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TRITERPENOIDS FROM THE STEMS OF Astragalus galegiformis

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Continuing an investigation of the chemical composition of individual parts of the plant Astragalus galegiformis L. (Fabaceae) growing in Georgia, we have studied the isoprenoids of the stems gathered in the flowering phase in the environs of Tbilisi.

The air-dry comminuted raw material was extracted with a tenfold amount of 80% ethanol. After evaporation of the ethanol, the residual liquid was treated with chloroform. The chloroform was distilled off, and the residue was precipitated from hot water, filtered off, dried to a syrupy mass, and chromatographed on a column of type L 100/160 silica gel (Czechoslovakia).

Four individual isoprenoids were isolated: one aglycon and three glycosides, and from their IR and PMR spectra these were assigned to the cycloartanes [1, 2].

Substance (1): $C_{30}H_{60}O_5$, M^+ 490, mp, 195–196°C (from methanol); $[\alpha]_D^{20}$ + 28.7 ± 2° (c 1.15; methanol). ν_{max}^{KBr}, cm^{-1}: 3460-3380 (OH), 3040 (CH_2 of a cyclopropene ring), PMR spectrum (δ, ppm); 0.22; 0.50 (^2J = 4.2 Hz); 0.89; 1.17; 1.22; 1.25; 1.41; 1.58; 1.79 (s, 7 × CH_3); 3.55 (q, ^3J = 4.8,; 11.2 Hz, H-3); 3.69 (sx, ^3J = 3.6; 9.6; 9.6 Hz, H-6); 4.70 (sx, Σ ^3J = 21 Hz, H-16); 3.83 (t, ^3J = 15 Hz H-24).

A comparison of the results obtained with the constants of cyclogalegigenin [3, 5] showed their identity.

Substance (2): $C_{37}H_{60}O_{10}$, M^+ 664, mp 223-226°C [from chloroform–methanol (1:1)], $[\alpha]_D^{24}$ + 40 ± 2° (c 1.0; pyridien). ν_{max}^{KBr}, cm^{-1}: 3530-3300 (OH), 3050 (CH_2 of a cyclopropene ring); 1755, 1245 (ester group).

Substance (3): $C_{35}H_{58}O_9$, M^+ 622, mp 252-254°C [from chloroform–methanol (1:1)], $[\alpha]_D^{24}$ + 32 ± 2° (c 1.0; pyridine).

On the basis of the results obtained, substances (2) and (3) were identified as cyclogaleginosides A and B [4, 5].

Substance (4) formed white acicular crystals with mp 184-188°C. It was cleaved by acid into cyclogalegigenin and D-xylose, and was also hydrolyzed by alkali. This glycoside is an acylated bioside, and the determination of its structure is continuing.

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STEROID COMPOUNDS FROM OPHIUROIDS.

III. SULFATED STEROIDS FROM Gorgonocephalus caryi

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Continuing an investigation of physiologically active compounds from ophiuroids [1, 2], we have studied the composition of the polar steroids from an ethanolic extract of Gorgonocephalus caryi ("Gorgon's head") collected in the summer of 1988 on the Kashevarov bank in the Sea of Okhotsk from a depth of 160-170 m. By extraction of the dry residue with ethanol, column chromatography on silica gel in the chloroform–methanol–water (3:1:0.05) system with the addition of ammonia to pH 7-8, and HPLC [Ultrasphere-Si, 10 × 250 mm, 1 ml/min, methanol–1.6% aqueous solution of sodium dihydrogen phosphate (25:1)], followed by column chromatography on Sephadex LH-20 in methanol, we isolated compound (I). A positive qualitative Liebermann-Burchard reaction confirmed that it belonged to the steroid series. Solvolytic desulfation on heating in a mixture pyridine and dioxane and the IR spectrum (KBr, 1235, 1064 cm^{-1}) showed the presence of sulfate groups in its molecule. The ^1H and ^{13}C NMR spectra of (I) coincided with those for the cholest-5-ene-3α,4β,21-triol 3α,21-di(sodium sulfate) isolated previously from Ophiura sarsi [2]. Atomic absorption analysis showed the presence of sodium ions in (I) as the counter-ions to the sulfate groups.

In addition, by a method described previously [3], we isolated the sulfated steroid (II), the R_f value of which on TLC and the chemical shifts of the signals of the protons in its ^1H NMR spectrum coincided with the corresponding characteristics for cholesterol sulfate. The desulfation of (II) by heating in the pyridine–dioxane system gave cholesterol.

Thus two compounds known previously have been isolated from the far-eastern ophiuroid Gorgonocephalus caryi: cholest-5-ene-3α,4β,21-triol 3α,21-di(sodium sulfate) and cholesterol sulfate.

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