SUMMARY

A new triterpene glucoside — foetoside C — has been isolated from the epigeal part of the plant *Thalictrum foetidum* and it has been shown to be oleanolic acid 28-O-[O-α-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] 3-O-[O-β-D-xylopyranosyl(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside].

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STEROID COMPOUNDS OF MARINE SPONGES. III. 24-ETHYL-25-METHYLCHOLESTA-5,22-DIEN-3β-OL — A NEW MARINE STEROL FROM THE SPONGE *Halichondria* sp.

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UDC 547.92:639.29

A new sterol — 24 ethyl-25-methylcholesta-5,22-dien-3β-ol — has been isolated by column chromatography on silica gel from extracts of the sponge *Halichondria* sp. Its structure has been established on the basis of an analysis of GLC-MS results and of PMR and ^{13}C NMR spectroscopy and has been confirmed by ozonolysis.

Continuing a study of the steroid compounds of sponges [1], we have isolated and determined the structure of a new sterol from the sponge *Halichondria* sp.

From ethanol and ethanol—chloroform extracts of the sponge *Halichondria* sp. by column chromatography on silica gel we obtained a free sterol fraction which, according to the results of GLC and of GLC-MS consisted of a single component.

The ^{13}C spectrum of the compound isolated (Table 1) and the molecular ion at 426 m/z in the mass spectrum showed that it contained 30 carbon atoms and two double bonds.

Peaks at 271, 255, and 213 m/z in the mass spectrum, and also the agreement of the signals of the C_1—C_{20} atoms in the ^{13}C NMR spectrum with the corresponding signals of the spectra of model Δ^5-monounsaturated steroids [2] indicated the presence of a cholestane nucleus with a 5,6- double bond.

In the high-resolution PMR spectrum (250 MHz) (Table 2) the signals of methyl groups (ppm 0.7 (3 H, s), 1.01 (3 H, s), 1.05 (3 H, d, J = 6.5 Hz), and 0.79 (3 H, t, J = 7.2 Hz) for the C-18, C-19, C-21, and C-29 methyl groups were close to the corresponding signals in the spectrum of stigmasterol [3]. The presence of a disubstituted double bond in the side chain was confirmed by a multiplet signal at 5.1 ppm (2 H, m).

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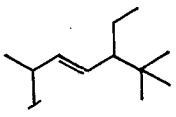
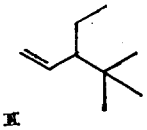
TABLE 1. ^{13}C NMR Spectrum of Sterol I

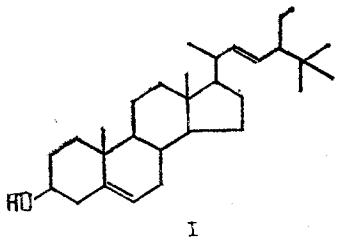
Atom	CS	Atom	CS	Atom	CS	Atom	CS
C-1	37,5	C-9	50,5	C-17	56,2	C-25	33,1
C-2	32,1	C-10	36,7	C-18	12,15	C-26	27,9
C-3	71,9	C-11	21,2	C-19	19,4	C-27	27,9
C-4	42,5	C-12	39,9	C-20	40,5	C-28	22,0
C-5	141	C-13	42,5	C-21	21,2	C-29	13,3
C-6	121,7	C-14	57,1	C-22	138,9	C-30	27,9
C-7	32,1	C-15	24,5	C-23	129,2		
C-8	32,1	C-16	28,9	C-24	56,2		

TABLE 2. PMR Spectra of Compounds (I) and (II)

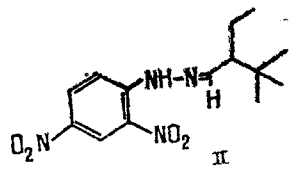
Compound	Me					H		
	C-18	C-19	C-21	C-29	C-26, 27, 30	C-3	C-6	C-22,23
 I	0,7 s	1,01 s	1,05 d J=6,5Hz	0,79 t J=7,2Hz	0,82 s	3,54 m	5,35 m	5,1 m
DNPH  II				0,9 t J=7,2Hz	0,97 s			

A singlet at 0.82 ppm (9 H) was due, as we assumed, to a tert-butyl group. The presence of such a group was confirmed by strong signals in the mass spectrum at 369 m/z ($M^+ - 57$), 370 ($M^+ - 56$), and 351 ($M^+ - 57 - 18$).

On the basis of the results obtained, the compound isolated was assigned the structure of 24-ethyl-25-methylcholesta-5,22-dien-3β-ol (I).



I



II

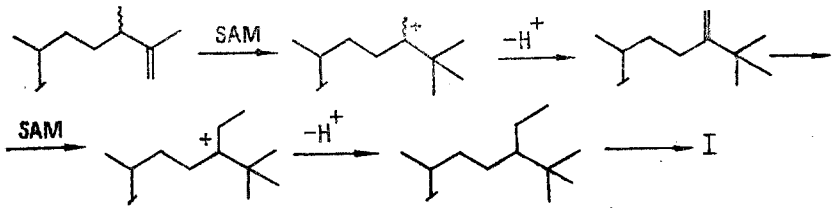
Absorption at 966 cm^{-1} in the IR spectra showed the trans configuration of the double bond in the side chain [4].

Additional confirmation of formula (I) was obtained after the ozonolysis of compound (I). The ozonolysis of compound (I) followed by treatment of the ozonides with zinc dust in acetic acid gave 2-ethyl-3,3-dimethylbutanal, which was isolated in the form of the 2,4-dinitrophenylhydrazone (II). The mass spectrum of (II) showed strong peaks at 308 m/z (M^+) and 252 m/z ($M^+ - 56$).

In the PMR spectrum of compound (II) (see Table 2), in addition to the signals of aromatic protons (7.95, 8.3, and 9.15 ppm), the signals of methyl groups were observed at 0.9 ppm (3H, t, J = 7.2 Hz, C-29) and 0.97 ppm (9 H, s, C-26, -27, -30) and the signals of a vinyl proton at 7.35 ppm, and also the signals of the protons of a methylene group at 1.45 ppm (1 H, m) and 1.7 ppm (1 H, m) and of a methine group at 2.05 ppm.

Recently Djerassi et al. have put forward the hypothesis that many of the unusual C_{30} and C_{31} sterols of sponges additionally alkylated in the side chain are biosynthesized as the result of the reaction of precursors of the type of codisterol or epicodisterol [5] with

S-adenosylmethionine (SAM). According to these ideas, the biogenesis of 24-ethyl-25-methylcholesta-5,22-dien-3β-ol (I) can be explained by the following scheme:



Further investigations and, in particular, the isolation of new steroid compounds that may be considered as intermediates in the biosynthesis of the sponge C_{30} and C_{31} sterols will show how true this hypothesis is.

EXPERIMENTAL

The sponges were collected at a depth of 2-3 m in the northwestern part of the island of Madagascar in December, 1981, during the expedition of the Scientific Research Ship, "Professor Bogorov."

The GLC analysis was performed on a Pye-Unicam 104 chromatograph with a 150 × 0.5 cm column containing 3% of SE-30 at 280°C. The carrier gas was argon, at the rate of 60 ml/min.

The chromato-mass-spectrometric study was performed on a LKB 9000S spectrometer at an ionizing voltage of 70 V using a 300 × 0.5 cm column containing 1.5% of SE-30. The temperature was 265°C, and the carrier gas helium at the rate of 30 ml/min.

PMR spectrum were determined on a Bruker WM-250 instrument, and ^{13}C NMR spectra on a Bruker HX-90E instrument in deuterochloroform with tetramethylsilane as internal standard.

IR spectra were recorded on a Specord IR-75 spectrometer, melting points on a stage of the "Boĕtius" type, and optical rotations on a Perkin-Elmer 141 polarimeter.

Isolation of 24-Ethyl-25-methylcholesta-5,22-dien-3β-ol (I). A comminuted sponge (dry weight 93 g) was extracted with ethanol. Then the extract was decanted off and concentrated in vacuum. The remaining tissue was re-extracted with a mixture of chloroform and methanol (2:1) for 48 h.

The extracts were combined and concentrated in vacuum to dryness. Column chromatography on silica gel L (40/100 μ) in the benzene–ethyl acetate (5:1) system yielded 260 mg (0.3% on the dry weight of the animals) of the sterol (I).

After recrystallization from ethyl acetate, mp 166-168°C, $[\alpha]_D^{20}$ −52° (c 0.4; chloroform).

Mass spectrum, m/z (%): 426 (M^+, 29); 411 (4); 408 (4); 393 (3); 370 (92); 369 (83); 351 (100); 300 (64); 285 (16); 282 (7); 271 (92); 255 (62); 231 (11); 213 (32).

Formation of 2-Ethyl-3,3-dimethylbutanal 2,4-Dinitrophenylhydrazone (II). Ozone was passed through a solution of 32 mg of (I) in 3 ml of CH_2Cl_2 and 0.7 ml of MeOH at −70°C until a permanent blue coloration had been obtained (50 min). Then the temperature of the solution was brought to that of the room and 1 ml of AcOH and 75 mg of zinc dust were added; the mixture was stirred for 1 h and the solution was filtered off and was treated with 1 ml of a solution of DNPH (1 g of DNPH in 3 ml of H_2SO_4 and 10 ml of EtOH) and was left at room temperature for 12 h. Then it was diluted with water and extracted with CH_2Cl_2, and the organic layer was washed with water, dried over $MgSO_4$, concentrated, and chromatographed on silica gel L (40/100 μ) in the hexane–benzene (3:1) system. This led to the isolation of 21 mg of the hydrazone (II), mp 128-129°C (from EtOH), $[\alpha]_D^{20}$ −11.5° (c 0.24; chloroform). Mass spectrum, m/z (%): 308 (M^+, 26); 293 (6); 252 (100); 235 (57), 217 (50); 208 (20).

SUMMARY

A new marine sterol has been isolated from the sponge *Halichondria* sp. and its structure has been established as 24-ethyl-25-methylcholesta-5,22-dien-3β-ol.

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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS *Silene*.

VI. α-ECDYSONE 22-SULFATE — A NEW ECDYSTEROID FROM *Silene brahuica*

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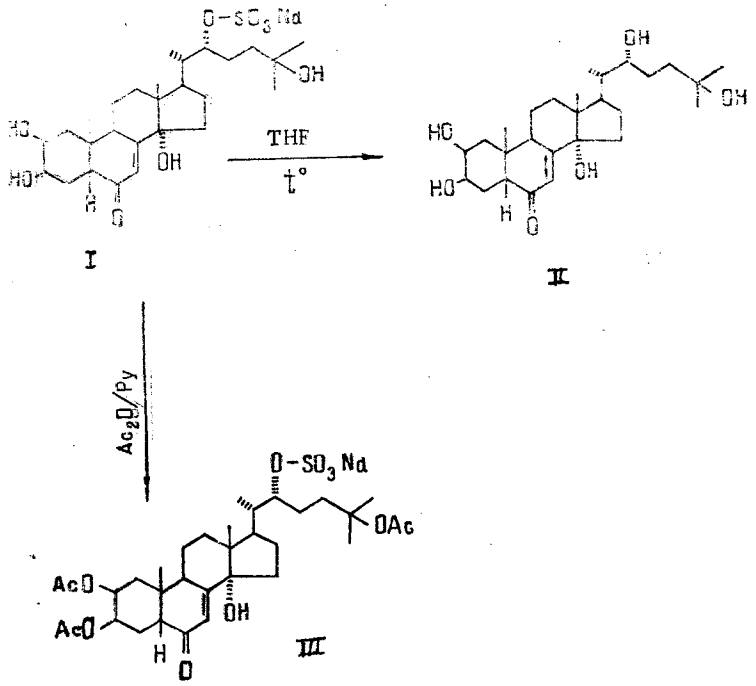
A phytoecdysteroid consisting of the sodium salt of α-ecdysone 22-sulfate has been isolated from the roots of *Silene brahuica* Boiss.

Continuing a study of the ecdysteroids of *Silene brahuica* Boiss. (family Caryophyllaceae) [1], we have isolated a new ecdysteroid (I) from the roots of this plant.



The IR spectrum of compound (I) showed, in addition to the maximum at 1652 cm^{-1} that is characteristic for ecdysteroids, absorption at 1235 cm^{-1} corresponding to a sulfate group [2]. The solvolytic cleavage of ecdysteroid (I) in tetrahydrofuran [3] gave a compound (II) identified as α-ecdysone. The SO_4^{2-} ion was detected in the reaction products by the test with $BaCl_2$. Consequently, ecdysteroid (I) contains a sulfate group.

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