Crystal Structure and Absolute Configuration of Two Cyclopropane Containing Marine Steroids

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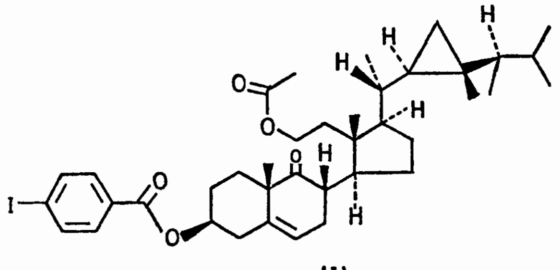
Summary The structures and absolute configurations of 9-oxo-9,11-secogorgost-5-ene-3β,11-diol 11-acetate and 23-demethylgorgosterol have been determined by single crystal *X*-ray diffraction studies on their *p*-iodobenzoate derivatives.

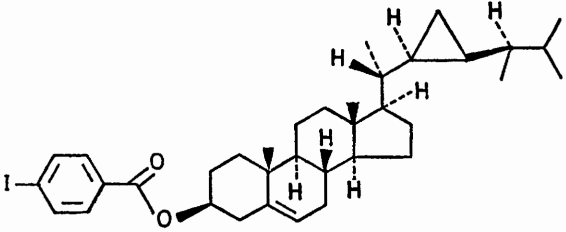
A NEW and growing class of marine steroids which exhibit unusual side chain structures, including the presence of a cyclopropane ring, have been reported.[1] In order to demonstrate unambiguously the relationship of two of these compounds to gorgosterol[1a,b] we now report our determinations of the molecular and crystal structures of the 3-*p*-iodobenzoate derivatives of 9-oxo-9,11-secogorgost-5-ene-3β,11-diol 11-acetate and 23-demethylgorgosterol.

The seco-derivative of gorgosterol occurs as the free dihydroxy-ketone in *Pseudopterogorgia americana*, a gorgonian which also contains a relatively high proportion of the new marine sterol gorgosterol. After purification as the 3,11-diacetate, a selective saponification afforded the free 3-ol which was esterified with *p*-iodobenzoyl chloride in pyridine to give (I). The *p*-iodobenzoate derivative (II) was prepared by a similar esterification of a sample of 23-demethylgorgosterol isolated from *Gorgonia flabellum* and *Gorgonia ventalina* as described in a previous report.[1c]

Diffraction intensity data for (I) were collected on a General Electric XRD-5 single crystal diffractometer and



(I)



(II)

data for (II) were collected on an Enraf Nonius CAD-3 automatic diffractometer. In each case the data were collected at room temperature by the moving-crystal, moving-counter technique with background counted on both sides of the peak, and both data sets were corrected for absorption using a Gaussian integration scheme. Crystallographic data are given in the Table.

Table

Compound	(I)	(II)
Space group	*P*1	$P2_12_12_1$
a,α(Å, °)	9·60(2), 97.37(9)	14·08(1), 90
b,β	15·62(4), 71·44(8)	39·15(1), 90
c,γ	6·68(1), 93·01(14)	5·987(3), 90
D_m, D_c (g cm^{-3})	1·2, 1·28	1·30, 1·29
Crystal size (mm)	0·12 × 0·26 × 0·30	0·03 × 0·13 × 0·45
μ (cm^{-1})	9·0	79·9
Radiation, filter	Mo-K_α, Zr	Cu-K_α, Ni
Total refln., obs.	2409, 2008	2459, 1872
Resolution ($\lambda/2\sin\theta$,Å)	0·93	0·94
Rw^+, Rw^- (%)	5·63, 5·80[a]	
Final *R* all data (%)	6·7	10·35
Final R_{obs} data (%)	5·5	7·44
E.s.d. in C–C bond (Å)	0·03	0·02

[a] Rw^+ calculated for the correct configuration, Rw^- incorrect.

Both structures were determined using normal heavy-atom and Fourier synthesis techniques. The structures were refined by least-squares procedures with anisotropic thermal parameters and anomalous dispersion corrections for the iodine atoms. In the case of (I), anisotropic thermal parameters were also used for ten carbon and oxygen atoms which showed large anisotropic motion in a difference Fourier synthesis. All other refined atoms were given isotropic thermal parameters. Hydrogens (except for methyl groups) were located and included, but not refined.

The absolute configuration of (I) was determined by use of Hamilton's[2] test with rejection of the alternate configuration at the 99·5% confidence level. The absolute configuration of (II) was determined according to the procedure of Bijvoet[3] using ten reflections which showed large differences in structure factor between Friedel pairs. There were no disagreements between observed and calculated signs for the differences between pairs.

(I) and (II) show the absolute configurations of the structures. The presence of a *trans* substituted cyclopropane ring in the side chain of both molecules as suggested for (II) by n.m.r. evidence is clearly demonstrated by the *X*-ray structures. The seco-derivative of gorgosterol is shown to be (22*R*,23*R*,24*R*)-22,23-methylene-23,24-dimethyl-9-oxo-9,11-secocholest-5-ene-3β,11-diol, and 23-demethylgorgosterol to be (22*R*,23*R*,24*R*)-22,23-methylene-24-methylcholest-5-en-3β-ol. This provides the first determination of the absolute configuration of this class of compounds by *X*-ray diffraction, and the configurations agree with those deduced for gorgosterol[1a,b] and acanthasterol[1d] from o.r.d. evidence.

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