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24,25,26,26-TETRAMETHYLCHOLEST-23-ENE-2β,3α,6α-TRIOL TRIS(SODIUM SULFATE) — A NEW POLYHYDROXYLATED STEROID FROM THE SPONGE HALICHONDRIIDAE GEN. SP.

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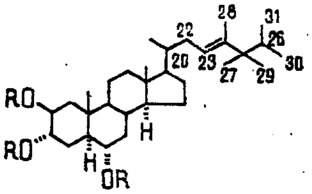
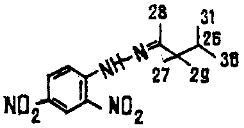
UDC 547.92

Sponges of the class Demospongiae form a rich source of steroid compounds of unique structure [1, 3]. From an aqueous ethanolic extract of the sponge *Halichondriidae* gen. sp., collected off the island of Socotra (People's Democratic Republic of Yemen) during the twelfth voyage of the Scientific-Research Vessel "Professor Bogorov," by column chromatography on Polikhrom 1 (50% ethanol) we have obtained the previously unknown 24,25,26,26-tetramethylcholest-23-ene-2β, 3α, 6α-triol tris (sodium sulfate) (Ia, $C_{31}H_{51}O_{12}S_3Na_3 \cdot 3H_2O$, mp 170-172°, $[\alpha]_D^{20}$ + 35.9° (c 0.46; pyridine). IR spectrum: λ^{KBr} 1236 cm^{-1} ($-OSO_3$). Mass spectrum (direct introduction, m/z, %): 420 ($M^+ - 3NaHSO_4$, 43); 377 ($M^+ - C_3H_7 - 3NaHSO_4$, 100).



$R = SO_3Na$ (Ic)
R = H (Ib)
$R = COCH_3$ (Ia)



II

Acid hydrolysis (9% HCl, 90°C, 1.5 h) of (I) gave sulfuric acid and the triol (Ib), $C_{31}H_{54}O_3$, mp 223-226°, $[\alpha]_D^{20}$ + 45.6° (c 0.45; ethanol). Mass spectrum (direct introduction, m/z, %): 431 ($M^+ - C_3H_7$, 13); 413 ($M^+ - C_3H_7 - H_2O$, 73); 395 ($M^+ - C_3H_7 - 2H_2O$, 80); 377 ($M^+ - C_3H_7 - 3H_2O$, 100).

The acetylation of (Ib) with acetic anhydride in pyridine led to the triacetate (Ic), $C_{37}H_{60}O_6$, mp 140-142°, $[\alpha]_D^{20}$ + 71.2° (c 0.43; ethanol). Mass spectrum (direct introduction, m/z, %): 557 ($M^+ - C_3H_7$, 16); 497 ($M^+ - C_3H_7 - C_3H_7 - CH_3COOH$, 43); 437 ($M^+ - C_3H_7 - 2CH_3COOH$, 95); 377 ($M^+ - C_3H_7 - 3CH_3COOH$, 100).

Recently Japanese authors [3] have obtained a compound similar to (Ia), 24ξ, 25-dimethylcholestane-2β, 3α, 6α-triol tris (sodium sulfate) (halistanol sulfate), from the sponge *Halichondria* cf. *moorei* [3]. A comparison of the ^{13}C NMR spectra of (Ia-c) with the corresponding spectra of halistanol sulfate, halistanol, and halistanol acetate showed their complete coincidence for the signals of the C_1-C_{20} atoms.

The structure of the side chain of (Ia) was shown by spectral methods (Bruker WM-250) and by ozonolysis. The presence of a $CH_3-\underset{|}{C}H-CH_2-CH=C<$ fragment in the side chain followed from differential decoupling and double resonance experiments for (Ib). Thus, when the vinyl proton (5.34 ppm) was irradiated by the method of differential decoupling the signals of the protons of the neighboring methylene group (C_{22}) appeared at 2.20 and 1.85 ppm. Irradiation at 2.20 or 1.85 ppm enabled the chemical shift of the C_{20} methine proton to be determined (1.52 ppm). Under double-resonance conditions, irradiation at 1.52 ppm converted the doublet signal of the C_{21} methyl group into a singlet. The presence of a methyl group at a double bond follows from the ^1H NMR spectra of (Ia-c), in which the corresponding singlet signal (3 H) is observed in the 1.49-1.52 ppm region.

The ozonolysis of (Ic) gave 3,3,4-trimethylpentan-2-one, which was isolated in the form of the 2,4-dinitrophenylhydrazone (II), $C_{14}H_{20}N_4O_4$, mp 153-154°C. Mass spectrum (direct introduction): M^+ 308 (100). Its ^1H NMR spectrum contained the signals of C_{30} and C_{31}

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methyl groups (0.86 ppm, J = 6.7 Hz, 6 H) of a C_{28} methyl group (2.01, s, 3 H), of C_{27} and C_{29} methyl groups (1.14 ppm, s, 6 H), and of a C_{26} methine group at 1.95 ppm (septet, J = 2.1 Hz, 1 H). Irradiation at 0.86 ppm converted the septet at 1.95 ppm into a singlet.

In the structure of its side chain, compound (Ia) that we have obtained has no analogs among natural steroids.

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KAEMPFEROL DERIVATIVES FROM THE FRUIT OF THE JAPANESE PAGODA TREE

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UDC 547.972

Buds of *Sophora japonica* L. (Japanese pagoda tree) are an industrial source of rutin — a valuable drug with a vitamin P action. The fruit of the plant contains an insignificant amount of rutin [1-3]. We have isolated the two quantitatively predominating glycosides from the fruit of the Japanese pagoda tree.

Compound (I), $C_{27}H_{30}O_{16}$, mp 198-201°C (from methanol) $[\alpha]_D^{20} - 69.1°$ (c 1.01; methanol). $\lambda_{max}^{CH_3OH}$: 267, 352.5 nm.

The acid hydrolysis of substance (I) in 0.5% sulfuric acid gave an aglycone with mp 275-277°C (M^+ 286), which was identified from its mobility on TLC and by spectral characteristics as kaempferol [4]. D-Glucose was detected as the sugar component. The GLC method [5] showed the presence of two D-glucose residues in compound (I).

The PMR spectrum of the trimethylsilyl ether of the diglycoside (I) (100 MHz, CCl_4, 0 — HMDS) showed signals of the protons of the aglycone: H-2', H-6' — 7.85 (2 H, d, J = 8 Hz); H-3', H-5' — 6.67 (2 H, d, J = 8 Hz); H-8 — 6.30 (d, J = 2Hz); H-6 — 5.97 (d, J = 2 Hz). The anomeric protons of the sugar resonated at 5.33 ppm (d, J = 7 Hz) and 5.94 ppm (d, J Hz). The 12 protons of the carbohydrate moiety were represented by signals in the 2.92-4.01 ppm region.

On the basis of the UV spectrum of the diglycoside (I) with diagnostic reagents ($\lambda_{max}^{CH_3OH}$: 275, 352.5; $\lambda_{max}^{CH_3ONa}$: 275, 330, 399; $\lambda_{max}^{AlCl_3}$: 275, 352.5, 400; $\lambda_{max}^{AlCl_3 + HCl}$: 275, 352.5, 400; λ_{max}^{NaOAc}: 263, 350; $\lambda_{max}^{H_3BO_3 + NaOAc}$: 263, 350 nm), it may be concluded that in the compound under consideration the hydroxy groups at C-5 and C-4 are free and those in positions 3 and 7 are substituted by D-glucose residues. According to the facts given, compound (I) is kaempferol 3,7-diglucoside.

This kaempferol glucoside has been isolated previously from peony [6] and guelder rose [7] flowers. The amount of (I) in the fruit of the Japanese pagoda tree amounts to from 5 to 7%.

Substance (II), $C_{32}H_{38}O_{20}$, mp 173-175°C (from methanol), $[\alpha]_D^{20} + 21.8°$ (c 0.45; methanol) was also a kaempferol glycoside and it contained two D-glucose and one L-rhamnose residues. The amount of (II) in the fruit was about 1%.

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