

# The Reactions of Lignin with Alkaline Hydrogen Peroxide. Part V.\* The Formation of Stilbenes

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Structures of the 1,2-diarylpropane-1,3-diol type constitute an important building unit in native lignins. In spruce as well as in birch lignin their frequency has been estimated to be approximately seven units per 100 phenylpropane units.<sup>2</sup> Hot alkaline<sup>3</sup> or acidic<sup>3</sup> treatment of the phenolic variants of such structures results in their conversion to stilbenes through elimination of formaldehyde and water. However, the exact conditions required for these conversions are unknown.

In the present work, the lignin model compound **1** (4,4'-dihydroxy-3,3'-dimethoxy- $\alpha$ -ethoxy- $\alpha'$ -hydroxymethylbiphenyl) was treated with hydrogen peroxide under mild alkaline conditions similar to those encountered during hydrogen peroxide bleaching of mechanical pulp (*e.g.*, presence of sodium metasilicate and diethylenetriaminepentaacetic acid). The rates of decomposition of **1** and the structures of the reaction products were determined at three pH values. In each experiment the temperature and pH were kept constant and the consumption of hydrogen peroxide and alkali analyzed as described previously.<sup>5</sup>

When the reactions were carried out at pH = 12 or pH = 14 (30 °C) first-order reaction plots gave straight lines with the rate constants given in Table 1. (The rate constant obtained at pH = 14 is approximately 10 times higher than the corresponding value for the formation of 2,4'-dihydroxy-3,3'-

Table 1. First-order reaction rate constants,  $k(\text{obs})$ , for the decomposition of **1** at 30 °C.

pH	$k(\text{obs})/10^{-3} \text{ min}^{-1}$
11.0	~ 0
12.0	8.2
14.0	23

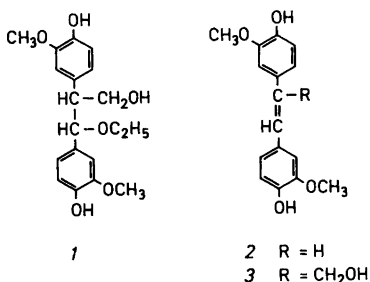
dimethoxy-5-(3-hydroxypropyl)stilbene from dihydro-dehydroniciferyl alcohol (2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-5-(3-hydroxypropyl)-7-methoxy-benzofuran).<sup>6</sup> At pH = 11 no reaction was observed even after 120 min (GLC).

After 4 h reaction time at pH = 12 or pH = 14 extracts of the reaction mixtures were analyzed by TLC using **1**, *trans*-4,4'-dihydroxy-3,3'-dimethoxystilbene (**2**) and 4,4'-dihydroxy-3,3'-dimethoxy- $\alpha$ -hydroxymethylstilbene (**3**) as reference compounds. At pH = 12 the only product formed was the stilbene **3** whereas at pH = 14, **2** and **3** were identified as major reaction products. The formation of these products is consistent with a mechanism proceeding *via* the methylene quinone corresponding to **1** (*cf.* Ref. 6), which subsequently eliminates formaldehyde (formation of **2**) or hydrogen (formation of **3**). No consumption of alkali or hydrogen peroxide was observed in any of the experiments which is in accordance with known features of the behaviour of mixtures of alkaline hydrogen peroxide and phenols in the presence of stabilizers.<sup>5</sup>

Phenolic stilbene structures, being vinylogous hydroquinones, should easily be oxidized by the action of oxygen (*cf.* Ref. 7). Thus the bleaching of mechanical pulps with hydrogen peroxide leads to the introduction of structures into lignin which are easily converted to quinones upon storage, particularly under the influence of light or heat (*cf.* Ref. 8).

*Experimental.* Compound **1** (mixture of two diastereoisomeric forms) was prepared according to Ref. 4. It contained an ethoxy group and not, as expected, a hydroxyl group in the  $\alpha$ -position to the aromatic ring (<sup>1</sup>H NMR, MS). Compounds **2** and **3** were prepared according to Ref. 9.

The treatment of **1** (120 mg, 0.345 mmol) with hydrogen peroxide and alkali in the presence of sodium metasilicate and diethylenetriaminepentaacetic acid was carried out as previously described.<sup>10</sup> In the GLC analyses of **1**, docosane was used as the internal standard. Reaction products (**2** and **3**) were identified by TLC analyses on silica gel in two different solvents (acetone – light petroleum (3:2), acetone-chloroform (1:1)).



\* Part IV. See Ref. 1.

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