

## The Catechol Group in Lignosulfonate

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The catechol group was proposed by Hayashi<sup>1)</sup> as a functional group in lignosulfonate for the gelling reaction with dichromate. This assignment was also supported by a similarity in the reactivity of lignosulfonate with catechol.<sup>2)</sup> Recently, several authors have also suggested the catechol group in lignosulfonate or in other lignin preparation.<sup>3)</sup> These works, however, have dealt with the catechol group only by means of indirect methods, and this group did not yet have general support.

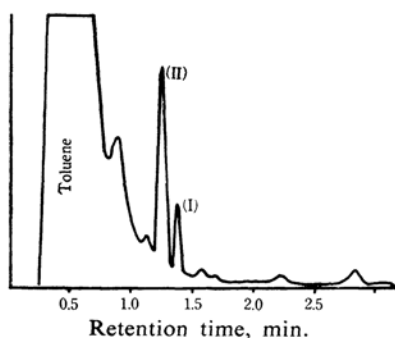


Fig. 1. Gas chromatogram of oxidation product of lignosulfonate.

Column: Apiezon Grease L 2.0 m.

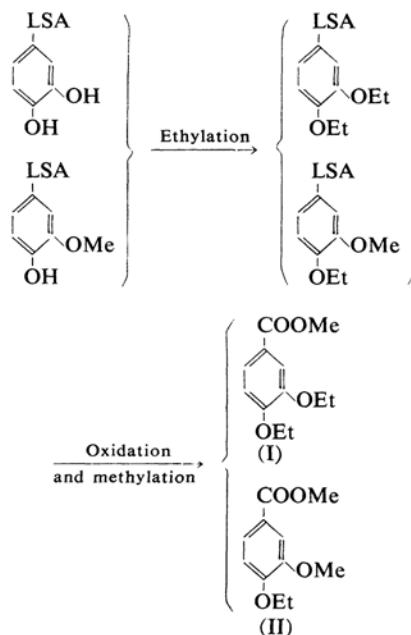
Column temp.: 250°C

Carrier gas: H<sub>2</sub>, 50 cc./min.

In order to establish the catechol group directly, softwood lignosulfonate was ethylated with diethyl sulfate, oxidized with potassium permanganate,<sup>4)</sup> and methylated with methanol; then the resultant products were examined by means of gas chromatography. An Apiezon

Grease L column was used at 250°C. The chromatogram obtained is given in Fig. 1.

Sufficient methyl 3,4-diethoxy-benzoate (I) was detected, along with methyl 3-methoxy-4-ethoxy-benzoate (II). Compounds I and II were derived from the pendant catechol group and the guaiacyl group in lignosulfonate respectively according to the following reaction scheme:



Thus the catechol group was directly confirmed in the lignosulfonate molecule by the formation of compound I.

Vanillyl alcohol was cooked in sulfite cooking liquor in order to ascertain the mechanism of catechol group formation. Methanol was obtained from the cooked liquor by gas chromatography, which corresponded to the 4% demethylation of the methoxyl group in vanillyl alcohol. I was also obtained from the

1) A. Hayashi, *J. Japan Wood Research Soc.*, in contribution (Studies on Lignosulfonate XX).

2) A. Hayashi, *ibid.*, in contribution (Studies on Lignosulfonate XXI and XXII).

3) I. Croon and B. Swan, *Svensk Papperstidn.*, **66**, 812 (1963); C. Steelink, T. Reid and C. Tollin, *J. Am. Chem. Soc.*, **85**, 4048 (1963); J. Marton, *Tappi*, **47**, 713 (1964).

4) K. Freudenberg, *Chem. Ber.*, **86**, 155 (1953).

cooked liquor treated in a method similar to that used for lignosulfonate. These results indicate that the catechol group results from the demethylation of the free guaiacyl group in lignin during the sulfite cooking process.

A detailed and quantitative investigation will be reported soon.

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