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The Reactions of Lignin During Sulphate Pulping

Part XI.* Reactions of Pinoresinol With Alkali and With White Liquor **

JOSEF GIERER and LEIF-ÅKE SMEDMAN***

Swedish Forest Products Research Laboratory, Chemistry Department, Box 5604, S-144 86 Stockholm, Sweden

The reactions under the conditions of alkali and sulphate pulping of (+)-pinoresinol, a model compound for structural units of the lignane type in lignin, have been studied. The following reaction products have been isolated and identified (as their acetates): (+)-epi-pinoresinol, guaiacol, 1,4-bis-(4-hydroxy-3-methoxy-phenyl)-buta-1,3-diene, and bis-(4-hydroxy-3-methoxy-phenyl)-methane. The formation of these compounds is interpreted in terms of mechanisms also operative in the alkaline degradation of other types of models. The significance of the two latter compounds as representatives for possible leucochromophoric systems in alkali and sulphate lignins is discussed.

Studies on the biosynthesis of lignin revealed that units of the pinoresinol and syringaresinol types may constitute prominent structural elements in this natural product.[1] Strong support for their occurrence has been provided by the isolation of pinoresinol [2] and syringaresinol [3] after mild acidic hydrolysis of spruce and beech wood, respectively. Furthermore, oxidation of various lignin preparations with nitric acid afforded small amounts of the di-γ-lactone of α,α'-bis(hydroxymethyl)-succinic acid [4] arising from the aliphatic portion of the above 2 lignane structures.[5] While the presence of structural elements of the pinoresinol type in spruce lignin appears established, no satisfactory method for their estimation is known. Therefore, their frequency is still a matter of controversy. The extremely low yields of pinoresinol obtained after hydrolytic degradations of lignin indicate that the majority of pinoresinol units are connected to their neighbours by carbon-carbon or diaryl ether linkages, resistant to the degradation conditions employed.[6]

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

*** Present address: Mo och Domsjö AB, Forskningslaboratoriet, 891 01 Örnsköldsvik, Sweden.

Pinoresinol has been used as model representing these structures, and its behaviour under the conditions of alkali pulping has been briefly reported in a previous communication of this series.[7] It has been stated that this compound is converted into a mixture of phenolic products. The present work deals with the characterisation of some of these degradation products and the possible importance of pinoresinol units as sources of leucochromophoric structures and condensable groups.

(+)-Pinoresinol was subjected to the conditions of alkali and sulphate pulping. After acetylation, the reaction products were separated by column chromatography and identified by NMR, mass, and IR spectroscopy.

RESULTS AND DISCUSSION

The results of the treatment of (+)-pinoresinol (used as diacetate) with white liquor at 180° for 3 h are summarised in Table 1. The various reaction paths are outlined in Scheme 1.

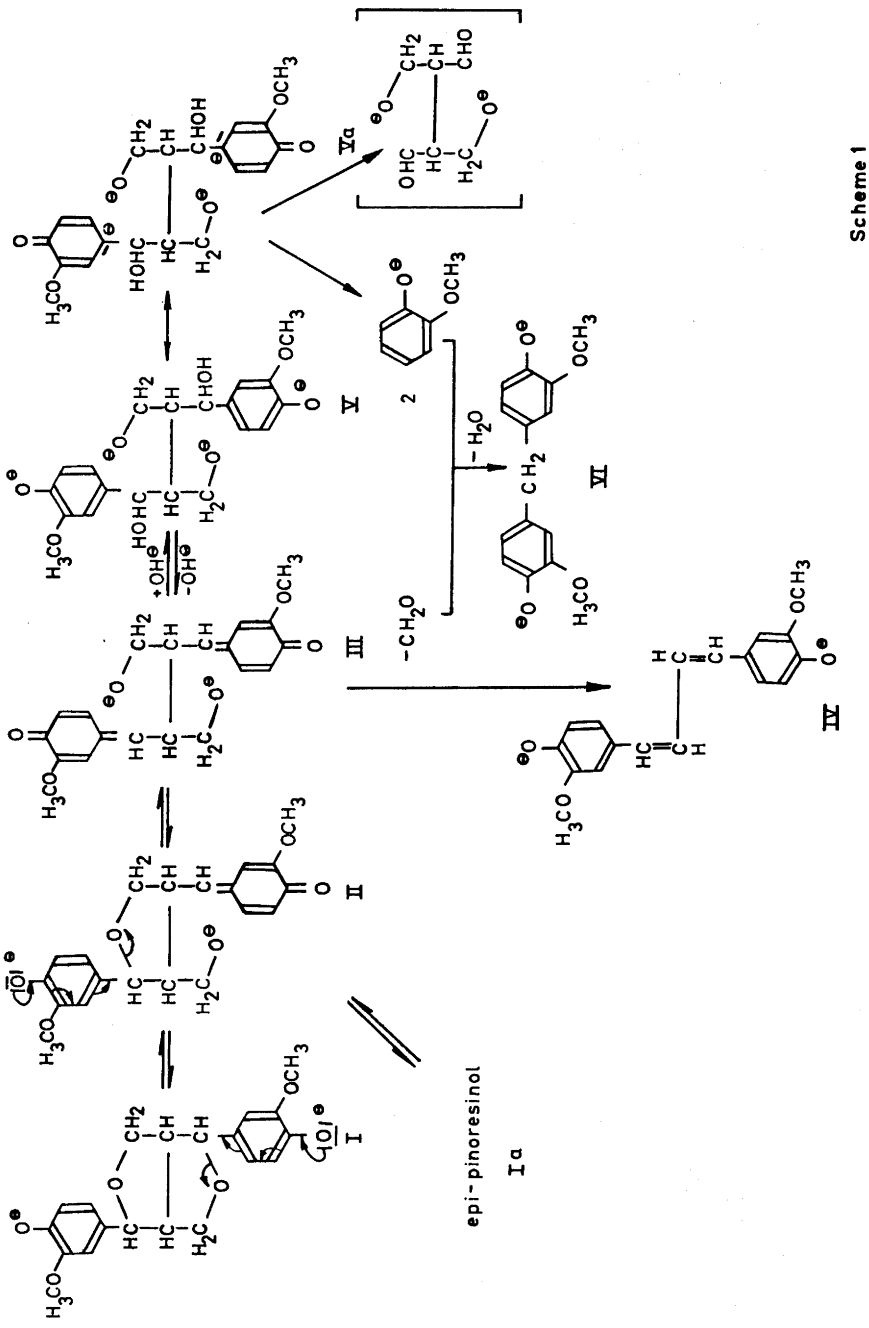
Table 1. Approximate composition of the reaction mixture from pinoresinol diacetate after treatment with white liquor at 180° for 3 h and acetylation.

Reaction product	Yield [a] (% by weight)	m.p. [b]
1,4-Bis-(4-acetoxy-3-methoxy)-buta-1,3-diene	6	185 – 190
(+)-Epi-pinoresinol diacetate	11	143 – 145
(+)-Pinoresinol diacetate	25	162 – 163
1-Acetoxy-2-methoxybenzene	12	
Bis-(4-acetoxy-3-methoxy-phenyl)-methane	5	119 – 121
Unidentified oligomeric compounds	33	
Unrecovered	8	

[a] After one chromatographic separation.
[b] After repeated purification by chromatography and recrystallisation.

On the basis of the results obtained after treatment of phenolic model compounds of the α-aryl and β-aryl ether types with alkali,[7] it could be predicted that the alkaline cleavage of the α-alkyl ether linkages in pinoresinol (I) might proceed *via* methylene quinone structures (II and III). These methylene quinone intermediates may then undergo various reactions resulting in stable products:

(1) Nucleophilic attack of the terminal alcoholate anion in II restores the hydrofurane ring. This reverse reaction is substantiated by the presence in the



Scheme 1. Reactions of pinoresinol with alkali.

reaction mixture of (+)-epi-pinoresinol, isolated and identified as its diacetate. In epi-pinoresinol, the configuration about one of the benzyl carbon atoms is inverted,[8] the aryl substituent being axial. The formation of this diastereoisomer implies opening of one of the tetrahydrofurane rings (I→II), inversion at the α-carbon atom, and closure of the tetrahydrofurane ring (II→Ia). The (+)-pinoresinol isolated (as diacetate) after the alkaline treatment should likewise be regarded as a product of ring closure of the (common) methylene quinone intermediate II rather than as unchanged starting material. Thus, the ratio (+)-pinoresinol/(+)-epi-pinoresinol most likely reflects the equilibrium existing between the two diastereoisomeric forms under the conditions employed. The intervention of methylene quinone structures during the alkaline degradation of pinoresinol (I) is also supported by the behaviour of the tetra-ol V which, on similar treatments, yields mixtures of the same reaction products in roughly the same proportions as does pinoresinol. These transformations also suggest methylene quinones (II and III) as intermediates. Conversely, treatment of (+)-pinoresinol dimethylether with alkali [7] or with white liquor [9] does not afford any epi-isomer due to the blocking of the methylene quinone pathway by the etherified phenolic hydroxyl groups.

Alkaline isomerisations in the lignane series have been known for a long time.[10,11] However, the partial conversion of lignanes into their diastereoisomers is usually performed in acidic medium, using alcoholic solutions of hydrogen chloride.[10–16] Under these conditions, the reactions follow a different course, presumably *via* benzylium ions, the formation of which does not require the presence of free phenolic hydroxyl groups *para* to the side chains. Consequently, in contrast to the alkali-promoted isomerisations, the acidic isomerisations are not restricted to phenolic lignanes. Thus, even the dimethylether of (+)-pinoresinol is partly converted into the corresponding diastereoisomer (dimethylether of (+)-epi-pinoresinol).[11,17]

(2) Hydroxyl ions, present in the cooking liquors, may compete with the alcoholate anions of the methylene quinone intermediates II and III for the electrophilic centers at the α-carbon atoms. This results in the formation of *p*-hydroxybenzyl alcohol groups (*e.g.* in V) which, presumably in the form of carbanions of the cyclohexadienone type (Va), eliminate the guaiacyl residues, leaving the aliphatic portion probably as (unstable) α,α′-bis-(hydroxymethyl) succinic aldehyde.[5] This mode of cleavage of the bond between the aromatic nucleus and the α-carbon atom is also given to a small extent by methylene quinone intermediates, formed from (phenolic) β-arylether and phenylcoumaran structures.[18] In the latter instance, it has been possible to isolate and identify not only the phenolic (guaiacol) but also the aldehydic cleavage product and its cyclic hemiacetal in the form of their acetates.[18]

(3) Instead of adding alcoholate or hydroxyl ions (see (1) and (2)), the methylene quinone intermediates II and III could be expected to be stabilised by elimination of formaldehyde [7,19] with formation of a conjugated system. In fact, 1,4-bis-(4-hydroxy-3-methoxy-phenyl)-buta-1,3-diene (IV) could be isolated from the reaction mixture (as its diacetate) and identified by spectroscopic methods. Catalytic hydrogenation (Pd/H_2) of the product afforded the expected 1,4-bis-(4-acetoxy-3-methoxy-phenyl)-butane.

The formaldehyde split off in the above reaction may give rise to various condensation reactions with phenolic degradation products yielding diaryl-

methane structures. The formation of bis-(4-hydroxy-3-methoxy-phenyl)-methane (VI), also isolated and identified as its diacetate, illustrates this type of reaction.

A considerable portion (33 %) of the starting compound was converted into an oligomeric fraction, the components of which have not so far been characterised.

No significant differences in the compositions of the reaction mixtures obtained after treatment of (+)-pinoresinol diacetate with white liquor and with alkali have been observed. This finding shows that the sulphide and hydrosulphide ions present in the white liquor do not exert any noticeable influence on the alkali-promoted transformations described above.[9]

The 1,4-diarylbutadiene IV and the diarylmethane VI represent leuco-chromophoric structures which may arise from pinoresinol units in lignin and, on oxidation, give rise to conjugated chromophores of the methylene quinone type (*e.g.* VII and VIII). Furthermore, the 1,4-diarylbutadiene IV may be dehydrogenated with cyclisation to form the corresponding, substituted arylnaphthalene IX,[20] in analogy to the dehydrogenative cyclisation of

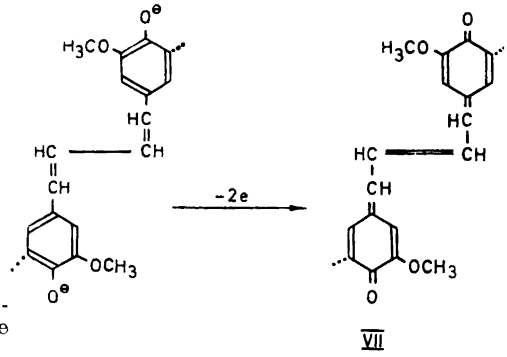


Fig. 1. Oxidation of 1,4-diaryl-buta-1,3-diene structures to conjugated methylene quinone structures.

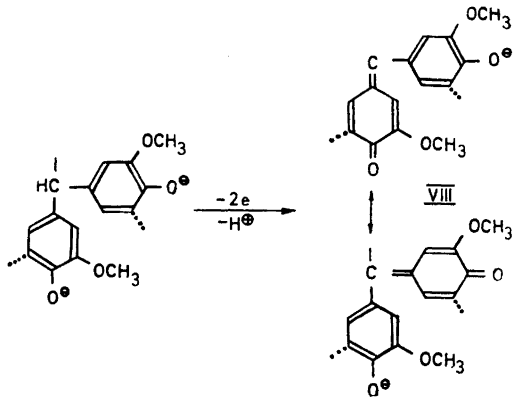


Fig. 2. Oxidation of diaryl-methane structures to aryl-substituted methylene quinone structures.

stilbenes to phenanthrenes.[21] The dihydroxy-phenylnaphthalene IX may possibly be oxidised to the phenylnaphthalene-dione X. Alternatively, the latter compound may arise by dehydrogenation and cyclisation of the conjugated bis-methylene quinone VII.

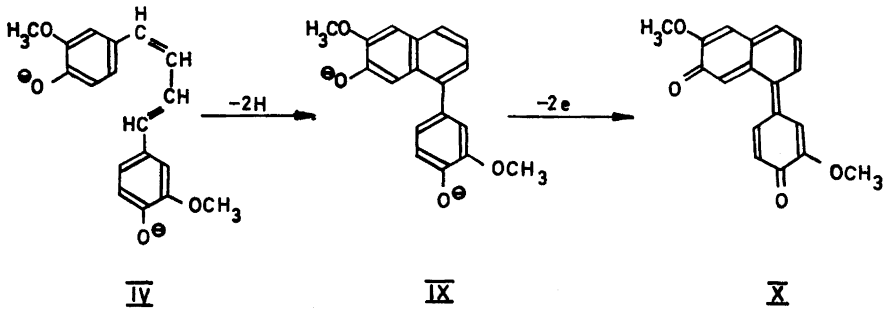


Fig. 3. Dehydrogenation of a 1,4-diaryl-buta-1,3-diene to an aryl-naphthalene, and oxidation of the latter to a dione.

From the results of the present work it may be concluded that the benzyl-alkyl ether linkages of the pinoresinol structures in lignin are extensively cleaved during alkali and sulphate pulping, giving rise to intermediate methylene quinone structures. The latter are converted into a great variety of stabilisation products, some of which constituting leucochromophoric structures. Thus, units of the pinoresinol type, although possibly present in small amounts only, may contribute considerably to the discoloration of lignins brought about by alkali and sulphate pulping. A study of the nature and reactivity of such leucochromophoric groups is currently being attempted.

EXPERIMENTAL

All melting points are corrected. Thin-layer chromatography and column chromatography were performed on silica gels, using either chloroform or mixtures of dichloro methane and ethyl ether as eluents. The analyses of the mixtures of acetylated compounds were carried out by gas liquid chromatography on a Carbowax-20M column (1 % Carbowax 20M on Chrom G 100/120 mesh). NMR spectra were recorded on a Perkin-Elmer R 12 spectrophotometer and mass spectra on a Perkin-Elmer M 10 mass spectrometer.

Model compounds. (+)-Pinoresinol diacetate was prepared from the resin of *Picea abies* and purified according to Ref. 22. Melting point and NMR spectrum excluded any contamination by (+)-epi-pinoresinol.

1,4-Bis-(4-hydroxy-3-methoxy-phenyl)-2,3-bis-(hydroxymethyl)-butan-1,4-diol (V) and bis-(4-hydroxy-3-methoxy-phenyl)-methane (VI) were prepared according to Refs. 23 and 24, respectively.

Cooking liquors. Sodium hydroxide (2 N) and "white liquor", containing NaOH (3.5 g) and $Na_2S.9\,H_2O$ (3.1 g), in water (100 ml) were used as cooking liquors.

Cooking procedure. The compound (100 mg) was dissolved in the cooking liquor (5 ml), and the solution was sealed in a glass ampoule in an atmosphere of nitrogen. The ampoule was then placed in a reaction vessel of stainless steel, partly filled with water. The autoclaves were placed in a preheated polyglycol bath (180°) and rotated for 3 h. After cooling, the ampoule was opened and the contents neutralised by addition of an excess of dry ice and then extracted with chloroform. The chloroform layer was washed with water, and after drying (Na_2SO_4) evaporated under reduced pressure.

The residue was acetylated with acetic anhydride-pyridine in the usual way. During the whole working-up procedure, air was carefully excluded and possible oxidation prevented by adding traces of $Na_2S_2O_4$. The acetylated reaction mixture was subjected to column chromatography. The isolated compounds were identified by m.p., IR, UV, NMR, and mass spectroscopy, as well as by comparison with authentic samples.

1,4-Bis-(4-acetoxy-3-methoxy-phenyl)-buta-1,3-diene (diacetate of IV) was obtained as colourless crystals, m.p. 185 – 190°, after recrystallisation from isopropanol. The mass spectrum showed distinct lines for the molecular ion (*m/e* 382) and for the successive loss of 2 ketene molecules (*m/e* 340 and *m/e* 298). The deacetylated molecular ion (*m/e* 298) gave rise to the base peak. In the NMR spectrum, the signals from aromatic protons (6 H) were centered at δ 7.03, and those from the olefinic protons (4 H, unresolved) at δ 7.25. The methoxyl and acetyl protons appeared as singlets at δ 3.87 (6 H) and δ 2.29 (6 H), respectively. The IR spectrum resembled those of *trans*-isoeugenol and of *trans*-stilbenes. The prominent peak at 980 cm^{-1} indicated a *trans-trans*-arrangement of the butadiene skeleton.[25]

1,4-Bis-(4-acetoxy-3-methoxy-phenyl)-butane. Catalytic hydrogenation (Pd/H_2) of the above compound afforded colourless crystals, m.p. 115 – 120°, after recrystallisation from ethanol. The mass spectrum showed the molecular ion (*m/e* 386) and the successive loss of two ketene molecules (*m/e*) 344 and 302). The deacetylated molecular ion exhibited the base peak (*m/e* 302). Other prominent peaks were located at *m/e* 316, 137 and 138. The NMR spectrum showed the signals from the aromatic protons centered at δ 6.60 (6 H), those from the methoxyl protons at δ 3.72 (6 H), and from the acetyl protons at δ 2.18 (6 H). The methylene protons exhibited two broad bands centered at δ 2.58 (4 H) and at δ 1.63 (4 H), attributable to the α- and β-protons, respectively.

The m.p., NMR and mass spectra of the other products (acetates of guaiacol, (+)-*epi*-pinoresinol and of compound VI) were in agreement with those of authentic samples.

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