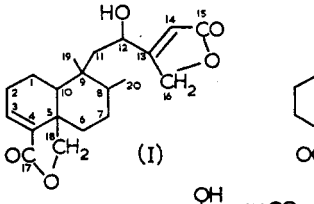
The Structure of Olearin, a Diterpene Dilactone

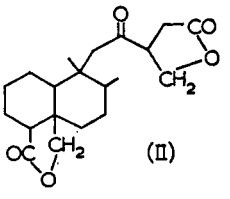
By J. T. PINHEY and R. F. SIMPSON

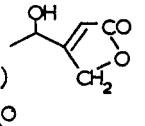
(Department of Organic Chemistry, University of Sydney, Sydney, Australia)

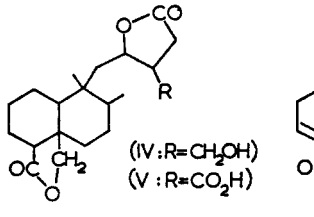
ON chemical and spectroscopic evidence we suggest structure (I) for olearin ($C_{20}H_{26}O_5$, m.p. 213°, $[\alpha]_D$ −120° in $CHCl_3$), a new, neutral diterpene of the columbin type,[1] isolated from *Olearia heterocarpa* S. T. Blake. The u.v. (λ_{max} 214 mμ, ϵ, 21,000) and i.r. absorption [ν_{max} 1787, 1740s, 1654w, 1630w cm.$^{-1}$ in Nujol] indicate the presence of two $\alpha\beta$-unsaturated ester groupings. The carbonyl absorption (ν_{max} 1762 cm.$^{-1}$ in $CHCl_3$) of tetrahydro-olearin, obtained by hydrogenation of (I), showed that both carbonyl groups are present in γ-lactone rings. The fifth oxygen of olearin is present in a readily acetylatable hydroxyl group which is secondary since tetrahydro-olearin may be oxidised to a ketone (II).

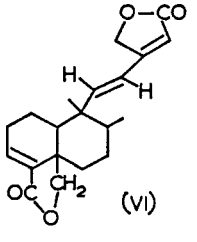
Part structure (III) was established in the following way. Treatment of the ketone (II) with







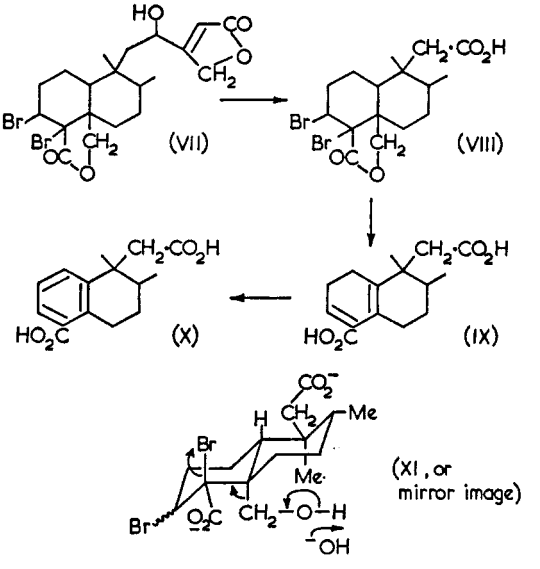




alkali gave rise to formaldehyde, presumably *via* a retro-aldol condensation. Thus the hydroxyl of the opened lactone must be β to the keto-group. In addition, strong acid or dissolution in dilute alkali followed by acidification converts tetrahydro-olearin to an isomer (IV) which also contains two γ-lactone rings (ν_{max} 1773 and 1765 cm.$^{-1}$ in $CHCl_3$) and which may be oxidised to a carboxylic acid (V).

The n.m.r. spectrum of olearin is consistent[2] with a β-substituted butenolide structure. The two C-16 protons appear as an AB system at δ 4·83 and δ 4·85 (J_{AB} = 18 c./sec.) while H-14 is a fine multiplet (allylic coupling) at δ 5·90. The remainder of the proposed structure is supported by n.m.r. data, which indicate the presence of one tertiary methyl, one secondary methyl, one vinyl proton adjacent to a CH_2 group ,and the grouping CH_2–O attached to a fully substituted carbon atom.

On heating the methanesulphonate of olearin in dimethyl sulphoxide[3] anhydro-olearin (VI) is formed in good yield. The *trans*-assignment for the introduced double bond follows from its n.m.r. spectrum (J_{AB} = 16·7 c./sec.). Both protons of this *trans*-ethylenic link appear as doublets, hence C-9 in olearin does not bear a proton, indicating a rearranged labdane skeleton.



Olearin readily adds bromine to yield dibromo-olearin (VII). The assignment of structure (VII) follows from the n.m.r. spectrum which shows a signal due to one vinyl proton at δ 5·97 (fine multiplet), indicating that the butenolide double bond is retained. Oxidation of dibromo-olearin with potassium permanganate in dry acetone produces the dibromo-acid (VIII; ν_{max} 1760 and 1717 cm.$^{-1}$ in Nujol) in good yield. In aqueous alkali at reflux (VIII) gives formaldehyde and a fair

yield of the diene (IX; λ_{max} 281 mμ, ϵ, 2407).[4] The n.m.r. spectrum of the dimethyl ester of (IX) has a signal due to one vinyl proton at δ 6·8 (multiplet). The conversion of (VIII) into (IX) must occur by a Grob fragmentation[5] (see XI)[6] followed by dehydrobromination. No doubt the facile fragmentation is due to a *trans* and diaxial arrangement of the bromine and hydroxymethyl group. The stereo-electronic arrangement is less favourable for debrominative decarboxylation and this reaction does not seem to compete.

Dehydrogenation of the dimethyl ester of the diene (IX) with dichlorodicyanoquinone, followed by hydrolysis gives a high yield of the tetralin dicarboxylic acid (X; λ_{max} 234 mμ, ϵ, 6260; 283 mμ, ϵ, 1300).[7] The structure assigned to (X) is consistent with the n.m.r. spectrum of the dimethyl ester, which has signals due to a secondary methyl (δ 1·0, doublet, J = 7 c./sec.), a tertiary methyl (δ 1·28), two protons adjacent to C=O (δ 2·76, broad singlet), two benzylic protons (δ 3·13, triplet) and three aromatic protons (δ 7·0—δ 7·8). In support of the structures proposed for the above compounds, the diene (IX), on dehydrogenation over 10% Pd/C, yields 1,2-dimethylnaphthalene.

The relative stereochemistry of olearin implied in (XI) is based on biogenetic considerations.[8,9]

(*Received, September 15th*, 1966; *Com.* 695.)

[1] D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 1956, 2085.
[2] N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, p. 45.
[3] D. N. Jones and M. A. Saeed, *J. Chem. Soc.*, 1963, 4657.
[4] For closely related homoannular dienes with similar u.v. absorption see G. A. Berchtold, J. Ciabattoni, and A.A. Tunick, *J. Org. Chem.*, 1965, **30**, 3679.
[5] C. A. Grob, "Proceedings and Discussions of the Kekulé Symposium", Butterworths, London, 1959, p. 114.
[6] The *trans*-ring junction is assumed on biogenetic grounds.
[7] The u.v. absorption of (X) corresponds closely to a similarly substituted tetralincarboxylic acid reported by S. W. Fenton, A. E. De Wald, and R. T. Arnold, *J. Amer. Chem. Soc.*, 1955, **77**, 979.
[8] D. H. R. Barton, H. T. Cheung, A. D. Cross, L. M. Jackman, and M. Martin-Smith, *J. Chem. Soc.*, 1961, 5061.
[9] T. G. Halsall, A. W. Oxford, and W. Rigby, *Chem. Comm.*, 1965, 218.