

carbazate  $^4$  ( $2 \times 10^{-3}$  mol) was added to a 40 % aqueous formaldehyde solution ( $4 \times 10^{-3}$  mol), with stirring. The reaction mixture was filtered immediately and allowed to stand for  $\frac{1}{2}$  h. The precipitated yellow oil was isolated by centrifugation, washed with water and dissolved in chloroform (10 ml). The solution was dried ( $\text{MgSO}_4$ ) and taken to dryness. The oily residue was redissolved in chloroform (4 ml), pentane added, and the turbid solution cooled to  $-18^\circ\text{C}$ . On scratching, a yellow crystalline compound (VIII) precipitated. Yield: 60–70 %. M.p.  $60-61^\circ\text{C}$ . (Found: C 19.81; H 3.43; N 11.78. Calc. for  $\text{C}_4\text{H}_8\text{N}_2\text{Se}_2$ : C 19.85; H 3.33; N 11.57).

*3-Methyl-1,3,4-selenadiazolidine-2-selone (V)*. A filtered, aqueous solution (5 ml) of methylhydrazinium 2-methyldiselenocarbazate  $^4$  ( $10^{-3}$  mol) was added to a 40 % aqueous formaldehyde solution ( $2 \times 10^{-3}$  mol), with stirring. The reaction mixture was allowed to stand for  $\frac{1}{2}$  h, after which the yellow precipitate was isolated by centrifugation, washed with water, and dried *in vacuo*. Yield: 90 %. The compound (V) was dissolved in the minimum amount of chloroform and precipitated with pentane. M.p.  $124-126^\circ\text{C}$ . (Found: C 16.07; H 2.61; N 12.30. Calc. for  $\text{C}_5\text{H}_8\text{N}_2\text{Se}_2$ : C 15.81; H 2.65; N 12.28).

*Methyl isopropylidene-2-methyldiselenocarbazate (IX)*. Ethanolic solutions of IV ( $10^{-3}$  mol) and potassium hydroxide ( $10^{-3}$  mol) were mixed, and the equivalent amount of methyl iodide added to the resulting solution. After  $\frac{1}{2}$  h the reaction mixture was filtered and the filtrate taken to dryness. The residue was extracted with pentane. This extract was dried ( $\text{MgSO}_4$ ) and the solvent evaporated. The yellow, crystalline residue (IX) was washed with pentane and dried *in vacuo*. Yield: 65 %. M.p.  $80-83^\circ\text{C}$ . (Found: C 26.43; H 4.53; N 10.49. Calc. for  $\text{C}_6\text{H}_{12}\text{N}_2\text{Se}_2$ : C 26.68; H 4.48; N 10.37).

Apart from the  $^{77}\text{Se}$  satellites around the  $\text{CH}_2-\text{Se}$  signal ( $J_{\text{Se}-\text{C}-\text{H}} = ca. 14$  Hz), the  $^1\text{H}$  NMR spectra of IX were almost identical to those of methyl isopropylidene-2-methyldithiocarbazate, $^1$  as was the IR spectrum in the  $\text{C}=\text{N}$  stretching region ( $1601$   $\text{cm}^{-1}$  and  $1624$   $\text{cm}^{-1}$ ). Accordingly, IX is acyclic.

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## Aromatic Hydroxylation Resulting from Attack of Lignin by a Brown-Rot Fungus

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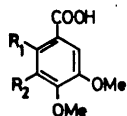
A valuable means for studying the aromatic substitution in lignins is the identification of methoxylated aromatic carboxylic acids formed on oxidative degradation of methylated samples. $^{1,2,c}$  In connection with investigations of the effects of brown-rot fungi on the chemical structure of lignin it was of interest to determine whether any significant differences were to be found between aromatic substitution patterns of sound and fungus-altered lignin.

Lignin isolated from wood of sweetgum (*Liquidambar styraciflua* L.) decayed by the brown-rot fungus *Lenzites trabea* Pers. ex Fries $^3$  ("enzymatically liberated lignin") has thus been compared with Björkman lignin (milled wood lignin) $^4$  of sound sweetgum wood. Following methylation, the lignins were oxidized with permanganate at pH 11–12 and then with hydrogen peroxide at pH 9–10, $^{2b}$  and the resulting acids methylated with diazomethane. The mixtures of methyl esters were examined by gas chromatography-mass spectrometry.

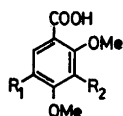
The gas chromatograms indicated close similarity between the two lignins in the products and in the approximate relative proportions of products. The major aromatic acids included veratric acid (I), tri-*O*-methylgallic acid (II), isohemipinic acid (III), metahemipinic acid (IV), and 3,4,5-trimethoxyphthalic acid (V). These acids are also major products formed on similar treatment of Björkman lignin of birch (*Betula verrucosa* Ehrh.). $^5$

In addition to the mutual chromatographic peaks, there were two significant peaks from the enzymatically liberated lignin that were not observed in the case of the ester mixture derived from Björkman lignin. The compounds responsible for

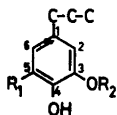
\* Present address: U. S. Forest Products Laboratory, Madison, Wisconsin, USA.



- I  $R_1 = R_2 = H$   
 II  $R_1 = H; R_2 = OMe$   
 III  $R_1 = H; R_2 = COOH$   
 IV  $R_1 = COOH; R_2 = H$   
 V  $R_1 = COOH; R_2 = OMe$



- VI  $R_1 = H; R_2 = OMe$   
 VII  $R_1 = R_2 = OMe$   
 IX  $R_1 = OMe; R_2 = H$



- VIII a  $R_1 = OCH_3; R_2 = H$  or Me  
 VIII b  $R_1 = H; R_2 = H$  or Me

these peaks have been identified by gas chromatography-mass spectrometry as the methyl esters of 2,3,4-trimethoxybenzoic acid (VI) and 2,3,4,5-tetramethoxybenzoic acid (VII). These clearly arose from structures which had been hydroxylated as a result of fungal action.

The hydroxylations occurred *ortho* to the side chains in the phenylpropane units of the lignin. It is not discernible from our data whether normal units (structures VIIIa and b,  $R_2 = Me$ ) or methoxyl-deficient units<sup>6a,b</sup> (structures VIIIa and b,  $R_2 = H$ ) or both were hydroxylated. Neither is the hydroxylation mechanism known. Evidently the origin of structures giving rise to 2,3,4,5-tetramethoxybenzoic acid (VII) involved hydroxylation at C-2 or C-6 of lignin units of type VIIIa. Similarly, the origin of structures giving rise to 2,3,4-trimethoxybenzoic acid (VI) involved hydroxylation at C-2 of VIIIb. Hydroxylation at C-6 of VIIIb did not occur; this would have led to 2,4,5-trimethoxybenzoic acid (IX), which was not detected in the mixture of esters derived from either lignin.

Investigations are underway to determine the nature of the hydroxylation reaction and to identify the structures giving rise to VI and VII.

**Experimental. Reference compounds.** For compounds I–VI, see Ref. 2c. 2,3,4,5-Tetramethoxybenzoic acid (VII), m.p. 85–86° (Ref. 7, m.p. 87–88°); asaronic acid (IX), m.p.

143–143.5° (Ref. 8, m.p. 142°). The respective methyl esters were prepared by methylation with diazomethane in methanol-ether.

**Lignins.** The enzymatically liberated lignin was a fraction (Fraction 3) prepared in connection with an earlier study.<sup>3</sup> Björkman lignin was prepared<sup>4</sup> from sound sweetgum sapwood.

**Methylation** of the lignins was accomplished with diazomethane in dimethylformamide in the manner used for ethylation with diazoethane.<sup>6b</sup> **Oxidation** of the methylated lignin<sup>5</sup> was done as described for ethylated lignins.<sup>6b</sup>

**Gas chromatography. Chromatograph:** Perkin-Elmer Model 880. **Column dimensions:** column A) 100 × 0.3 cm o.d., column B) 180 × 0.3 cm o.d. stainless steel tubing. **Solid support:** A) Chromosorb G, acid-washed and treated with dimethyldichlorosilane, 80–100 mesh; B) Gas-Chrom Z, 80–100 mesh. **Stationary phase:** A) General Electric SE-30, 5% by weight of solid support; B) combination of SE-30, 1% by weight of solid support, and General Electric XE-60, 2% by weight of solid support. **Temperatures:** Injection 300°, Detector 230°. **Column:** A) 170° constant, or 160–250°, 5°/min; B) 180° constant. **Carrier gas:** N<sub>2</sub>, 25 ml/min. **Detector:** Differential flame ionization. Compounds I–VII were analyzed with column A. The absence of compound IX could not be established with column A, but was possible with column B, which permitted authentic IX to be well separated from compounds obtained on methylation-oxidation of the lignins.

**Identification of methyl esters.** Compounds I–VII, as methyl esters, were identified by comparison of retention times and mass spectra with those of synthesized materials. Mass spectra were taken with an LKB 9000 gas chromatograph-mass spectrometer unit.

**Retention times of methyl esters.** (Retention times are expressed relative to that of the methyl ester of III). Column A (constant temperature of 180°) I–VI;<sup>2c</sup> VII 0.64; IX 0.65. Column B (constant temperature of 180°) I 0.26; II 0.40; III 1.00; IV 1.59; V 1.59; VI 0.34; VII 0.46; IX 0.73.

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## High Pressure Synthesis of $\text{Nb}_3\text{O}_7\text{F}$ with $\text{U}_3\text{O}_8$ -type Structure

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Structure determinations of niobium oxide fluorides have revealed the existence of six-coordinated metal atoms in  $\text{Nb}_3\text{O}_7\text{F}$ <sup>1</sup> and mixtures of six- and four-coordinated niobium atoms in the structures of  $\text{Nb}_{17}\text{O}_{43}\text{F}_3$ ,<sup>2</sup>  $\text{Nb}_{21}\text{O}_{77}\text{F}_3$ ,<sup>2</sup>  $\text{Nb}_{45}\text{O}_{161}\text{F}_3$ ,<sup>3</sup> and  $\text{Nb}_{59}\text{O}_{147}\text{F}_3$ .<sup>3</sup> All these structures are related to the  $\text{ReO}_3$  type of structure.  $\text{Nb}_3\text{O}_7\text{F}$  shows crystallographic shear in one dimension, while the others are of the Wadsley block type with shear in two dimensions.

Recently, Holmberg<sup>4</sup> has determined the structure of  $\text{Nb}_{23}\text{O}_{65}\text{F}_3$  with the niobium atoms in six- as well as in seven-coordination, and there is no obvious relation to the  $\text{ReO}_3$  structure.

Several compounds of intermediate compositions have also been found to exist in the system  $\text{Ta}_2\text{O}_5\text{F}$ — $\text{Ta}_2\text{O}_5$ . The compound

$\text{Ta}_2\text{O}_5\text{F}$  was reported<sup>5</sup> to occur in two different forms, one of the  $\text{LiNb}_3\text{O}_{11}\text{F}$  structure type,<sup>6</sup> the other of a type related to  $\text{U}_3\text{O}_8$ .<sup>7</sup> Both of these have six- as well as seven-coordinated metal atoms. These structures are packed more densely than those of the corresponding niobium oxide fluoride structures that are based on the  $\text{ReO}_3$ -type building units.

The starting materials used were  $H\text{-Nb}_2\text{O}_5$  and  $\text{NbO}_2\text{F}$ ; the latter was prepared according to Ref. 8. A sample of  $\text{Nb}_3\text{O}_7\text{F}$  was obtained by heating a mixture of  $\text{NbO}_2\text{F}$  and  $H\text{-Nb}_2\text{O}_5$  (mole ratio 1:1) at 850°C in a sealed nickel capsule.

The pressure experiments were performed in a girdle apparatus<sup>9</sup> at 25 kb in the temperature range 850–1100°C. Mixtures of  $H\text{-Nb}_2\text{O}_5$  and  $\text{NbO}_2\text{F}$  in the mole ratio 1:1 as well as samples of  $\text{Nb}_3\text{O}_7\text{F}$  were exposed to the pressure for 2–14 h. Crystalline materials were always obtained and X-ray powder analysis at atmospheric pressure and room temperature indicated the presence of a new phase. A reaction time in excess of 3 h at 900°C resulted in a slight reduction of the products as evidenced by dark coloration.

Weissenberg photographs of a single crystal, selected from a white nonreduced sample prepared at 900°C and 20 kb, were taken with  $\text{CuK}\alpha$  radiation with the  $a$  axis chosen parallel to the rotation axis ( $a = 3.9$  Å). The Laue symmetry was  $mmm$ . On the Weissenberg photographs  $0kl$  and  $1kl$  and the powder photograph (*v. infra*) the following reflections were absent:

$$hkl \text{ for } k+l = 2n+1$$

Thus probable space groups are  $A222$ ,  $A2mm$ ,  $Amm2$ , and  $Ammm$ .

The cell constants were derived from a powder photograph, taken with a Hägg-Guinier camera, using  $\text{CuK}\alpha_1$  radiation. All lines were indexed on the basis of an orthorhombic cell, with the following edge lengths:

$$\begin{aligned} a &= 3.927 \pm 1 \text{ \AA}; & b &= 10.514 \pm 1 \text{ \AA}; \\ c &= 6.475 \pm 1 \text{ \AA}; & V &= 267.4 \text{ \AA}^3 \end{aligned}$$

The indexed powder pattern is given in Table 1. The density of the sample determined from the loss of weight in benzene was 5.23 g cm<sup>-3</sup>, which corresponds to two formula units of  $\text{Nb}_3\text{O}_7\text{F}$  per unit cell ( $d_{\text{calc}} = 5.08$  g cm<sup>-3</sup>).

The composition of the starting materials as well as the observed density, suggests the formula  $\text{Nb}_3\text{O}_7\text{F}$ . The unit cell dimen-