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CAULERPOL, A DITERPENE ALCOHOL, RELATED TO VITAMIN A, FROM CAULERPA BROWNII (ALGAE)

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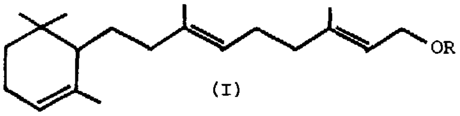
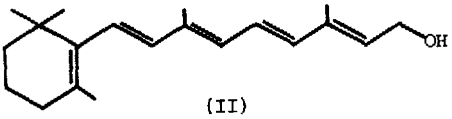
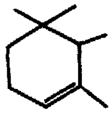
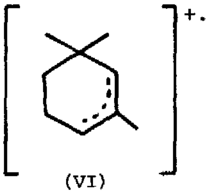
During investigations into the constituents of marine algae occurring in Tasmanian waters we have isolated a diterpene alcohol from Caulerpa brownii for which we propose the name caulerpol. The spectroscopic and degradative evidence for caulerpol are consistent with structure (1) (R=H) which is closely related to that of retinol (11).


(I)


(II)


(III)


(VI)

Several Caulerpa species (chlorophyta) have been previously investigated and shown to contain triterpenes[1] and xanthophylls[2] as well as nitrogen-containing compounds[3,4]. We now report the isolation of the first diterpene from this genus.

Freshly collected Caulerpa brownii (from Cook's Corner, Freycinet Peninsula, East Coast of Tasmania) was exhaustively extracted at 0° with chloroform-methanol (1:1, v/v). The concentrated extract was partitioned between hexane and aqueous methanol and the hexane-soluble material purified by dry column chromatography on silica gel eluted with hexane-chloroform to yield caulerpol (9.5% based on dry weight), together with the acetate 1 (R = Ac).

Caulerpol was obtained as a colourless oil; b.p. 120° (0.1 mm); $[a]_D^{MeOH}$ -84.8°; m.s. m/e 290 (M^+) which analysed for $C_{20}H_{34}O$. The i.r. spectrum (ν_{max} 3170, 1000 cm^{-1}) indicated the presence of a hydroxyl group and trans-substituted double bonds.

The ^1H n.m.r. of caulerpol (CCl_4) showed signals due to three olefinic protons at δ5.35, 5.26, 5.08 (Each 1H,m), a signal due to a $=CH-\underline{CH_2}-OH$ group at δ4.01 (2H,d,J=7.5Hz) coupled to the signal at δ5.26, three methyl groups attached to double bonds at δ1.65 (6H,s) and δ1.58 (3H,s) and two methyl singlets at δ0.91 and 0.85. The remainder of the spectrum comprised nine methine and methylene protons centred at δ1.97, a four proton multiplet centred at δ1.40 and a broad singlet (O-H) at δ2-3 (concentration dependant) which was exchanged by D_2O.

Caulerpol was therefore a monocyclic diterpene and structure (1, R=H) was consistent with all the data. Comparison of the ^1H n.m.r. data for (I) with the published values for (III)[5] supported the presence of this partial ring system and the positions of the exocyclic Sp^2 bound methyl groups were in close agreement to those predicted by the rules of Bates and Gale[6] for all trans stereochemistry in (I).

The ^{13}C n.m.r. of (I) supported the proposed structure and side chain stereochemistry (139.3(s), 136.9(s), 136.1(s), 123.8(d,2C), 120.0(d), 59.3(t), 49.1, 40.6, 39.7, 32.7, 31.8, 30.0, 27.5, 26.5, 23.2, 16.2 p.p.m.). The relevant region of the spectrum closely paralleled that reported for farnesol[7] and other resonances were entirely consistent with those expected of the substituted cyclo-hexane ring. The mass spectrum of I showed a strong fragment ion at m/e 123 which could be rationalised as ion IV.

Further support for the proposed structure was obtained by ozonolysis which gave levulinic acid, identified by g.l.c. of its methyl ester and preparation of the D.N.P. Acetylation of caulerpol gave the acetate (I, R=Ac) which was identical (i.r., m.s., ^1H n.m.r.) with a second component, separated in 0.3% yield from the algal extract.

A compound of structure I is reasonable on biosynthetic grounds and is closely related to that of retinol (II, vitamin A). It is interesting to note that retinol occurs in nature only in animal organisms and caulerpol would appear to be the first compound reported with the same carbon skeleton from plant sources.

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