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THE STRUCTURE OF (-)-OLIVIL

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IN a recent note[1], (-)-olivil was formulated as (I) on the basis of catalytic hydrogenolysis of (-)-olivil dimethyl ether to a triol identical with that obtained by hydrogenolysis of (+)-gmelinol (II)[2], and on the fission of (-)-olivil dimethyl ether by lead tetra-acetate.

The 60 mc. nuclear magnetic resonance spectrum of (-)-olivil dimethyl ether[3] in deuterochloroform using tetramethylsilane as internal reference showed a doublet at 5.29 τ (J = 7.5 c.p.s.). Numerous comparison spectra of lignans show this to be due to the hydrogen on the benzyl carbon atom of the benzyl ether group. Also, since this hydrogen shows as a doublet, the carbon atom adjacent to it must carry one hydrogen. This requirement is not accommodated by structure (I) for (-)-olivil,

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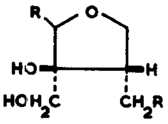
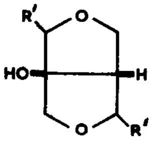
[1] K.Freudenberg and K.Weinges, Tetrahedron Letters, **1962**, 1077.

[2] A.J.Birch, G.K.Hughes and E.Smith, Austral.J.Chem. **7**, 83, (1954).

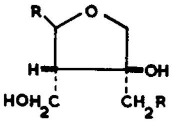
[3] I am grateful to Professor R.D.Haworth for provision of a specimen of olivil dimethyl ether.



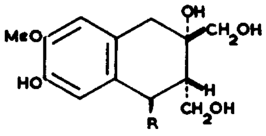
I



II

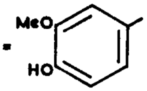


III

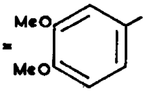


IV

R =



R′ =



but is satisfied by structure (III), which would also give rise to the observed triol on hydrogenolysis. The structure of (+)-cycloolivil therefore is (IV).

The reaction of (-)-olivil dimethyl ether with lead tetraacetate can not be a 1,2-glycol fission, and probably proceeds via initial attack at either of the benzyl carbon atoms.

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