STEROL COMPOSITION OF Pyrosoma giganteum

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UDC 547.925:549.93

Continuing an investigation of the steroid composition of marine organisms [2], we have studied the sterol fraction of the hemichordate Pyrosoma giganteum (class Thaliacea, subclass Pyrosoma, family Pyrosomidae), collected by means of a Sigsbee trawl in April, 1991 during the 13th cruise of the Scientific Resarch Ship "Akademik Oparin" in the region of the submarine mountain Kito-Kokho in the Philippine Sea from a depth of 326 m.

The free steroid fraction was isolated as described in [2]. Then part of the free steroids was acetylated by acetic anhydride in pyridine (1:1). The resulting mixture of sterol acetates was separated by preparative TLC (hexane–benzene (4:1)) on silica gel impregnated with silver nitrate and was analyzed by GLC-MS using a method analogous to one described previously [2].

The steroid components were identified from the mass spectra of the acetates with consideration of their chromatographic behavior in capillary GLC (phase OV-101, temperature 280°C).

A total of 21 steroid components was isolated from P. giganteum, including 19 known steroids that had been identified previously. The results of the analysis are given in Table 1.

TABLE 1. Composition of the Steroid Fraction of Pyrosoma giganteum

Sterols	Structural features	M+	RRT	%
24-Norcholesta-5,22-dien-3β-ol	$C_{26}\Delta^{5,22}$	—	0,69	0.89
24-Nor-5α-cholest-22-en-3β-ol	$C_{26}\Delta^{22}$	414	0,72	
24-Methyl-27-norcholesta-5,22-dien-3β-ol	$C_{27}\Delta^{5,22}$	—	0,89	4,92
24-Methyl-27-nor-5α-cholest-22-en-3β-ol	$C_{27}\Delta^{22}$	428	0,91	
Cholesta-5,22-dien-3β-ol	$C_{27}\Delta^{5,22}$	—	0,92	9,04
Cholesta-22-en-3β-ol	$C_{27}\Delta^{22}$	428	0,94	3.75
Cholesterol	$C_{27}\Delta^{5}$	—	1,00	12.43
Cholestanol	$C_{27}\Delta^{0}$	430	1,02	10,65
24-Methylcholesta-5,22-diel-3β-ol	$C_{28}\Delta^{5,22}$	—	1,09	21,16
24-Methylcholest-22-en-3β-ol	$C_{28}\Delta^{22}$	442	1,12	4,53
Unidentified C_{28} nonsaturated sterol	$C_{28}\Delta^{x}$	—	1.16	0,02
24-Methylcholesta-5,24(28)-dien-3β-ol	$C_{28}\Delta^{5,24(28)}$	—	1,22	6,92
24-Methylcholest-5-en-3β-ol	$C_{28}\Delta^{5}$	—	1,23	3,10
Unidentified C_{28} diunsaturaed sterol	$C_{28}\Delta^{x,y}$	—	1,27	0,89
24-Methylcholestanol	$C_{28}\Delta^{0}$	444	1,29	
24-Ethylcholesta-5,22-dien-3β-ol	$C_{29}\Delta^{5,22}$	—	1,33	5,18
24-Ethylcholest-22-en-3β-ol	$C_{29}\Delta^{22}$	456	1,33	
24-Ethylcholest-5-en-3β-ol	$C_{29}\Delta^{5}$	—	1,49	6.34
24-Ethylcholestanol	$C_{29}\Delta^{0}$	458	1,53	6,12
24-Ethylcholesta-5,24(28)-dien-3β-ol	$C_{29}\Delta^{5,24(28)}$	—	1,66	0,46
24-Propylidenecholest-5,14(28)-dien-3β-ol	$C_{30}\Delta^{5,24(28)}$	—	1,74	1,57

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 589-590, September-October, 1992. Original article submitted November 6, 1991.

0009-3130/92/2805-0517$12.50

As can be seen from the table, the sterol fraction of the pyrosoma studied consisted of C_{26}-C_{30} steroid alcohols and was characterized by a high level not only of C_{27} but also of C_{28} compounds. The sterols isolated were stanols and Δ^{5}-, Δ^{22}-, $\Delta^{5,22}$-, and $\Delta^{5,24(28)}$-derivatives.

The steroid composition of P. giganteum has not been studied previously. However, the sterol fraction of a related species – Pyrosoma sp., living in the Atlantic Ocean – has been investigated [3]. The total sterols of O. giganteum and P. sp. proved to be similar. The composition of the total sterols of these free-floating colonial animals probably depends on their systematic position.

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A NEW ACETYLATED GLYCOSIDE FROM THE HOLOTHURIAN Cucumaria japonica

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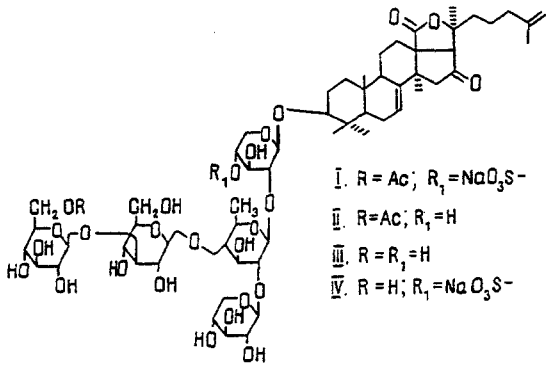
UDC 547.996:593.96

Continuing an investigation of the triterpene glycosides from the holothurian Cucumaria japonica [1], we have established the chemical structure of a new glycoside – cucumarioside A_1-2 (I). Compound (I) is a new holostane glycoside containing an acetylated monosaccharide residue in the carbohydrate chain.



The fraction of weakly polar glycosides containing (I) was obtained by chromatographing the total glycosides on silica gel [1]. It was not susceptible to further separation by the usual methods, but the desulfation of this fraction, followed by separation on silica gel [$CHCl_3$:CH_3OH (5:1)] and HPLC (Silasorb C-18, 60% C_2H_5OH), led to the isolation of the individual derivative (II), mp 201-203°C, $[\alpha]_{578}$ −96° (c 10; pyridine).

A comparison of the ^{13}C NMR spectra of (II) and of the desulfated derivative of cucumarioside A_1-2 (III) [1] permitted the conclusion that in (II), as compared with (III), an acetate group (170.4 and 20.6 ppm) was attached to the C-6 atom of the terminal glucose residue. In actual fact, in (II) the C-6 signal was shifted from 62.5 to 64.5 ppm and the C-5 signal from 78.1 to 75.1 ppm, which is explained by the acetylation effect [2]. Moreover, the assignment of these signals to the terminal glucose was confirmed by taking a series of

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Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 590-591, September-October, 1992. Original article submitted November 12, 1991.

0009-3130/92/2805-0518$12.50