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24-DEMETHYLDINOSTEROL: AN UNUSUAL STEROL FROM THE DINOFLAGELLATE, GONYAULAX DIAGENESIS.

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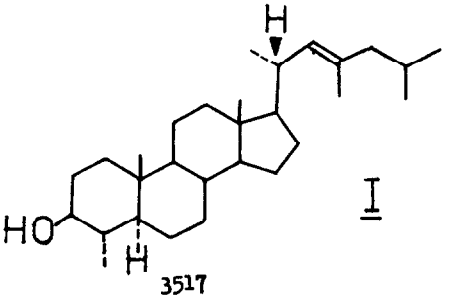
The origin of unusual sterols (e.g. gorgosterol[1], acanthasterol[2], etc.) in marine invertebrates has been a subject of much discussion.[3,4] Recently the presence of an other unusual sterol--dinosterol has been reported from the toxic dinoflagellate Gonyaulax tamarensis[5]. In our search for sterols with unusual side chains we decided to study a number of dinoflagellates for their sterol composition. Dinoflagellates along with diatoms constitute what is commonly known as phytoplanktons, and are part of the marine food chain.

Unialgal cultures of the dinoflagellate, Gonyaulax diagenesis were grown on NIH-15 medium.[6] The chloroform extract of the dinoflagellate upon saponification afforded a sterol fraction which consisted of three major sterols--cholesterol(38.7%), isofucosterol (28.7%) and a new C-29 sterol(12.5%).[7] The 24-demethyldinosterol (I) was purified by a high performance chromatographic method and crystallized from $CHCl_3$:MeOH. M.P. 183-185°C, $[\alpha]_D \pm 3°$ (c 0.45 in $CHCl_3$), $C_{29}H_{50}O$ (Calculated m/e 414.38616, found 414.38518). The mass spectrum pattern of I m/e 316 (74%, $C_{22}H_{36}O$), 287 (100%, $C_{20}H_{31}O$), 271 (66%, $C_{20}H_{31}$), 229 (22%, $C_{17}H_{25}$) reminded us of dinosterol[5] and gorgosterol.[1] The 100MHz PMR spectrum of I showed the presence of six alkyl linked methyl groups, [δ0.69(3H,S); δ0.79(3H,d,J=7Hz); δ 0.84(3H,S); δ0.85(3H, d,J=7Hz); δ0.9 6H,d,J=6Hz], a vinyl methyl (δ1.55,d,J=1.4Hz) and a hydroxyl proton at δ3.0, and an olefinic proton (δ 4.95, 1H, m, J = 1.2, 10.5Hz). The PMR spectrum of I suggests the presence of a side chain with a partial structure of -CH-CH=C(CH_3)- and was similar to that of dinosterol.[5] The only difference between the two was the absence of one methyl signal in the spectrum of I. The presence of a double bond at C-22 was established by the ozonolysis of I followed by $NaHB_4$ reduction of the product. The M.S. of the resulting diol 348(M^+, 75%) showed a fragmentation pattern [m/e 333(19%); 330(17%) 248(100%); 247(70%) and 229(55%)] similar to that reported for the diol from dinosterol.[5]



I

Compound I was characterized as 24-demethyl dinosterol (4α, 23-dimethyl-5α-cholest-22-en-3β-ol), on the basis of the PMR and the mass spectral data which was very similar to that of dinosterol.

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