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TRITERPENE GLYCOSIDES AND THEIR GENINS FROM *Thalictrum foetidum*.

I. THE STRUCTURE OF FOETOSIDE C

T. V. Ganenko, M. I. Isaev,
T. T. Gorovits, A. S. Gromova,
V. I. Lutskii, A. A. Semenov,
and N. K. Abubakirov

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A new glycoside — foetoside C — has been isolated from the epigeal part of *Thalictrum foetidum* L. and, on the basis of chemical transformations and spectral characteristics its structure has been established as oleanolic acid 28-[O-α-D-glycopyranosyl-(1 → 6)-O-β-D-glucopyranoside] 3-O-[O-β-D-xylopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside].

From the epigeal part of *Thalictrum foetidum* L. (Ranunculaceae) we have isolated triterpene glycosides A, B, and C. In the present paper we consider the structure of the glycoside that we have called foetoside C (I). When glycoside (I) was subjected to acid hydrolysis, oleanolic acid (V) was identified as the aglycone [1]. It was found by GLC [2] that foetoside C contains D-glucose, D-xylose, L-arabinose, and L-rhamnose residues in a ratio of 2:1:1:1.

The alkaline hydrolysis of the pentaoside (I) led to the formation of the progenin (II), the carbohydrate components of which were, according to GLC [2], D-xylose, L-arabinose, and L-rhamnose (1:1:1). Consequently, foetoside C is a bisdesmosidic glycoside the acyloside chain of which includes two D-glucose residues.

The Smith degradation of glycoside (I) [3] led to the formation of oleanolic acid (V), which showed the absence of branching in the sugar chain.

Glycoside (II) was subjected to stepwise hydrolysis. From the hydrolysis products were isolated substance (VI), identified as oleanolic acid 3-O-α-L-arabinopyranoside [4], and a progenin (VII) containing L-arabinose and L-rhamnose residues.

The Hakomori methylation of glycoside (VII) [5] gave the hexa-O-methyl derivative (IX) (M^+ 818). From the products of the methanolysis of the permethylated (IX) was isolated methyl oleanolate (VIII). In a hydrolysate 2,3,4-tri-O-methyl-L-rhamnopyranose and 3,4-dimethyl-L-arabinopyranose were detected by GLC [6]. The presence of the latter compound was confirmed by a positive Bonner reaction [7]. A calculation of molecular rotation differences showed the α configuration of the anomeric carbon atom of the L-rhamnopyranose residue [8].

The facts given determine the glycoside (VII) as oleanolic acid 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside], which has been described previously [4]. A good

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 458-463, July-August, 1984. Original article submitted July 4, 1983.

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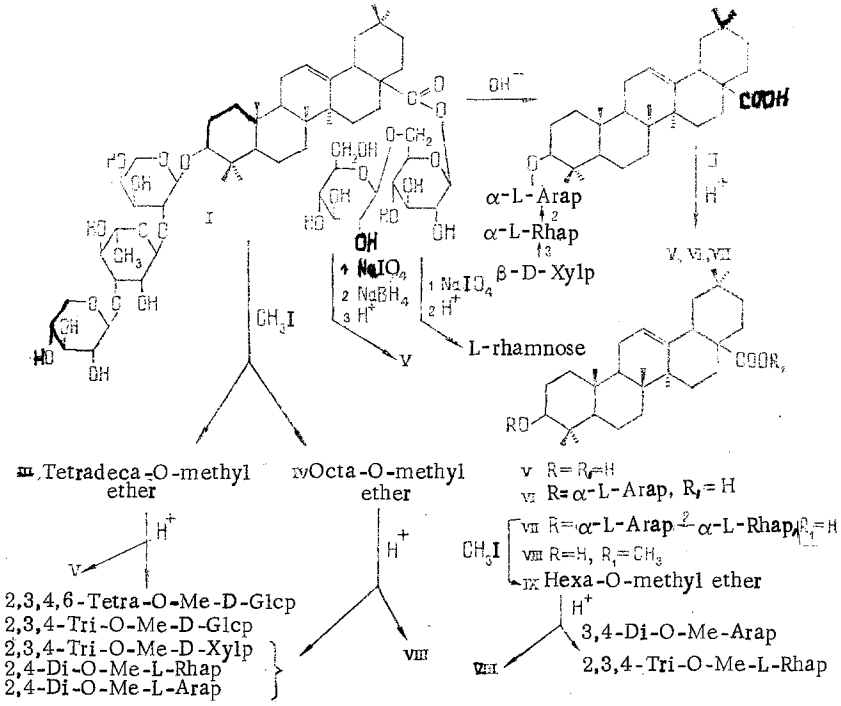

agreement of the physicochemical constants of the glycoside (VII) with those given in the literature [4] also confirmed their identity.

The Hakomori methylation of foetoside C [5] gave the octa-O-methyl derivative (IV) (M^+ 978) and the tetradeca-O-methyl derivative (III) (M^+ 1386). Compound (III) is the permethylate of the pentaoside (I), and substance (IV), formed as the result of the cleavage of the acyloside bond is the permethylate of the trioside (II).

The methanolysis of the octa-O-methyl derivative (IV) yielded methyl oleanolate (VIII). Three carbohydrate components were isolated from the hydrolysate by column chromatography. Among them, 2,3,4-tri-O-methyl-D-xylopyranose and 3,4-di-O-methyl-L-arabinopyranose were identified with the aid of GLC [6] and TLC in the presence of authentic samples. The third compound must obviously be a di-O-methylated derivative of L-rhamnose. Since L-rhamnose was detected in the products of the periodate cleavage of foetoside C (I) followed by acid hydrolysis, the terminal D-xylose residue must be linked to a L-rhamnose residue by a 1 → 3 bond. Consequently, this partially methylated sugar was 2,4-di-O-methyl-L-rhamnopyranose.

The PMR spectrum of the octa-O-methyl derivative (IV) showed at 4.32 and 4.37 ppm the signals of the anomeric protons of L-arabinopyranose and D-xylopyranose residues in the form of two partially overlapping doublets with spin–spin coupling constants (SSCCs) ^3J = 7.5 Hz. It followed from this that the glycosidic center of the D-xylose residue had the β configuration [9]. The molecular rotation increment confirmed the conclusion of the β configuration of the anomeric carbon atom of the D-xylose residue [8].

Thus, progenin (II) was oleanolic acid 3-O-[O-β-D-xylopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside]. A glycoside of this structure has been isolated from *Clematis chinensis* Osbeck [10].

To determine the structure of the acyloside chain of foetoside C (I), the tetradeca-O-methyl derivative (III) was subjected to acid hydrolysis. After the isolation of the oleanolic acid, in addition to the methylated sugars obtained from the permethylate (IV), 2,3,4,6-tetra-O-methyl-D-glucopyranose and 2,3,4-tri-O-methyl-D-glucopyranose were detected by the GLC method.

In the PMR spectrum of the tetradeca-O-methyl derivative (III) the anomeric protons of the D-glucopyranose residues resonated at 4.75 and 5.68 ppm in the form of doublets with the SSCC ^3J = 7.5 Hz, which shows the β configuration of both glycosidic links [9].

Thus foetoside C has, according to the experimental facts given, the structure of oleanolic acid 28-O-[O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] 3-O-[O-β-D-xylopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside].

EXPERIMENTAL

General Remarks. Thin-layer chromatography (TLC) was performed on a fixed (with 13% of gypsum) layer of type L silica gel and on Silufol plates. For column chromatography we used silica gel of the same brand with a grain size of 50-100 μm and the following solvent systems: 1) chloroform–methanol–water (70:23:4); 2) chloroform–methanol–water (70:12:1); 3) chloroform–methanol (15:1); 4) benzene–acetone (7:1); 5) chloroform–acetone (15:2); 6) benzene–acetone (7:3); and 7) chloroform–methanol (20:1).

Triterpenoids were detected in TLC by spraying with a 20% methanolic solution of tungstophosphoric acid or with a 5% solution of vanillin in 50% phosphoric acid followed by heating at 100-110°C for 3-5 min, and sugars and their derviatives with o-toluidine salicylate or with aniline phthalate.

Gas-liquid chromatography was performed on a Chrom-5 chromatograph. The monosaccharides were chromatographed in the form of trimethylsilyl ethers of methyl glycosides [2] on a column (2.5 m × 3 mm) filled with Inerton AW-DMCS with 5% of the silicon phase SE-30. The temperature of the thermostat was 175°C, and the carrier gas was helium at a rate of flow of 60 ml/min.

The methyl glycosides of the methylated sugars were obtained by boiling the methyl ethers in anhydrous methanol containing 5% of hydrogen chloride for 4 h. The methyl glycosides of the methylated sugars were chromatographed on a column (1.2 m × 3 mm) filled with Celite impregnated with 20% of poly(butane-1,4-diyl succinate) (phase 1) and on a column of similar size containing Chromaton N-AW impregnated with 10% of 5F-4E poly(phenyl ether) (phase 2). The temperatures of the thermostat were respectively, 160 and 180°C and the rate of flow of helium 50 ml/min.

The retention times (T_{rel}) for the methylated methyl glycosides were calculated in relation to the retention time of methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside [6].

Mass spectra were obtained on a MKh-1310 instrument at an ionizing voltage of 50 V and a temperature of 150-180°C. IR spectra were recorded on a UR-20 instrument in KBr or Nujol, and PMR spectra in deuterochloroform or deuteropyridine on a JNM-4H-100/100 MHz instrument (δ, ppm; 0 — HMDS).

Isolation of the Triterpenoids. The air-dry epigeal part of the plant *Thalictrum foetidum* L. collected in the flowering period on the shores of Lake Baikal (village of B. Goloustnoe) (5.5 kg) was exhaustively extracted with 80% methanol (40 liters). The aqueous methanolic extract was concentrated and extracted with butanol. The butanolic extract was passed through alumina and evaporated to dryness, and the residue was dissolved in methanol and precipitated with acetone. This gave 43.89 g of purified combined triterpene glycosides, which amounted to 0.81% on the weight of the air-dry raw material. Repeated chromatography of the combined material on a column (system 1) yielded the individual glycosides A, B, and C.

Foetoside C (I) — substance C — $C_{58}H_{94}O_{25}$, mp 212-214°C (from aqueous butanol), $[\alpha]_D^{22}$ −23.5 ± 2° (c 1.36; methanol. ν_{max}^{KBr}, cm^{-1}: 3500-3290 (OH), 1740, 1255 (ester group). According to GLC [2], glycoside (I) contained D-glucose, D-xylose, L-arabinose, and L-rhamnose residues in a ratio of 1.00:0.38:0.56:0.55.

Oleanolic Acid 3-O-[O-β-D-Xylopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside (II) from (I). Foetoside C (1.8 g) was hydrolyzed in 150 ml of a 5% solution of sodium hydroxide in 70% ethanol at room temperature for 5 days. Then the solution was diluted with water and the ethanol was evaporated off. The aqueous solution was treated with butanol. The butanolic extract was washed with water to neutrality, and, after the solvents had been distilled off, the residue was chromatographed on a column with elution by system 2. This yielded 878 mg of progenin (II) $C_{46}H_{74}O_{15}$, mp 239-241°C (from methanol), $[\alpha]_D^{22}$ −5.7 ± 2° (c 1.4; methanol). ν_{max}^{KBr}, cm^{-1}: 3500-3360 (OH), 1690 (C=O of a carboxy group). GLC [2] showed the presence of glycoside (II) of D-xylose, L-arabinose, and L-rhamnose residues in a ratio of 1.00:1.14:1.08. $[M]_{DII}$ −49.36°; $[M]_{DVII}$ +73.4°;

$\Delta[M]_{C(II-VII)}$ −122.8°; the $[M]_D$ values of the methyl glycosides of D-xylopyranose are: α, +253°; β, −108° [4]. Literature figures for (II) [10]: mp 241-243°C, $[\alpha]_D$ −4.5° (c 0.1; methanol).

Partial Hydrolysis of the Progenin (II). Glycoside (II) (828 mg) was hydrolyzed in 50 ml of a 0.25% methanolic solution of sulfuric acid at the boiling point of the reaction mixture for 1.5 h. The hydrolysate was diluted with water, the methanol was distilled off, and the aqueous residue was treated with chloroform. The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column with elution by chloroform. This yielded 348 mg of oleanolic acid with mp 301-302°C (from ethanol), $[\alpha]_D^{24}$ +75 ± 2° (c 1.2; chloroform–methanol, 1:1).

When the elution of the column was continued with system 3, 52 mg of progenin (VI) was obtained. The further washing of the column with system 2 led to 23 mg of the progenin (VII).

Oleanolic Acid 3-O-α-L-Arabinopyranoside (VI). After recrystallization from methanol, progenin (VI) had mp 250-252°C, $[\alpha]_D^{22}$ +41.6 ± 2° (c 1.21; methanol). GLC [2] showed the presence of one L-arabinose residue. $[M]_{DV}$ +342° $[M]_{DVI}$ +244.6; $\Delta[M]_{D(VI-V)}$ −97.4°. The $[M]_D$ values for the methyl L-arabinopyranosides are: α, +28°; β, +403° [4]. Literature figures for oleanolic acid 3-O-α-L-arabinopyranoside [4]: mp 255-259°C (from methanol); $[\alpha]_D$ +49° (c 0.78; methanol).

Oleanolic Acid 3-O-[O-α-L-Rhamnopyranosyl-(1 → 2)-O-α-L-arabinopyranoside] (VII). Glycoside (VII) was recrystallized from methanol: mp 232-234°C, $[\alpha]_D^{22}$ +10 ± 2° (c 1.2; methanol). According to GLC [2], the glycoside contained one L-arabinose and one L-rhamnose residue. $[M]_{DVII}$ +73.4°; $\Delta[M]_{D(VII-VI)}$ −171.2°; $[M]_D$ for methyl L-rhamnopyranosides: α, −109°; β, +169° [4]. Literature figures oleanolic acid 3-O-[O-α-L-rhamnopyranoside-(1 → 2)-α-L-arabinopyranoside] [4]: mp 222-225°C, $[\alpha]_D$ +9° (c 1.83; methanol).

The Hexa-O-methyl Derivative (IX) from (VII). A solution of 43 mg of glycoside (VII) in 10 ml of dimethyl sulfoxide was treated with 50 mg of sodium hydride and stirred for 1 h. Then 0.5 ml of methyl iodide was added dropwise to the reaction mixture and stirring was continued for another 5 h. The reaction products were poured into 10 ml of a 2% solution of sodium hyposulfite, diluted with water, and extracted with chloroform. The chloroform extract was washed with water, dried with anhydrous sodium sulfate, and evaporated. The dry residue was purified by column chromatography with elution by system 4. This gave 37 g of the amorphous hexa-O-methyl derivative (IX), (M^+ 818), $[\alpha]_D^{23}$ +20 ± 2° (c 0.8; methanol).

Hydrolysis of the Permethylate (IX). The permethylate (IX) (30 mg) was hydrolyzed with a 0.5% methanolic solution of sulfuric acid (10 ml) at the boil for 5 h. After cooling, the reaction mixture was diluted with a twofold volume of water and the methanol was evaporated off. The precipitate that deposited was filtered off and washed with water. It was recrystallized from methanol giving 11 mg of the methyl oleanolate with mp 196-197°C.

The filtrate was evaporated to a volume of 10 ml and was heated in the boiling water bath for 3 h. After neutralization with ARA-8p anion-exchanger and evaporation, the following were identified in the hydrolysate by the GLC method [6]: 2,3,4-tri-O-methyl-L-rhamnopyranose, with T_{rel} 0.44 (phase 1) and 0.44 (phase 2), and 3,4-di-O-methyl-L-arabinopyranose with T_{rel} 2.18 (phase 1) and 1.07 (phase 2).

TLC in system 5 likewise showed the presence of the methylated sugars mentioned. The 3,4-di-O-methyl-L-arabinopyranose gave a positive Bonner reaction [7].

Smith Degradation of Foetoside C (I). A solution of 200 mg of glycoside (I) in 25 ml of methanol was treated with 500 mg of sodium periodate in 10 ml of water, and the mixture was left for 24 h. To destroy the excess of oxidant, 1 ml of glycerol was added to the reaction mixture, and it was then diluted with water. The reaction products were extracted with butanol. After the solvent had been distilled off, 50 ml of methanol and then 0.5 g of sodium tetrahydroborate were added to the residue and the mixture was left at room temperature for 12 h. Then the solution was acidified with dilute sulfuric acid to pH 2, and after 12 h it was diluted with a twofold volume of water. The methanol was evaporated off and the resulting precipitate was filtered off, washed with water, and dried. The product was identified by TLC (systems 2 and 3) in the presence of an authentic sample as oleanolic acid.

Oxidative Cleavage of Foetoside C (I). A solution of 25 mg of foetoside C in 2 ml of methanol was treated with 60 mg of sodium periodate in 1 ml of water, and the mixture was left at room temperature for 2 days. The excess oxidant was destroyed with a few drops of ethylene glycol and, after dilution with water, the products were extracted with butanol. After the solvents had been distilled off the residue was dried and subjected to methanolysis in 3 ml of absolute methanol containing 5% of hydrogen chloride and boiled for 12 h. L-Rhamnose was identified in the reaction products by GLC [2].

The Tetradeca-O-methyl (III) and Octa-O-methyl (IV) Derivatives of (I). With constant stirring, 700 mg of sodium hydride was added in small portions to a solution of 700 mg of foetoside C (I) in 100 of dry dimethyl sulfoxide, after which the reaction mixture was stirred for another 1.5 h. Then 10 ml of methyl iodide was added dropwise and stirring was continued for another 7 h. All the operations were carried out at room temperature. The reaction products were poured into 140 ml of 2% solution of sodium hyposulfite, after dilution with 100 ml of water, the mixture was exhaustively extracted with chloroform. The chloroform extract was washed with water, dried with anhydrous sodium sulfate, and evaporated to dryness. The residue (863 mg) was chromatographed on a column with elution by system 4. This yielded 102 mg of the amorphous octa-O-methyl derivative (IV), $C_{54}H_{90}O_{15}$, $[\alpha]_D^{22}$ −9.3 ± 2 (0.86; methanol); ν_{max}^{KBr}, cm^{-1}: 1730, 1260 (ester group). M^+ 978. PMR ($CDCl_3$, ppm); 0.65 (3 H, s, CH_3), 0.74 (3 H, s, CH_3), 0.84 (9 H, s, 3 × CH_3), 0.91 (3 H, s, CH_3), 1.05 (3 H, s, CH_3), 1.17 (3 H, d, $^3J \approx 5$ Hz, CH_3 of L-rhamnose), 3.33-3.51 (8 × OCH_3), 4.32 (1 H, d, $^3J = 7.5$ Hz, anomeric proton of L-arabinopyranose), 4.37 (1 H, d, $^3J = 7.5$ Hz, anomeric proton of D-xylopyranose), 4.95 (1 H, broadened s, anomeric proton of L-rhamnopyranose), 5.15 (1 H, broadened s, H-12).

The further washing of the column with system 6 led to 545 mg of the noncrystalline tetra-O-methyl derivative (III), $C_{72}H_{122}O_{25}$, $[\alpha]_D^{22}$ −13.3 ± 2° (c 1.5; methanol). ν_{max}^{Nujol}, cm^{-1}: 1745, 1260 (ester group). M^+ 1386. PMR (C_5D_5N, ppm): 0.81 (9 H, s, 3 × CH_3); 0.85 (3 H, s, CH_3), 0.96 (3 H, s, CH_3), 1.15 (6 H, s, 2 × CH_3), 1.29 (3 H, d, $^3J \approx 5$ Hz, CH_3 of L-rhamnose), 3.19-3.54 (14 × OCH_3), 4.38 (1 H, d, $^3J = 7.5$ Hz, anomeric proton of L-arabinopyranose), 4.48 (1 H, d, $^3J = 7.5$ Hz, anomeric proton of D-xylopyranose), 4.73 (1 H, d, $^3J = 7.5$ Hz, anomeric proton of terminal D-glucopyranose), 5.22 (1 H, m, $W_{1/2} \approx 10$ Hz, H-12), 5.55 (1 H, broadened s, anomeric proton of L-rhamnopyranose), 5.68 (1 H, d, $^3J = 7.5$ Hz, anomeric proton of a D-glucopyranose residue attached through the carboxy group).

Hydrolysis of the Octa-O-methyl Derivative (IV). The permethylate (IV) (30 mg) was hydrolyzed with 10 ml of a 0.5% methanolic solution of sulfuric acid at the boil for 6 h. After cooling, 30 ml of water was added to the solution and the methanol was evaporated off. The precipitate that deposited was recrystallized to give 6 mg of methyl oleanolate with mp 196-197°C, which was identified by its melting point, and also by TLC in comparison with an authentic sample (systems 3 and 7).

The filtrate was evaporated to a volume of 10 ml and was then heated in the water bath for 4 h. Then it was neutralized with ARA-8p anion-exchanger. The aqueous solution was evaporated to dryness and the residue was chromatographed on a column with elution by system 5. This gave three individual methylated sugars (fractions I, II, and III). The following were determined by GLC [6]: in fraction I — 2,3,4-tri-O-methyl-D-xylopyranose with T_{rel} 0.47, 0.58 (phase 1) and 0.44, 0.55 (phase 2); in fraction III — 3,4-di-O-methyl-L-arabinopyranose with T_{rel} 2.18 (phase 1) and 1.07 (phase 2). The methyl ether of the carbohydrate present in fraction II had T_{rel} 1.17 (phase 1); 0.67 (phase 2) and was considered to be 2,4-di-O-methyl-L-rhamnopyranose, since the oxidative cleavage of foetoside C led to the formation of L-rhamnose.

Hydrolysis of the Tetradeca-O-methyl Ether (III). The permethylate (III) (79 mg) was hydrolyzed with 15 ml of 5% methanolic sulfuric acid at the boiling point of the reaction mixture for 6 h. After the usual working up, 20 mg of oleanolic acid with mp 301-302°C (from ethanol) was isolated from the hydrolysis products.

In the hydrolysate after the appropriate treatment the following were identified by GLC [6]: 2,3,4,6-tetra-O-methyl-D-glucopyranose, T_{rel} 1.00 and 1.40 (phase 1) and 1.00 and 1.31 (phase 2); 2,3,4-tri-O-methyl-D-glucopyranose, T_{rel} 2.59 and 3.66 (phase 1) and 1.84 (phase 2); 2,3,4-tri-O-methyl-D-xylopyranose, T_{rel} 0.47 and 0.58 (phase 1), 0.44 and 0.55 (phase 2); 3,4-di-O-methyl-L-arabinopyranose, T_{rel} 2.18 (phase 1); and 2,4-di-O-methyl-L-rhamnopyranose, T_{rel} 1.17 (phase 1) and 0.67 (phase 2).

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.

L. K. Shubina, T. N. Makar'eva, and V. A. Stonik

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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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