 2 H) 3.83 (s, 3 H), 3.75 (s, 3 H), 1.22 (t, 3 H). MS: 316 (32, M^+), 287 (14), 285 (15), 270 (100, $M - C_2H_5OH$).

The second fraction contained compound X, identical with the main product of oxidation from compound II using oxygen in alkali as oxidant. It was characterised as the diacetate by m.p., NMR and mass spectra (see above).

Compound III (400 mg), dissolved in anhydrous ethanol (20 ml), was similarly oxidised with DDQ⁵ (341 mg). The red crystalline precipitate formed was centrifuged off and washed with small portions of ethanol. The *3,3'*-dimethoxy-4,4'-stilbenequinone (XVI) thus obtained (300 mg, 75 %) did not have a sharp melting point (182–185 °C) (lit. 195–205 °C and 202–206 °C)⁵ but was chromatographically pure.

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