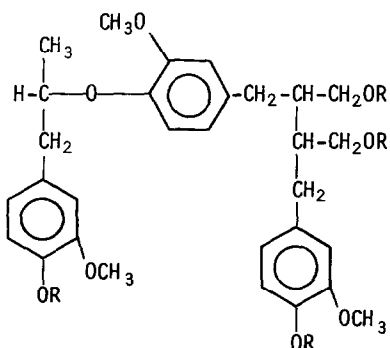


LIGNIN AND RELATED COMPOUNDS VII. THE ISOLATION OF  
A TRIMERIC LIGNIN COMPOUND BY THE HYDROGENOLYSIS OF SPRUCE WOOD

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In earlier reports<sup>1,2</sup> several low molecular weight monomeric products obtained by the hydrogenolysis of spruce lignin over a rhodium-on-charcoal catalyst were identified. A study of the higher molecular weight fraction has revealed the presence of a trimeric compound (1). A portion (21.4 g) of the combined chloroform-soluble fraction (42.2 g) obtained by the hydrogenolysis of pre-extracted spruce wood meal [ten runs each using wood meal (20 g), Rh-C catalyst (1.5 g), dioxane-water (1:1 v/v)(300 ml), hydrogen (initial pressure 500 psi), 5 hr at 195°] was fractionated in a 100-tube Craig countercurrent extraction apparatus using Skelly C as the upper mobile phase (25 ml per tube) and dioxane-water (3:2) as the lower phase (25 ml per tube). G.l.c. analysis of a sample of the combined eluted fractions 1-21 showed the presence of the well recognized lignin dimer, 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-di-n-propylbiphenyl.

A further portion (13.2 g) of fractions 1-21 was refractionated in the same apparatus using methanol-water (3:2 v/v) as the upper phase and methylene chloride as the lower phase. From eluted fractions 21-25 (4.85 g) the trimer was isolated as follows. A sample was dissolved in chloroform, spotted on thin-layer plates (silica gel G with fluorescence indicator, 0.25 mm thickness) and developed with methanol-chloroform (1:9 v/v). A spot,  $R_f = 0.41$ , was extracted with methanol-chloroform (2:3 v/v), filtered and the solvent evaporated. The residue was acetylated, reapplied to similar thin-layer plates and developed using benzene-acetone (2:1 v/v). The material represented by a spot,  $R_f = 0.60$ , was extracted and characterized as (2) by its NMR and mass spectra.



(1) R = H

(2) R = COCH<sub>3</sub>

The NMR spectrum (in CDCl<sub>3</sub>) showed absorptions at  $\delta$ :0.8-1.1 (3H, CH<sub>3</sub>),  $\delta$ 1.4-1.6 (2H, -CH-),  $\delta$ 1.8-2.1 (6H, CH<sub>3</sub>-CO-O-C),  $\delta$ 2.2-2.3 (6H, CH<sub>3</sub>-CO-O-C<sub>6</sub>),  $\delta$ 2.4-2.8 (6H, -C-CH<sub>2</sub>-C<sub>6</sub>),  $\delta$ 3.7-3.9

(1H,  $\overset{|}{\text{C}}\text{H}-\text{O}-\text{C}_6\text{H}_4$ , 9H,  $\text{CH}_3-\text{O}$ ),  $\delta$ 4.1-4.3 (4H,  $-\overset{|}{\text{C}}-\text{CH}_2-\text{O}$ ),  $\delta$ 6.8-7.3 (9H, aromatic). The mass spectrum suggested a molecular formula of  $\text{C}_{38}\text{H}_{46}\text{O}_{12}$  (molecular ion 694) with a base peak of mass 137 (4-hydroxy-3-methoxyphenylmethyl radical ion). Other prominent peaks represented fragment masses of 652 and 610 (loss of one or two ketene molecules), 488 ( $\text{C}_\beta$ -aryl ether cleavage with hydrogen transfer), 446 (loss of ketene from 488), 265 ( $\text{C}_\beta-\text{C}_\beta$  cleavage of 488), 301 ( $\text{C}_\alpha-\text{C}_\beta$  cleavage of 652 and 610, and 164 (loss of 137 from 301).

Other similar trimeric compounds have been isolated from the products of the catalytic hydrogenolysis and mild hydrolysis of softwood lignin. Sakakibara and coworkers<sup>3,4,5,6,7</sup>, using a copper chromite catalyst, reported the isolation of compounds with  $\text{C}_\beta-\text{C}_5$  and  $\text{C}_\beta-\text{C}_1$ ,  $\text{C}_5-\text{C}_5$  and  $\text{C}_\beta-\text{C}_5$ , and  $\text{C}_\beta-\text{C}_5$  and  $\text{C}_\beta-\text{C}_5$  linkages. By hydrolysis, Sano and Sakakibara<sup>8</sup> isolated a trimer with  $\text{C}_\beta-\text{C}_5$  (coumaran ring) and  $\text{C}_\beta-\text{C}_1$  linkages and both these workers<sup>9</sup> and Nimz<sup>10</sup> reported the presence of the same trimer with  $\text{C}_\beta$ -aryl ether and  $\text{C}_\beta-\text{C}_1$  linkages. The isolation therefore of (1) from spruce lignin with its previously unreported  $\text{C}_\beta-\text{C}_\beta$  and  $\text{C}_\beta$ -aryl ether linkages adds further support to the radical theory and the random nature of lignin biosynthesis.

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