2-(2-Methoxy-4-n-propylphenoxy)propan-1-ol as a New Spruce Lignin Hydrogenolysis Product

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Summary 2-(2-Methoxy-4-n-propylphenoxy)propan-1-ol has been isolated from the products of the hydrogenolysis of spruce lignin over a rhodium–charcoal catalyst.

IN an earlier report[1] the main low-molecular-weight products obtained by the hydrogenolysis of spruce lignin over rhodium–charcoal catalyst were identified. We have begun a study of the nature of the less abundant but higher-molecular-weight lignin products. The chloroform-soluble fraction obtained by the hydrogenolysis of pre-extracted spruce wood meal [wood meal (20 g.), Rh–C catalyst (1·5 g), dioxan–water (1 : 1 v/v) (300 ml.), hydrogen (initial pressure 500 lb./in^2), 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 dioxan–water (3 : 2) as the lower phase (25 ml. per tube). This technique permitted of the separation of the less polar compounds from those possessing a higher content of hydroxy-groups. Thus in the combined eluted fractions 1–21 was found, in a 0·8% yield of the lignin, 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-di-n-propylbiphenyl (m.p. 149—150°, reported[2] m.p. 149·5—150·5°) and in fractions 6—75 was found 4-n-propylguaiacol, whereas the other main hydrogenolysis product, dihydroconiferyl alcohol, remained in transfer tubes 18—38 in the machine even after 1110 transfers had been completed. The presence of the above dimeric unit, in the products of spruce lignin hydrogenolysis, had also been recorded previously in these laboratories.[3]

G.l.c. analyses of the eluted fractions 42—75 revealed the presence of a new compound whose retention time was between those of typically monomeric and dimeric products. This compound was isolated by means of g.l.c. using a Varian Aerograph Model 90-P apparatus with a 6 ft. × $\frac{1}{4}$ in. column of 10% Apiezon N on Chromosorb W at 200°. Other compounds that were similarly isolated from this fraction were identified as 4-methylguaiacol, 4-n-propylphenol, 4-ethylguaiacol, and 4-n-propylguaiacol by their retention times and mass spectra, and by comparison with authentic samples.

This new compound was identified as (I) by its mass and n.m.r. spectra. The mass spectrum suggested a molecular formula of $C_{13}H_{20}O_3$ (molecular ion 224) with a base peak of mass 137 (α–β cleavage of side-chain with loss of 29 mass units and cleavage of the ether linkage with hydrogen ion transfer with loss of 58 mass units). Other prominent peaks represented fragment masses of 166, 138, 122, 107, 77, 41, 39, 31, 29, and 27. The n.m.r. spectrum (in $CDCl_3$) showed absorptions at τ 2·95—3·2, m, 3H; 5·7—6·0, m, 1H; 6·09, s, 3H; 6·33,d, 2H; 7·43, tr, 2H; 7·5, broad, 1H; 8·0—8·3, m, 2H; 8·67, d, 3H; and 9·05, tr, 3H.

On irradiation at τ 5·85 (2-H) the doublets at τ 6·33 and 8·67 collapsed into singlets and irradiation at τ 8·2 (H_β) collapsed the triplets at τ 7·43 and 9·05, also into singlets.

The structure was confirmed by synthesis. Ethyl 2-(2-methoxy-4-n-propylphenoxy)propionate (II) was obtained by the condensation, in ethanol, of ethyl α-bromopropionate with the sodium salt of 4-n-propylguaiacol. This ester, b.p.$_{0\cdot8}$ 129—130°, was reduced with $LiAlH_4$ to give (I) as a colourless oil, b.p.$_{0\cdot5}$ 110—111° which gave identical mass and n.m.r. spectra with those of the compound isolated from the hydrogenolysis products.

(I) $R{=}CH_2OH$
(II) $R{=}CO_2Et$

Compound (I) has been obtained in a yield of 0·2—0·3% of the spruce lignin. The isolation of this new degradation product lends support to the presence in lignin of the recently suggested[4,5] glyceraldehyde 2-aryl ether unit, from which it could easily arise by dehydration followed by hydrogenation.

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† Petroleum b.p. 80–100°.

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