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MARINE ORGANIC CHEMISTRY, IV. STRUCTURE OF THE PRINCIPAL AGLYCONES FROM THE STARFISH *MEYENASTER GELATINOSUS*

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Continuing with our work on biologically active compounds of marine origin (1, 2), we have been working on saponin constituents of the Chilean starfish *Meyenaster gelatinosus* Meyen and have isolated, by acid hydrolysis of the saponin mixture, two steroidal sapogenins: dihydromarthasterone and asterone.

EXPERIMENTAL

ANIMAL COLLECTION AND EXTRACTION.—Starfish collected in Cocholgue (36°36′S; 72°59′W) were identified by comparison with samples of *M. gelatinosus* deposited in the Zoological Museum, Universidad de Concepción, and then were chopped and extracted with 50% aqueous EtOH.

ISOLATION OF THE SAPOGENINS.—Hydrolysis of the crude extracts with 2.5 N HCl at 100° for 3 h furnished a mixture of water-insoluble aglycones, which was partially separated by silica gel column chromatography using petroleum ether-EtOAc mixtures as eluant, and the aglycones were further purified by medium pressure liquid chromatography on silica gel.

IDENTIFICATION OF THE SAPOGENINS.—The major aglycone crystallized from MeOH, mp 196-199°; M^+ 332.2351 $C_{21}H_{32}O_3$; ir ν max (nujol) 3250, 1700, 1240, 1060, 825 cm^{-1}. Its mass spectrum contained an acetyl base peak *m/z* 43 and important peaks at *m/z* 230, 229, and 211 characteristic of cleavage of the D ring and dehydration of pregnane-20-one. Also peaks due to loss of H_2O and methyl groups at *m/z* 314(M^+-H_2O), 296(M^+-2H_2O), 281(M^+-2H_2O-CH_3). Its ^{1}H-nmr spectrum (90 MHz, $CDCl_3$) depicted two quaternary methyl groups at 0.55 (s, 3H, H-18) and 0.95 (s, 3H, H-19), an acyl at 2.13 (s, 3H, $COCH_3$), two secondary carbinol methines at 3.57 (br, m, 2H, H-3 and H-6), and an olefinic proton at 5.38 (br, t, 1H, H-11).

These data indicate that this compound is asterone (3).

Another steroidal compound was also isolated, M^+ 416 $C_{27}H_{44}O_3$; ir ν max (KBr) 3330, 1710 cm^{-1}. Its mass spectrum contained a peak at *m/z* 316 (M^+-100, McLafferty rearrangement) and also peaks at 416 (M^+), 301, 298, 285, 283, 267, 245.

Its ^{1}H-nmr spectrum (270 MHz, $CDCl_3$) depicted 0.63 (s, 13-CH_3), 0.94 [20-CH_3, 25-$(CH_3)_2$]; 0.95 (s, 10-CH_3), a carbinol methine at 3.62 (H-3 and H-6), and an olefinic proton at 5.32 ppm (H-11).

These data and co-chromatography with an authentic sample indicate that this compound is dihydromarthasterone which was first reported in *Marthasterias glacialis* (4).

Cholesterol and Δ^7-cholestenol (lathosterol) were also isolated; their structure determination was based on their physical constants.

Work on the saponins of *M. gelatinosus* is currently in progress.

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