PSOLUSOSIDE A - A NEW TRITERPENE GLYCOSIDE FROM THE HOLOTHURIAN Psolus fabricii

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Having continued a chemical study of holothurians of the sublittoral of the island of Onekotan [1] we have isolated a triterpene glycoside fraction from the holothurian *Psolus fabricii* Düben et Koren, collected in August-September, 1982 off the Okhotsk shore of the island of Onekotan (Kurile islands) at a depth of 100 m with a scallop dredge.

The holothurians were extracted with hot ethanol, and the extract was concentrated in vacuum and was then lyophilized. The lyophilizate was extracted at the boil with chloroform—methanol (1:1), and the extract was evaporated and filtered through silica gel in the chloroform—ethanol—water (100:100:17) system. The filtrate was evaporated, and the residue was dissolved in water and chromatographed on columns with the polytetrafluoroethylene powder Polikhrom-1 (water—50% ethanol) and then with silica gel (chloroform—ethanol—water (100:100:17)). This gave the total glycosides, by chromatography of which on silica gel in the chloroform—methanol—water (75:25:1) system we isolated the main component of the fraction, which we have called psolusoside A (I), mp 208-211°C (from ethanol), $[\alpha]_D^{25}$ -73°, (c 0.01; pyridine).

The acid hydrolysis of (I) with 12% HCl (100°C, 2 h), extraction of the water-insoluble products with chloroform, followed by chromatography on silica gel (benzene-ethyl acetate (85:15) gave the combined aglycone (II and III), which were identified from their ¹³C NMR spectrum.

In actual fact, in the ¹³C NMR spectrum there were signals of two types of double bonds in the side chain — $\Delta^{24}(^{25})$:123.3 ppm, (C-24, d) and 132 ppm (C-25, s) and $\Delta^{25}(^{26})$:145.2 ppm (C-25, s) and 110.5 ppm (C-26, t). Hydrogenation of (II) and (III) together led to the genin (IV) with mp 260-262°C (from methanol), which was identified by means of its mass and PMR spectra and also its melting point as the known 3 β -hydroxyholost-9(11)-en-16-one [2].

The monosaccharides obtained by the hydrolysis of the glycoside (I) were analyzed by GLC-MS in the form of the peracetates of the corresponding aldononitriles and were identified as quinovose, xylose, 3-0-methylglucose, and glucose (1:1:1:1). Found for the monosaccharides $[\alpha]_D^{25}$ +42° (c 0.01; water). Calculated for the sum of the D- forms of the same monosaccharides (1:1:1:1): $[\alpha]_D^{25}$ +40°.

In the ^{13}C NMR spectrum of glycoside (I) the signal of the aglycone moiety coincided with the corresponding signals of the main components of the glycosidic fraction of Stichopus japonicus, the native genin of which is (II) [3]. On this basis, the native genin of psolusoside A was determined as 3 β -hydroxyholosta-9(11),25(26)-dien-16-one (II). The aglycone of (III) was consequently artifactual, formed by the migration of the double bond from the 25(26) to the 24(25) position under the conditions of acid hydrolysis as described by Kalinovskii et al. [3].

Thus, the sum of the triterpene glycosides from P. fabricii contain as their main component psolusoside A — a tetraoside of 3β -hydroxyholosta-9(11),25(26)-diene-16-one the monosaccharide residues of which are those of D-quinovose, D-xylose, 3-0-methyl-D-glucose, and D-glucose. No triterpene glycosides have previously been known from representatives of the family Psolidae.

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ROHDEXIN A FROM Convallaria keiskei

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Having continued an investigation of the herb *Convallaria keiskei* Miq. (Far Eastern lily-of-the-valley), by the partition chromatography of a chloroform-ethanolic (9:1) extract on silica gel [stationary phase: water, mobile phase: the methyl ethyl ketone-benzene (1:2)-(1:1) system], we have isolated a cardenolide with the empirical formula $C_{29}H_{44}O_{9}$, mp 248-252°C, $[\alpha]_D^{20}$ -22° (c 1.0; methanol). With 84% sulfuric acid it formed colorations changing with time: 1 min - red-brown; 10-15 min - blue-green; 30-45 min - greenish blue; 60 min - light green; 90 min - greenish grey.

On acid hydrolysis by Mannich and Siwert's method [1], the substance was cleaved into L-rhamnose and an aglycone $C_{23}H_{34}O_5$, mp 265-270°C, $[\alpha]_D^{2^1}$ +21.5° (c 0.5; methanol), which proved to be identical with sarmentogenin. As was established from the molecular rotation difference, the sugar component was attached to the genin by an α -glycosidic bond [3]. The compound isolated was sarmentogenin 3-0- α -L-rhamnoside. A comparison of physicochemical properties, IR spectra, R_f values on paper chromatography in various solvent systems, and a mixed melting point confirmed its identity with rohdexin A, which has been obtained previously from Ornithogalum magnum [2] and Rohdea japonica [4].

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