CAUDINOSIDE A — A NEW TRITERPENE GLYCOSIDE FROM THE HOLOTHURIAN *Paracaudina ransonetii*

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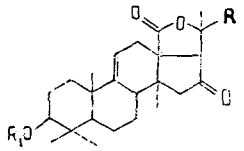
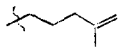
Continuing a chemical study of the holothurians of the Far Eastern seas of the USSR [1, 2], we have isolated a triterpene glycoside fraction from the holothurian *Paracaudina ransonetii* (Marenzella), family Caudinideae, order Molpadonia, collected in August, 1982, in Posyet Bay, Sea of Japan, from a depth of 3-5 m.

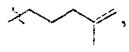
The total glycosides were obtained by the procedure described in [1]. High-performance reversed-phase liquid chromatography (Du Pont 8800 chromatograph, Zorbax C-8 column, 4.6 × 250 mm, mobile phase 20% ethanol, rate of elution 1 ml/min, concentration of glycosides 4.5 mg/ml, solution in water, volume of the sample 0.2 ml, UV detector, λ 230 nm) led to the isolation of glycoside (I), mp 227-230°C, decomp. (ethanol), $[\alpha]_D^{20}$ −8° (c 0.1; pyridine). The acid hydrolysis of (I) with 12% HCl (100°C, 2 h), extraction of the water-insoluble products with chloroform, and subsequent chromatography on silica gel (benzene—ethyl acetate (85:15)) gave the combined aglycons (II) and (III), which were identified from their PMR spectra. In actual fact, in the PMR spectrum the signals of two types of double bonds in the side chain were observed $\Delta^{24(25)}$; 5.07 ppm (H-24, m); and also $\Delta^{25(26)}$; 4.67 ppm (H-26, m) and 4.71 ppm (H-26, m). The hydrogenation of the combined (II) and (III) led to the genin (IV), mp 257-260°C (methanol), identified from its melting point and its PMR and mass spectra as the known 3β-hydroxyholost-9(11-en-16-one [3].

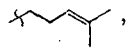
The monosaccharides obtained on the hydrolysis of glycoside (I) were analyzed by GLC-MS in the form of the corresponding aldononitrile peracetates and were determined as D-quinovose, D-xylose, D-3-O-methylglucose, and D-glucose (1:1:1:3).

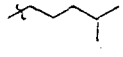


I. R = 

R_1 = [D-Xyl, D-Quin, D-Glc (3), D-3-O-MeGlc]

II. R =  , R_1 = H

III. R =  , R_1 = H

IV. R =  , R_1 = H

The ^{13}C NMR spectrum of (I) taken in dimethyl sulfoxide contained the signals of six anomeric carbon atoms: 100.6, 103.0, 103.4, 103.6 (2), and 104.1 ppm.

The signals of the aglycon moiety in this spectrum coincided with the corresponding signals of the main components of the glycosidic fractions of *Stichopus japonicus* and *Psolus fabricii*, the native genins of which are (II) [4, 2]. On this basis, the native genin of caudinoside A was determined as 3β-hydroxyholosta-9(11),25-dien-16-one (II). The aglycone (III) was therefore an artifact 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 in [4].

Thus, the sum of the triterpene glycosides from *P. ransonetii* contain as their main component caudinoside A — a hexaoside of 3β-hydroxyholosta-9(11),25-dien-16-one. No triterpene glycosides from representatives of the order Molpadonia have previously been known.

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