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CONSTITUTION OF PEUCEPHYLLIN, A NEW TYPE OF GERMACRANOLIDE FROM PEUCEPHYLLUM SCHOTTII

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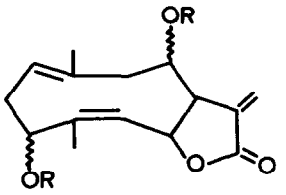
Examination of the chloroform extract of Peucephyllum schottii Gray, has resulted in the separation of a new type of germacranolide, designated peucephyllin. We now report its structure.

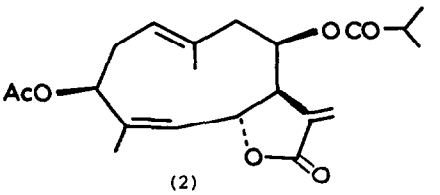
Chromatography over silica gel gave peucephyllin, $C_{21}H_{28}O_6$, as needles m.p.120.5-121.5° (from EtOAc), $[\alpha]_D^{22}$ - 140.9 ($CHCl_3$, c 1.00). Extensive spectral data, and particularly inspection of Eu(dpm)$_3$ expanded and decoupled ^{1}H n.m.r. data suggested gross structure (1a) for the germacranolide. Catalytic hydrogenation led to dihydropeucephyllin $C_{21}H_{30}O_6$, m.p. 167-168°, and saponification produced 2-methylpropionic acid.[1] Acetylation of the diol obtained from saponification of peucephyllin, gave a germacranolide diacetate, different in its p.m.r. spectrum from chihuahuin acetate[2] and eupaformonin acetate.[3,4]

The structure and relative stereochemistry of peucephyllin were fully established by single crystal X-ray analysis. Peucephyllin crystallised in the space group P2, with a = 9.71, b = 11.56, c = 10.08 °A, β = 110.13° and Z = 2. Intensity data were collected with Mo-Kα radiation using an automatic four-circle diffractometer, and 1357 reflections were considered observed. The structure was determined by direct methods using the Multan program,[5] and refined by block-diagonal least-squares to a current R index of 12.4%. The Figure shows the resulting structure of peucephyllin and also its conformation in the crystal

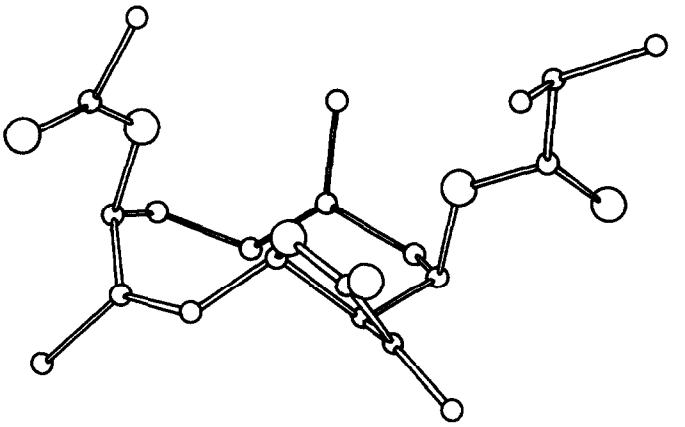
Peucephyllin is a new member of the trans-1(10), cis-4(5) germacranolides ("heliangolide" sub group).[6] Up to now, all other "heliangolide" sesquiterpenes have contained a 1(10) epoxide group and generally a 3β-hydroxyl group.[7] If, as in all known



(1) a R,R,=Ac, $COPr^1$
b R=α-Ac, R,=β-OH



(2)



naturally occurring germacranolides, the 7-H is α-orientated, then both the 3-OAc and 8-$OCOPr^1$ are β-orientated in peucephyllin, i.e the asymmetric carbon atoms have the configurations 3S, 6S, 7R and 8R. Peucephyllin is structurally similar to eupaformonin (1b) isolated recently from Eupatorium formosamon Hay.[2]

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References

1. Identified as the methyl ester by co-g.l.c. with authentic methyl 2-methylpropionate.
2 W Renold, H. Yoshioka and T J Mabry, J Org. Chem., 1970, 35, 4264
3 A.T McPhail, K.D. Onan, K.H. Lee, T Ibuka and H C Huang, Tetrahedron Letters, 1974, 3206 We thank Dr. Lee for a sample of eupaformonin acetate for comparison.
4. Dihydropeucephyllin was recovered unchanged after heating at 220° for 7 min., and also after u.v irradiation
5. G. Germain, P. Main and M M Woolfson, Acta Cryst 1971, A27, 368
6 S Neidle and D Roberts. Chem. Comm., 1972, 140, 142.
7 See ref 3 for a complete list of other 'heliangolides'.