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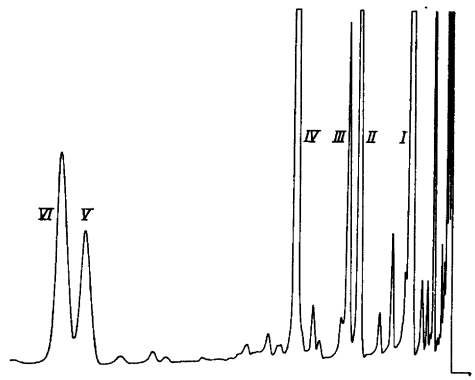


Fig. 1.

Gas Chromatographic Analysis of Lignin Oxidation Products. The Diphenyl Ether Linkage in Lignin

SAM LARSSON and
GERHARD E. MIKSCHE

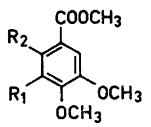
Department of Organic Chemistry, Chalmers Institute of Technology and University of Göteborg, Göteborg, Sweden

In connection with studies on the behaviour of lignin in pulping, we intended to follow possible condensation reactions by examining the aromatic carboxylic acids formed on permanganate oxidation of the methylated lignins. This type of lignin degradation and the careful separation of the arising mixture of aromatic carboxylic acids by distribution between solvents, column chromatography, and crystallization has been reported by Freudenberg *et al.*[1,2] For our purpose, it was desirable to replace this tedious combination of separation procedures by gas chromatographic analysis, which also could be expected to give more quantitative information.

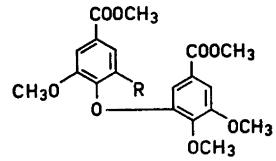
In the work of Freudenberg *et al.*, the permanganate oxidation was carried out at pH 6—7. We found that considerably higher yields of the aromatic carboxylic acids were obtained if the oxidation was carried out at pH 12. However, the mixture of degradation products obtained at this pH value was found to contain appreciable amounts of phenylglyoxylic acids. These could be degraded to the corresponding aromatic carboxylic acids by subsequent treatment with 5 % H_2O_2 at pH 9—10. Finally, the mixture of carboxylic acids was methylated with diazomethane.

Gas chromatography of the mixture of methyl esters under the conditions given below effected good separation (Fig. 1). In Table 1, the amounts of the more prominent methyl esters obtained from diazomethane methylated Björkman lignin (spruce) as well as from Björkman lignin (spruce) pretreated in two different ways are given. The main products from the oxidative degradation thus are the methyl esters of veratric acid (I), isohemipinic acid (II), metahemipinic acid (III), 3′,4,5-trimethoxy-3,4′-oxydibenzoic acid (V) and 5,5′-dehydro-diveratric acid (VI).

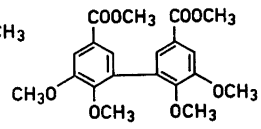
The tetramethyl ester of pyromellitic acid (IV) was added as internal standard for the quantitative determination. The significance of the relative amounts of



I $R_1 = R_2 = H$
II $R_1 = COOCH_3$, $R_2 = H$
III $R_1 = H$, $R_2 = COOCH_3$



V R = H
VII R = OCH3



VI

Table 1. Methyl esters (mg/100 mg of lignin).

	I	II	III	V	VI
Björkman lignin, methylated with diazomethane	7.7	1.6	0.8	1.2	1.8
Björkman lignin, treated with 1 M NaOH for 3 h at 170°, followed by methylation with dimethyl sulfate	23.4	5.8	1.1	2.0	2.8
Björkman lignin, treated with 0.2 M HCl in dioxane-water 9:1 (refluxing for 4 h), followed by methylation with dimethyl sulfate	20.6	1.6	1.8	2.2	1.7

degradation products will be discussed in a forthcoming paper.

The diphenyl ether linkage. In the process of lignin formation, phenoxyl radicals are formed by enzymatic dehydrogenation of *p*-hydroxycinnamyl alcohols and their oligomeric coupling products, *i.e.* phenols mainly containing saturated side chains. The possibility of coupling of phenoxyl radicals to form diphenyl ether structures has been considered.[3,4] Indeed, among the products from the oxidative degradation of methylated, alkali-treated and re-methylated wood meal, Freudenberg and co-workers [2] detected the diphenyl ether acid corresponding to methyl ester V. The yield of this acid, however, was very small (< 0.1 %).

Our results clearly show that diphenyl ether structures actually are of appreciable importance in coniferous lignin, comparable to that of the biphenyl structures. This is in accordance with experiments on the enzymatic dehydrogenation of 2-methoxy-4-propylphenol reported by Pew.[5]

Similarly, oxidative degradation of Björkman lignin from birch followed by methylation with diazomethane was found to give the dimethyl ester of 3′,4,5,5′-tetramethoxy-3,4′-oxydibenzoic acid[6] (VII) as one of the major products.

Conditions of gas-liquid chromatography. Chromatograph: Perkin-Elmer Model 880. *Column dimensions:* 150 × 0.3 cm o.d. stainless steel tubing. *Solid support:* Chromosorb G, acid washed and treated with dimethyldichlorosilane, 80—100 mesh. *Stationary phase:* Silicone elastomer SE-54, General Electric (1.5 % by weight of the solid support). *Temperatures:* Injection: 300°. Detector: 230°. Column: 160—230° (5°/min), then isothermal at 230°. *Carrier gas:* N_2, 30 ml/min. *Detector:* Differential flame ionization detector. The instrument was used with two packed columns.

Identification of components. The mass spectra of components I, II, III, V, VI, VII have been obtained on a LKB gas chromatograph-mass spectrometer unit and shown to be identical with the mass spectra of the sythesized known compounds.

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