The Reactions of Lignin during Bleaching

Part I. Chlorination of Model Compounds of the β-Arylether Type

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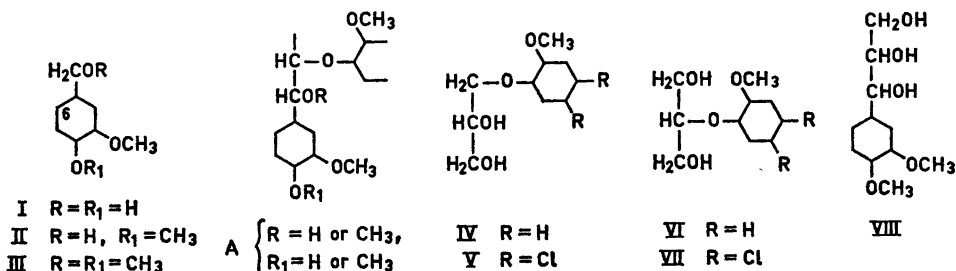*Swedish Forest Products Research Laboratory, Department of Wood Chemistry,
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The chlorination of model compounds of the β-arylether type (A)
by elemental chlorine in glacial acetic acid has been studied.

β-Arylethers containing a hydroxyl group at the α-carbon atom are
rapidly chlorinated, the linkage between the aromatic nucleus and
the α-carbon atom being split by electrophilic displacement (*cf.* also
Refs.[1,2]). The resulting chlorination products (tetrachloroguaiacol,
dichloro-veratrole and the dichloro-guaiacylethers of glycolaldehyde
and glyceraldehyde) have been isolated and characterised.

The importance of this cleavage reaction for the degradation of
lignin during acidic bleaching is briefly discussed.

U nder the conditions of technical bleaching lignin undergoes a great variety
of reactions which finally lead to its degradation into water- and alkali-
soluble fragments. If the common chloro-containing bleaching agents are used,
the main types of reaction observed are chlorination, hydrolytic cleavage, and
oxidation. These main reactions may take place at the same time or at different
times, attacking the same or different reactive sites in the lignin molecules.
If a certain reaction is to be studied in more detail, it seems convenient to
limit the number of reactive sites by investigating the actual reaction with
appropriate model compounds and to inhibit concurrent reactions by selecting
suitable reaction conditions.

I   R = R₁ = H
II   R = H, R₁ = CH₃
III R = R₁ = CH₃

A { R = H or CH₃,
     R₁ = H or CH₃

IV   R = H
V   R = Cl

VI   R = H
VII R = Cl

VIII

Sarkanen and Dence [1,2] studied the behaviour of simple p-hydroxy- and p-methoxy-benzylalcohols (I, II) and -benzyl-alkylethers (*e.g.* III) towards elemental chlorine in aqueous solutions of pH 1. They found that the initial reactions are substitution by chlorine at C(6) of the aromatic nucleus and electrophilic displacement of the hydroxymethyl group (as formaldehyde) by chlorine. This initial phase was suggested to be followed by demethylation and subsequent oxidation of the resulting chlorocatechols to chlorobenzo-quinones.

These model experiments with primary benzylalcohols and benzylalkyl-ethers do not account for the effect(s), which substituents in β- (and/or γ-) position(s) of the lignin side-chains may exert on the course of the acidic chlo-rination.[2] In particular, the fission of the linkage between the aromatic nucleus and the α-carbon atom (the electrophilic displacement of the side-chain by chlorine) may be expected to be influenced by the presence of substituents at the β- (and γ-) atom(s).

The present work is primarily concerned with the reactions of model compounds of the β-arylether type (A) with elemental chlorine at room tem-perature. In order to reduce the number of reactions taking place the treatments were carried out using glacial acetic acid as a solvent. The course of the reac-tion was followed by iodometric titration of the excess chlorine actually present. When possible, the reaction products were isolated and identified.

RESULTS AND DISCUSSION

The chlorination reactions were found to proceed rapidly for the first five minutes, and then either more slowly or not at all (see Fig. 1). When glacial acetic acid was used as solvent, the only reaction was chlorination of the aromatic nuclei and displacement of substituents. No cleavage of arylether linkages or oxidation of side-chains was observed.

Phenols were chlorinated in all positions available for substitution. Thus, creosol (p-methyl-guaiacol), when treated with increasing amounts of chlorine
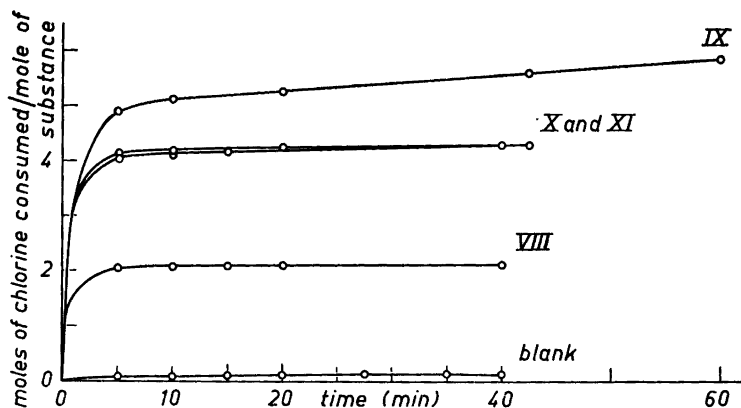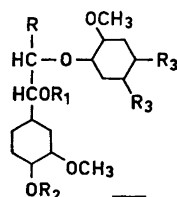

Fig. 1. Chlorination of model compounds in glacial acetic acid at room temperature.
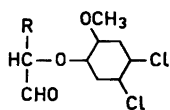
yielded successively monochloro-, dichloro-, and trichloro-creosol (cf. also complete chlorination of guaiacol[3] and I[1]). In contrast, the chlorination of phenol ethers is restricted to free positions *para* to the etherified phenolic hydroxyl group(s). Veratrole was rapidly converted into 4,5-dichloro-vera-trole,[1,2] which remained unchanged when exposed to further chlorination under the same conditions. Essentially the same behaviour was shown by the phenolic and/or non-phenolic nuclei in model compounds IV, VI, VIII, IX, X, XI, XIV (see below).

The α- and β-guaiacylethers of glycerol (IV and VI) yielded the expected dichloro-products V and VII, respectively, indicating that the guaiacyl-glycerylether bonds are stable and that side-chains of the (substituted) gly-cerol type are not oxidised under the conditions used. Alkaline hydrolysis of IV and VI (cf. Ref.[4]) gave 4,5-dichloroguaiacol and glycerol.

Glycerol was not attacked by chlorine in glacial acetic acid. The 3,4-dimethoxy-phenyl derivative VIII, however, afforded glyceraldehyde (paper chromatography) and an almost quantitative yield of 4,5-dichloroveratrole. This result shows that the elimination of side-chains (as aldehydes) is a general reaction of *p*-alkoxy- (and *p*-hydroxy-) benzylalcohols, given not only by the lowest representatives of this series (primary benzylalcohols, II and I), but also by those having a neighbouring oxygen containing substituent.

IX   R = R₁ = R₂ = R₃ = H
X   R = R₁ = R₃ = H, R₂ = CH₃
XI   R = CH₂OH, R₁ = R₃ = H, R₂ = CH₃
XII R = R₃ = H, R₁ = R₂ = CH₃

XIII R = CH₂OH, R₁ = R₂ = CH₃, R₃ = H
XIV R = R₁ = H, R₂ = CH₃, R₃ = Cl
XV   as X but CO instead of HCOH
XVI as XIV but CO instead of HCOH

XVII   R = H
XVIII R = CH₂OH

In view of the importance generally attributed to β-arylether structures, special emphasis was laid on the study of the behaviour of benzylalcohols containing an aroxyl substituent at the β-carbon atom. The β-guaiacylether of α-(3,4-dimethoxy-phenyl)-ethyleneglycol (X) consumed 4 moles of chlorine per mole of substance and was cleaved into 4,5-dichloro-veratrole and glycol-aldehyde-(4,5-dichloro-guaiacyl)-ether (XVII). The latter was identified by comparison with authentic material, prepared by reacting 4,5-dichloro-guaiacol with monochloroacetaldehyde-diethylacetal followed by removal of the acetal group. The products gave identical dinitrophenylhydrazones (m.p.'s,

thin-layer chromatography). When the dichloro-derivative XIV, a possible intermediate in the reaction of X, was chlorinated, the consumption of chlorine amounted to only 2 moles per mole of substance (see Fig. 1) and the same splitting products (4,5-dichloro-veratrole and the aldehyde XVII) were obtained as from X.

Analogously, the β-guaiacylether of α-(3,4-dimethoxy-phenyl)-glycerol (XI) consumed 4 moles of chlorine per mole of substance and was cleaved into 4,5-dichloro-veratrole and the α-(4,5-dichloro-guaiacyl)-ether of glycer-aldehyde (XVIII). The latter was identified by reduction to the β-(4,5-dichloro-guaiacyl)-ether of glycerol (VII) with sodium borohydride and comparison of the reduction product with the chlorination product obtained from glycerol-β-guaiacylether (m.p. and mixed m.p.).

Chlorination of the phenolic β-guaiacylether IX gives rise to the same alde-hydic cleavage product (XVII) as was formed from the corresponding non-phenolic compound (X). However, instead of 4 moles (see above) 6 moles of chlorine per mole of substance were consumed (uptake of the last mole being very slow, Fig. 1) and tetrachloro-guaiacol could be isolated from the reaction mixture.

In order to further determine the scope of the elimination reaction the corresponding benzyl-methylethers XII and XIII were treated in the same manner. Only small amounts of 4,5-dichloroveratrole (10—15 %) were formed, the main reactions being chlorinations without rupture of the bond between the aromatic nuclei and the α-carbon atoms of the side-chains. The same was essentially true for a β-guaiacylether, containing an α-carbonyl group (XV).

Thus, the side-chains are replaced by chlorine when p-hydroxy- and p-alkoxy-benzylalcohols containing an aroxyl substituent at the neighbouring ($=\beta$-) carbon atom are chlorinated under the conditions mentioned.

Of all phenylpropane units in lignin (phenolic and non-phenolic, "con-densed"[5] and "non-condensed") about one fifth are thought to possess a free hydroxyl group at the α-carbon atom of the side-chain.[6] Electrophilic dis-placement of the side-chains by the action of chlorine may be assumed to take place with all structures of the benzylalcohol type, irrespective of whether the phenolic hydroxyl group in $para$-position is free or etherified, whether the 5-position is substituted or unsubstituted, and whether the β-carbon atom is linked to a bulky substituent or not. Hence, it may be expected that about every fifth lignin unit will suffer cleavage of the bond between the aromatic nucleus and the α-carbon atom of the side-chain. Further, some splitting of benzyl-alkyl- and/or benzyl-arylether structures may also occur, but this reaction has not been sufficiently studied with suitable model substances.

EXPERIMENTAL

All melting points are corrected. Evaporations were carried out *in vacuo*.

Preparation of chlorinated reference compounds

Glycolaldehyde-(4,5-dichloro-guaiacyl)-ether (XVII). Equimolar amounts of 4,5-dichloro-guaiacol (m.p. 72—73°), monochloroacetaldehyde-diethylacetal and sodium

ethoxide dissolved in anhydrous ethanol were heated in an autoclave at 160° for 15 h. The solution was filtered to remove the sodium chloride and concentrated. Chloroform was added to the residue and the chloroform solution washed with water. After drying (Na_2SO_4) and evaporation of the solvent the oily residue was distilled *in vacuo* $(137°/10^{-2}$ mm Hg) giving *glycolaldehyde-(4,5-dichloro-guaiacyl)-ether-diethylacetal* as a colourless oil (yield 80 %). (Found: C 50.81; H 5.98; O 20.61; Cl 22.49. $C_{13}H_{18}O_4Cl_2$ requires: C 50.52; H 5.82; O 20.79; Cl 22.95).

The diethylacetal (1.57 g) was dissolved in glacial acetic acid (4 ml) and concentrated hydrochloric acid (0.2 ml) added to the solution. After 2 days the solution was poured into water and the resulting emulsion extracted with chloroform. Evaporation of the dried (Na_2SO_4) chloroform extract afforded a colourless oil (1.17 g, 97 %), which on standing in the refrigerator solidified. Distillation of the crude aldehyde *in vacuo* $(100-110°/10^{-2}$ mm Hg) yielded needles (m.p. 78.5−81.5°), difficult to purify by recrystallisation. (Found: C 45.91; H 3.62; O 20.62; Cl 30.31. $C_9H_8O_3Cl_2$ requires: C 45.98; H 3.40; O 20.84; Cl 30.20).

ω-(4,5-Dichloro-2-methoxy-phenoxy)-acetoveratrone (XVI). Potassium carbonate (3 g) and sodium sulphate (1 g) were added to a solution of ω-bromo-acetoveratrone (3 g) and 4,5-dichloroguaiacol (3 g) in anhydrous acetone (70 ml). The suspension was stirred and boiled under reflux for 1 h. Water was added and the solution extracted with chloroform. The extract was washed first with dilute sodium hydroxide and then with water, dried (Na_2SO_4), and the solvent evaporated to yield crystals (3.8 g, 89 %), m.p. 130−131°. (Found: Cl 19.24; OCH_3 24.54. $C_{17}H_{16}O_5Cl_2$ requires: Cl 19.12; OCH_3 25.01).

α-(3,4-Dimethoxy-phenyl)-ethyleneglycol-β-(4,5-dichloro-guaiacyl)-ether (XIV). Sodium borohydride (1.5 g) was added to a solution of ω-(4,5-dichloro-2-methoxy-phenoxy)-acetoveratrone (XVI, 1 g) in anhydrous ethanol (50 ml). After stirring the mixture at room temperature overnight it was diluted with water (150 ml) and extracted with chloroform. The chloroform solution was washed with water, dried (Na_2SO_4), and evaporated. The resulting crystals were recrystallised from benzene-light petroleum and melted at 144−145° (yield 850 mg, 85 %). (Found: Cl 18.65; OCH_3 24.45. $C_{17}H_{18}O_5Cl_2$ requires: Cl 19.01; OCH_3 24.93).

Treatment of model compounds with elemental chlorine in glacial acetic acid

The chlorinations were carried out at room temperature by adding a 50−100 % excess of chlorine dissolved in glacial acetic acid to a solution of the substance (1−5 mmoles) in glacial acetic acid (25−50 ml). The reactions were followed by iodometric titration of the excess of chlorine with 0.1 N thiosulphate. In most experiments the reactions were stopped at the end of the rapid phase (after 5−10 min) by addition of a 0.1 N solution of sodium thiosulphate. Water was added, the reaction mixtures extracted with chloroform and the chloroform extracts washed with water until free from acids. After drying (Na_2SO_4), the chloroform was evaporated and the yields determined by weighing the residues. Most compounds gave yields approaching the theoretical (calculated on the basis of the extent of chlorination expected and corrected for the samples withdrawn for titration).

The compositions of the oily residues were investigated by thin-layer chromatography and the method for the separation of the reaction mixture into its components was chosen according to the chromatographic results. Usually, preparative chromatography on silica gel G (Stahl) (in columns and/or in layers of 1 mm thickness) proved to be the most effective tool for separation.

Chlorination of creosol with 1, 2, and 3 moles of chlorine per mole of substance yielded mono- (m.p. 69.5−70.5°), di- (m.p. 88.5−89.5°) and tri- (m.p. 113−114.5°) chlorocreosol, respectively.

When veratrole was reacted with an excess of chlorine (4 moles per mole of substance) only 4,5-dichloro-veratrole (m.p. 83−84°) was obtained, even after a reaction time of 2 h.

Chlorination of the glycerol-α-guaiacylether (IV) and glycerol-β-guaiacylether (VI) with an excess of chlorine afforded only the corresponding dichloro-products, *α-(4,5-dichloro-guaiacyl)-glycerolether (V)*, as needles from ethyl acetate-hexane, m.p. 100−101°. (Found: C 45.07; H 4.47; O 23.90; Cl 26.57. $C_{10}H_{12}O_4Cl_2$ requires: C 44.97; H 4.49; O 23.96; Cl 26.56), and *β-(4,5-dichloro-guaiacyl)-glycerolether (VII)*, as needles from

ethyl acetate-hexane, m.p. 80—81.5°. (Found: C 45.10; H 4.53; O 23.93; Cl 26.31).Heat-
ing of V and VII with 2 N NaOH at 170° for 2 h (cf. Ref.[4]) gave quantitative yields of
4,5-dichloro-guaiacol (m.p. 72—73°), identical with the chlorination product (mixed m.p.)
prepared from guaiacol and thionyl chloride.[7] The presence of glycerol in the cooking
liquors was shown by paper chromatography.

Treatment of a-(3,4-dimethoxy-phenyl)-glycerol (VIII) with an excess of chlorine
gave a quantitative yield of 4,5-dichloro-veratrole (m.p. 83—84°), identical with the prod-
uct obtained by chlorination of veratrole (see above). After removal of the dichloro-
veratrole and of most of the acetic acid, the solution was neutralised and evaporated
to dryness. The residue was extracted with anhydrous ethanol and the presence of gly-
ceraldehyde in the extract shown by paper chromatography. Treatment of the extract
with borohydride yielded glycerol (paper chromatography).

a-(3,4-Dimethoxy-phenyl)-ethyleneglycol-β-guaiacylether (X), chlorinated with 8
moles of chlorine per mole of substance and worked up in the usual manner yielded a
yellowish oil (96 %), which was separated into its components by preparative thin-layer
chromatography (solvent: chloroform). The two main zones were located by ultraviolet
light, removed from the plates with a spatula and the substances extracted with chloro-
form. 4,5-Dichloro-veratrole, the faster migrating component, was obtained in 80 %
yield (m.p. 82—84°), glycolaldehyde-(4,5-dichloro-guaiacyl)-ether (XVII) in 92 % yield.
For characterisation, aldehyde XVII was separated from the reaction mixture by
exhaustively extracting the chloroform solution of the crude oil with a saturated
aqueous solution of sodium bisulphite. After one week a white precipitate which
had formed in the bisulphite extract was filtered off, dissolved in a small amount of
water, a 0.3 % solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid
added and the mixture kept for one week. The resulting yellow precipitate was filtered
off, washed with water, and recrystallised from acetone. The 2,4-dinitrophenylhy-
drazone of glycolaldehyde-(4,5-dichloro-guaiacyl)-ether was obtained as yellow plates
(m.p. 175° decomposition) identical with the 2,4-dinitrophenylhydrazone prepared from
the authentic aldehyde XVII. (Found: N 13.41; Cl 17.29; OCH_3 7.24. $C_{15}H_{12}O_6N_4Cl_2$
requires: N 13.42; Cl 17.15; OCH_3 7.47). After removal of the aldehyde XVII 4,5-
dichloro-veratrole was isolated by evaporation of the chloroform solution and
sublimation of the resulting residue in vacuo (bath temp. 70°/10⁻³ mm Hg).

The dichloro-derivative of X (XIV) was split by chlorine to yield the same chlorinated
products (4,5-dichloro-veratrole and glycolaldehyde-(4,5-dichloro-guaiacyl)-ether (XVII)
in about the same yields, as was the parent compound (X) (thin-layer chromatography,
m.p.). Only 2 moles of chlorine per mole of substance were consumed. The same working-
up procedure was followed.

The method of preparative thin-layer chromatography was also applied to separate
the chlorinated products obtained from a-(3-methoxy-4-hydroxy-phenyl)-ethyleneglycol-
β-guaiacylether (IX). Glycolaldehyde-(4,5-dichloro-guaiacyl)-ether (XVII) was identified
as its 2,4-dinitrophenylhydrazone (thin-layer chromatography, analysis) (yield 80 %),
and tetrachloro-guaiacol (yield 77 %, m.p. 128—130°) by mixed m.p. with an authentic
sample.[8] Six moles of chlorine per mole of substance were consumed.

Chlorination of a-(3,4-dimethoxy-phenyl)-glycerol-β-guaiacylether (XI) yielded a
pale yellow precipitate, when the reaction mixture was poured into water. Attempts to
separate the expected chlorinated products (4,5-dichloro-veratrole and glyceraldehyde-a-
(4,5-dichloroguaiacyl)-ether (XVIII) and to characterise the latter in a manner analogous
to that described for the corresponding glycolaldehyde derivative(XVII) were unsuccess-
ful, due to the instability of XVIII (cf. Ref.[8]). The crude material was therefore dissolved
in 80 % ethanol, treated with an excess of sodium borohydride and the resulting reac-
tion mixture separated by preparative thin-layer chromatography, as described above.
4,5-Dichloro-veratrole (yield 66 %, m.p. 83—84°) and β-(4,5-dichloro-guaiacyl)-glycerol-
ether (VII) (yield 67 %, m.p. 80—81°) were obtained and identified by mixed m.p. with
authentic samples.

Chlorination of the a-methylethers XII and XIII resulted only in poor yields (10—
15 %) of 4,5-dichloro-veratrole in spite of the fact that at least 4 moles of chlorine per
mole of substance were consumed. The main chlorinated products were not characterised.

When treated with an excess of chlorine, the carbonyl compound XV consumed 3 moles per mole of substance. No 4,5-dichloro-veratrole could be isolated, and the main chlorinated product still exhibited a strong α-carbonyl band in the IR at 1680 cm^{-1}, indicating that no splitting of the side-chain had taken place.

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