Acansterol: A Cyclopropane-containing Marine Sterol from *Acanthaster planci*

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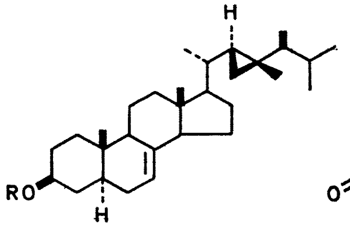
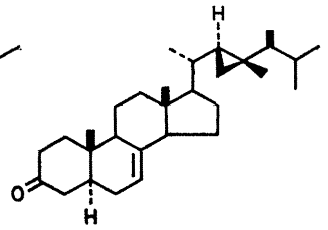
Summary From an extract of *Acanthaster planci* a new cyclopropane-containing sterol has been isolated and its structure elucidated.

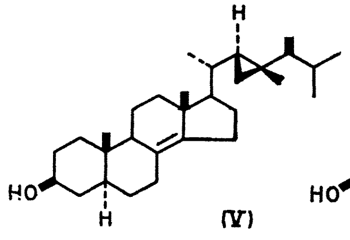
IN the course of a continuing search for biogenetically interesting marine sterols,[1-3] preparative gas chromatography of the sterol portion of *Acanthaster planci* (collected in Tahiti) furnished a new sterol (now named Acansterol) to which structure (I) is assigned on the following spectral and chemical evidence.

Acansterol (I) [$C_{30}H_{50}O$, M^+ 426·3728 (required 426·3861), $M - CH_3$ 411·35937 (required 411·36267), m.p. 179—180°, λ_{max} (KBr) 3375 cm^{-1}, $[\alpha]^{21}_{D}$ 5 ± 3° (*c* 0·65 g/100 ml chloroform) typical of Δ^7-sterols[4]] gave a positive Liebermann–Burchard reaction and could be precipitated with digitonin. Its mass spectrum showed the usual peaks at *m/e* 299—301, 271—273, 255—257, 231 (ring D fission) and 213 (231 − H_2O) characteristic of a conventional steroidal nucleus[5] with an unsaturated side-chain,[6] and also ions at *m/e* 411 ($M - CH_3$), 383 ($M - C_3H_7$), 355 ($M - C_5H_{11}$), 328 ($M - C_7H_{16}$), and 314 ($M - C_8H_{18}$) characteristic of the gorgosterol side-chain. The n.m.r. spectrum (100 MHz) in deuteriobenzene depicted the presence of three quaternary methyl groups (τ 9·16, 9·03, and 8·87, s, 3H each), one isopropyl function (τ 8·89, d, *J* 6·0 Hz, 6H coupled to a complex at 8·16), two superimposed secondary methyl groups (8·77, d, *J* 7 Hz, 6H coupled to a high-field multiplet at 9·90, and a complex signal at 8·24), a secondary carbinol methine (6·45, c, m) and an olefinic proton (4·51, dt, coupled to protons at 8·09). In addition, the n.m.r. spectrum showed high-field signals at τ 9·89 (d, d, *J* 3·0, 5·5 Hz, 1H), 9·70—9·50 (m, *J* 8·5, 7 Hz, 2H) and 9·30 (d, d, *J* 3·0, 8·5 Hz, 1H). Results of decoupling experiments† suggested the protons to be on a cyclopropane ring and to bear the same relationship to each other as in gorgosterol.[1]

Acansterol (I) furnished a mono *p*-bromobenzoate (II), m.p. 230—232°, M^+ 608, 610, and a mono *p*-iodobenzoate (III), m.p. 219—221°, M^+ 656. Oxidation with chromium trioxide in pyridine[7] gave acansterone (IV), [M^+ 424, m.p. 192—194°, λ_{max} ($CHCl_3$) 1705 cm^{-1} transparent in the u.v. region, no base shift and hence not a $\beta\gamma$-unsaturated ketone], which showed all of the mass spectral peaks associated with the steroidal nucleus and gorgosterol side-chain (see above) but shifted to lower mass-units by two, and an o.r.d. curve similar to that of Δ^7-ergosten-3-one.[8] On stirring with Pd/C in ethyl acetate under hydrogen, acansterol (I) was isomerized to a compound (V) (M^+ 426, m.p. 159—160°), whose mass spectrum contained all the ions of acansterol but with pronounced intensity changes [*e.g.*, *m/e* 271 base peak in (I) as against *m/e* 426 (M^+) in (V)]. The n.m.r. spectrum of (V) in deuteriobenzene (100 MHz) exhibited high-field cyclopropane protons [τ 9·87 (d, d, *J* 3·5 and 5·5 Hz), 9·67—9·45 (m, *J* 6·5, 8·5 Hz), and 9·27 (d, d, *J* 8·5, 3·5 Hz)], three quaternary methyl groups (9·08, 3H and 8·83, 6H, s), an isopropyl function (8·85, d, *J*, 6·5 Hz), two secondary methyl groups (8·75, d, *J* 6·5 Hz, 6H), a secondary carbinol methine (6·39, m, 1H) and notably no olefinic proton signals.


(I) R = H
(II) R = *p*-Br·C_6H_4·CO−
(III) R = *p*-I·C_6H_4·CO−


(IV)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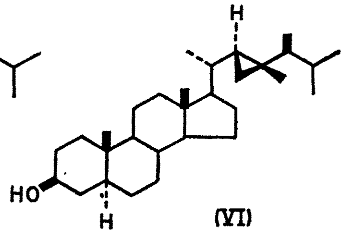
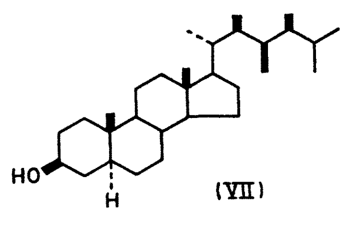

(VI)


(VII)

Prolonged hydrogenation (48 h, room temp. and atmospheric pressure) of (I) in a mixture of ethyl acetate, acetic acid, and hydrochloric acid over platinum furnished a dihydro-(VI) and a tetrahydro-(VII) derivative. The former (m.p. 164—167°, M^+ 428) showed identical g.l.c. retention times and mass spectra to those of dihydrogorgosterol[1] (m.p. 165—167°). Compound (VII), m.p. 152—156°, M^+ 430, showed peaks in its mass spectrum at *m/e* 387 ($M - C_3H_7$), 359 ($M - C_5H_{11}$), 331 ($M - C_7H_{15}$), and 303 ($M - C_9H_{19}$) suggesting the presence of a C_{11} side-chain

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† Kindly performed by Dr. M. Bramwell under the supervision of Dr. L. J. Durham at Stanford University. Benzene was used as a lock signal and was assumed to be 7·37 p.p.m. from Me_4Si.

carrying methyl groups at every carbon atom of the side-chain.

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