NEW TRITERPENE AGLYCON FROM THE HOLOTHURIAN Duasmodactyla kurilenis

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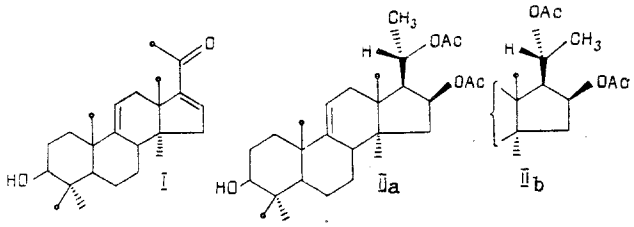
Under the conditions of the mild acid hydrolysis of the sum of the triterpene glycosides from the holothurian Duasmodactyla kurilenis a new genin has been obtained the structure of which has been determined as 16β,20(S)-diacetoxy-4,4,14-trimethylpregn-9(11)-en-3β-ol by IR, UV, and mass spectroscopy, and high-resolution ^{13}C and ^{1}H NMR.

We have previously [1] described the isolation of the artefactual nonholostane genin (I) after acid hydrolysis of the sum of the triterpene glycosides from the holothurian Duasmodactyla kurilenis. By changing the conditions of hydrolysis, from the same total glycosides we have obtained the new genin (IIa), which we proposed to call nemogenin (from the site of collection of the animals).



The IR, mass, and UV spectra of (IIa) showed that in comparison with (I), it lacked an α,β-unsaturated ketone fragment but had two acetate groups (mass spectrum, m/z: 460 (M^+); 400 ($M^+ - CH_3COOH$); 340 ($M^+ - 2CH_3COOH$).

The structure of (IIa) was established by comparing its ^{1}H and ^{13}C NMR spectra with the spectra of (I) and the spectra of model compounds: lanost-9(11)-en-3β-ol (II) [2] and 3β,16β-diacetoxyholosta-8,25-dien (IV) [3]. A comparison of the ^{13}C NMR spectra of (I), (IIa), and (III) showed that the C-1–C-14, C-18, C-19, and C-30–C-32 signals were close or coincided in the spectra of these substances. In addition, the presence of 9(11) double bond was also confirmed by the signals in the ^{1}H NMR spectrum of H-11 (5.25 ppm), CH_3-18 (0.84 ppm), and CH_3-19 (1.06 ppm), and the presence of hydroxy group by H-3 signal at 3.22 ppm.

The C-15–C-17 signals in the spectrum of (IIa) were close to the corresponding signals in the spectrum of (IV), which permitted the assumption of the presence of one of the two acetate groups in position 16β. This conclusion was confirmed by difference decoupling, and it was established that the second acetate group was localized at C-20.

In actual fact, difference decoupling on the multiplet at 5.20 ppm (H-20) revealed a doublet of doublets at 2.33 ppm (H-17) and the signal of a methyl group (C-21) in the form of a doublet with J = 6.4 Hz at 1.26 ppm. In its turn, decoupling on the multiplet at 5.40 ppm (H-16) revealed a doublet of doublets at 2.33 ppm (H-17) and a doublet of doublets at 2.17 (H-15α) and 1.42 ppm (H-15β).

The values of the spin-spin coupling constants of H-16 and H-27 indicated their α-configuration [3, 4]. This was confirmed by the results of a measurement of the nuclear Overhauser effect (NOE). On irradiation with a frequency corresponding to the H-16 signal, enhancements were obtained of the signals of H-17 and H-15α and of the methyl group at 0.79 ppm (C-32).

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TABLE 1. ^{13}C NMR Spectrum of Genin (IIa) (solvent pyridine; $\delta_{TMS} = 0$)

Atom	IIa	Atom	IIa	Atom	IIa
C-1	36,1	C-10	39,9	C-19	22,5
C-2	28,3	C-11	114,2	C-20	69,5
C-3	77,9	C-12	36,5	C-21	19,7
C-4	39,7	C-13	45,8	C-30	28,8
C-5	52,9	C-14	48,3	C-31	16,5
C-6	21,6	C-15	43,9	C-32	19,1
C-7	28,6	C-16	73,9	O-Ac	170,0
C-8	41,5	C-17	53,4		21,1
C-9	149,3	C-18	15,5		

TABLE 2. ^{1}H NMR Spectrum of the Genin (IIa) (solvent chloroform; $\delta_{TMS} = 0$)

Position of the protons	δ	Position of the protons	δ	Spin-spin coupling constant
H-3	3,22 dd	CH_3-19	1,06 s	$J_{15\alpha, 15\beta}$=12,8
H-11	5,25 m	CH_3-21	1,26 d	$J_{16, 15\alpha}$=8,4
H-15α	2,17 dd	CH_3-30	1,00 s	$J_{16, 15\beta}$=5,0
H-15β	1,42 dd	CH_3-31	0,86 s	$J_{16, 17}$=7,7
H-16	5,40 td	CH_3-32	0,79 s	$J_{17, 20}$=10,8
H-17	2,33 dd	O-Ac	1,94 s	$J_{20, 21}$=6,4
H-20	5,20 m		1,96 s	
CH_3-18	0,84 s			

For the asymmetric center at C-20 two stereoisomers are possible: (IIa), (IIb). A study of models of the isomers, a determination of interatomic distances, and the performance of NOE experiments permitted the unambiguous statement that we had isolated the isomer (IIa), since for isomer (IIb) after irradiation of H-16 a change in the intensity of the CH_3-21 doublet signal would have taken place.

EXPERIMENTAL

The spectral analyses were performed under the conditions described in [1].

The animals were collected in August, 1983, at a depth of 70-120 m in a traverse of Nemo Bay, island of Onekotan (Kurile Islands).

Isolation of the Glycoside Fraction. The sum of the triterpene glycosides was obtained by the procedure described in [1].

Acid Hydrolysis of the Sum of the Glycosides. A solution of 500 mg of the glycosidic sum in a mixture of 50 ml of 1 N H_2SO_4 and 20 ml of butanol was stirred vigorously on the boiling water bath for 1 h and was then cooled and the butanol layer was separated off. The aqueous layer was extracted twice with 5 ml of butanol, and the butanol extracts were combined. They were then washed with water (10 ml), with 1% $NaHCO_3$ solution (2 × 10 ml), and again with water (2 × 5 ml) and were evaporated to dryness. The dry residue was chromatographed on silica gel in the benzene–ethyl acetate (85:15) system. This gave 7.5 mg of genin (IIa) with mp 238-240°C, $[\alpha]_D^{20}$ +91° (c 1.0; chloroform).

SUMMARY

Under the conditions of mild acid hydrolysis of the sum of the triterpene glycosides from the holothurian Duasmodactyla kurilenis a new genin has been obtained the structure of which has been determined as 16β,20(S)-diacetoxy-4,4,14-trimethylpregn-9(11)-en-3β-ol.

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STRUCTURE OF PSOLUSOSIDE B — A NONHOLOSTANE TRITERPENE GLYCOSIDE OF THE HOLOTHURIAN GENUS Psolus

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The structure of psolusoside B — a minor triterpene oligoglycoside from the holothurian Psolus fabricii and the main glycoside from Psolus sp. has been determined by the methods of partial acid hydrolysis, methylation, ^{13}C NMR, and FAB mass spectrometry as 20S-acetoxy-3β-{2'-O-[O-β-D-glucopyranosyl-(1 → 4)-O-β-D-glucopyranosyl]-4'-O-(6"-O-sulfato-β-D-glucopyranosyl)-β-D-xylopyranosyloxy}holosta-7,25-diene-18,16-carbolactone. 3β-[O-(3"'-O-Methyl-6"'-O-sulfato-β-D-glucopyranosyl)-(1 → 3)-O-(6"-O-sulfato-β-D-glucopyranosyl)-(1 → 4)-O-β-D-quinovopyranosyl-(1 → 2)-β-D-xylopyranosyloxy]holosta-9(11),25-dien-16-one (psolusoside A), known previously for Psolus fabricii, has been identified in a holothurian — Psolus sp. — from Kraternaya Bay (island of Ushishir).

We have previously reported on the determination of the structure of psolusoside A (I) — the main triterpene glycoside of the Far Eastern holothurian Psolus fabricii Düben et Koren [1, 2]. Continuing a study of the glycoside fraction of this holothurian, we have isolated a minor component which has been called psolusoside B (II). After the acid hydrolysis of its hydrated desulfated derivative we obtained an artefactual genin, 20S-acetoxy-3β-hydroxylanost-7-ene-18,16-carbolactone (III) (onekotanogenin), and the structure of the native aglycon was determined as 20S-acetoxy-3β-hydroxylanosta-7,25-diene-18,16-carbolactone (IV) [3].

In the present paper we describe the determination of the constitution of the carbohydrate chain of psolusoside B and give its complete structure.

The acid hydrolysis of (II) led to the total monosaccharides, which were identified by the GLC-MS method in the form of aldononitrile peracetates as xylose and glucose (1:3). The FAB mass spectrum of (II) contained intense $M^- - Na - H$ ion at 1209 m/z, which confirmed the results of monosaccharide analysis.

After solvolysis by heating in a mixture of pyridine and dioxane, (II) gave the desulfated derivative (V) the FAB mass spectrum of which contained the $M^- - H$ peak at 1129 m/z showing the presence of only one sulfate group in psolusoside B.

After (V) had been methylated by Hakomori's method followed by the methanolysis and acetylation of the products, the methyl α- and β-glycopyranosides of 2,4-di-O-acetyl-3-O-methylxylose, 4-O-acetyl-2,3,6-tri-O-methylglucose, and 2,3,4,6-tetra-O-methylglucose, which were identified by the GLC-MS method, were obtained. It followed from this that the carbohydrate chain in glycoside (II) was branched at the xylose residue and had glucose residues at its ends. On the periodate oxidation and hydrolysis of (II), all the glucose residues were decomposed.

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