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STRUCTURE OF PSOLUSOSIDE A — THE MAIN TRITERPENE GLYCOSIDE FROM THE HOLOTHURIAN *Psolus fabricii*

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The structure of psolusoside A — the main component of the glycosidic fraction from the holothurian *Psolus fabricii* Duben et Koren — has been determined as 3β-O-[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.

Continuing a chemical study of holothurians of the sublittoral of the island of Onekotan [1, 2] we have established the complete structure of psolusoside A — the main component of the glycosidic fraction from the holothurian *Psolus fabricii*. We had shown previously that this glycoside was a tetraoside of 3β-hydroxyholosta-9(11),25-dien-16-one, and tis monosaccharide residues were determined as those of D-xylose, D-quinovose, 3-O-methyl-D-glucose, and D-glucose [1]. We have now completed the interpretation of the structures of the carbohydrate chain of psolusoside A (I). (Formula, top, following page.)

The result of the solvolytic cleavage of psolusoside A with a mixture of pyridine and dioxane (1:1) indicated the presence of sulfate groups in the glycoside [3]. This solvolysis gave the desulfated derivative (II).

The Hakomori methylation of (II) [4] followed by methanolysis and acetylation led to the formation of methyl 2-O-acetyl-3,4-di-O-methyl-α- and -β-xylopyranosides, methyl 4-O-acetyl-2,3-di-O-methyl-α- and β-quinovopyranosides, methyl 3-O-acetyl-2,4,6-tri-O-methyl-α- and -β-glucopyranosides, and methyl 2,3,4,6-tetra-O-methyl-α- and -β-glucopyranosides, which were identified by GLC and chromato-mass spectroscopy. The results obtained showed that the carbohydrate chain was unbranched, and the terminal position was occupied by a 3-O-methylglucose residue.

On periodate oxidation of glycoside (I) followed by acid hydrolysis, the xylose and quinovose residues were destroyed, which indicated the absence of sulfate groups attached to these monosaccharide residues. The number and positions of the sulfate groups were established by comparing the ^{13}C NMR spectra of the desulfated derivative (II) and the glycoside (I) (Table 1).

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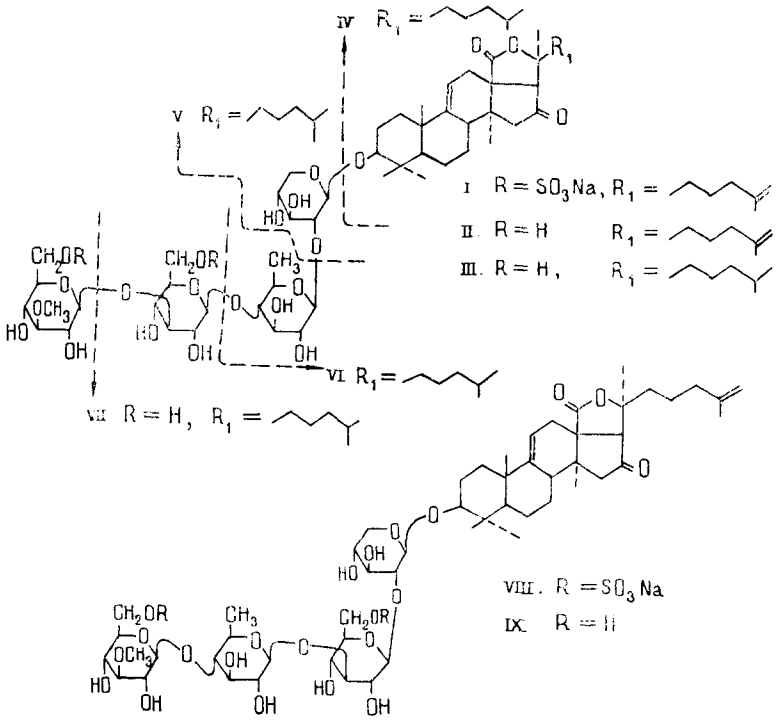

The C-6 signal of the 3-O-methylglucose residue (66.0 ppm) and the C-6 signal of the glucose residue (65.8 ppm) of glycoside (I) were shifted downfield in comparison with the corresponding signals in the spectrum of derivative (II) (60.9 ppm). The C-5 signal of the 3-O-methylglucose residue (75.1 ppm) and the C-5 signal of the glucose residue (74.4 ppm) were shifted upfield in the spectrum of (I) relative to the analogous signals of (II) at 76.9 and 76.6 ppm. These shifts are characteristic for the α and β effects of sulfate groups [5] and indicated that there were two such groups in the carbohydrate chain of glycoside (I) and they were attached at the C-6 positions of the 3-O-methylglucose and glucose residues. The counter-ion at the sulfate groups of (I) was, according to the results of atomic absorption spectroscopy, sodium.

The signals of the anomeric carbons at 104.0, 104.5, 103.1, and 103.9 ppm in the ^{13}C NMR spectrum of (I) showed the β configurations of the glycosidic bonds [5].

To determine the sequence of the xylose, quinovose, and glucose residues, we performed partial acid hydrolysis of the hydrogenated desulfated derivative (III) with 2 N sulfuric acid in the presence of butanol. This gave the aglycone (IV), a progenin (V) giving xylose on acid hydrolysis, a progenin (VI) the acid hydrolysis of which gave xylose and quinovose, and a progenin (VII) the monosaccharide residues of which were determined as xylose, quinovose, and glucose. It followed unambiguously from these facts that the xylose residue was attached directly to the aglycone, the quinovose residue to the xylose, the glucose residue to the quinovose, and, in its turn, the 3-O-methylglucose residue to the glucose.

Tables 1 and 2 give the ^{1}H and ^{13}C NRM spectra of the aglycone (IV) and of the progenins (V), (VI), and (VII), which confirm their structures. In a comparison of the spectrum of the progenins it was found that that of the bioside (VI) contained signals showing the presence of a secondary methyl group in the second monosaccharide (18.5 ppm in the ^{13}C spectrum; 1.72 ppm, d, J = 5.6 Hz, in the ^{1}H NMR spectrum). Analogous signals were observed in the spectrum of the trioside (VII) (18.4 ppm in the ^{13}C NMR spectrum; 1.8 ppm, d, in the ^{1}H NMR spectrum).

The position of the glucose residue was additionally confirmed by the results of the methylation of the progenin (VII) which, when followed by methanolysis and acetylation, formed methyl 2-O-acetyl-3,4-di-O-methyl-α- and -β-xylopyranosides, methyl 4-O-acetyl-2,3-di-O-methyl-α- and -β-quinovopyranosides, and methyl 2,3,4,6-tetra-O-methyl-α- and -β-glucopyranosides.

When our preliminary communication [1] had been sent for printing and the present paper was in the stage of being completed, a paper appeared from a group of Canadian workers [6] on the structure of the main component of the glycosidic fraction of the holothurian *Psolus fabricii* collected in the Gulf of St. Lawrence and called by them psoluthurin A (VIII).

TABLE 1. ^{13}C NMR Spectra of Compounds (IV) and (VII) (300 K, C_5D_5N); (II), (V), and (VI), (333 K, C_5D_5N), and (I) (300 K, DMSO-d_6, δ_{DMSO} = 39.6 ppm); II^+ — the Spectrum of (II) Taken in DMSO-d_6

Atom	I	II+	II	IV	V	VI	VII	Atom	I	II+	II	V	VI	VII
C_1	35,9	35,7	36,4	36,5	36,6	36,6	36,6	C_1^1	104,0[a]	104,0[a]	105,4	107,0	105,5	105,6[a]
C_2	26,6	26,6	26,9	28,6	27,1	27,2	27,2	C_2^1	82,7	82,4	83,9	75,1	83,8	84,4
C_3	88,3	88,1	88,8	78,0	88,8	89,0	89,0	C_3^1	76,7	76,6	77,8	78,0	77,9	78,2[c]
C_4	*	*	40,0	39,8	39,9	40,0	39,9	C_4^1	69,5	69,5	70,7	71,1	71,0	70,9
C_5	52,5	52,3	53,2	52,8	53,3	53,3	53,2	C_5^1	65,6	65,4	66,5	66,7	66,6	66,8
C_6	20,5	20,4	21,3	21,4	21,3	21,3	21,3	C_1^2	104,5[a]	104,3[a]	105,4		106,1	105,7[a]
C_7	28,0	27,8	28,5	28,6	28,4	28,4	28,3	C_2^2	75,0[b]	75,0[b]	76,3[b]		76,8	76,5[b]
C_8	38,2	38,1	38,9	38,8	39,0	39,0	38,9	C_3^2	74,4[b]	74,4[b]	75,9[a]		77,9	76,1[b]
C_9	151,0	151,1	151,5	151,5	151,8	151,8	151,6	C_4^2	85,8[c]	86,1[a]	87,1		77,0	87,4
C_{10}	*	*	40,0	40,2	40,0	40,0	40,1	C_5^2	70,4	70,3	71,7		73,4	71,8
C_{11}	110,6	110,6	111,0	111,1	111,2	111,0	111,2	C_6^2	17,4	17,5	18,1		18,5	18,4
C_{12}	31,2	31,2	32,3	32,2	32,4	32,4	32,3	C_1^3	103,1	103,1	104,6			105,5[a]
C_{13}	55,1	55,0	55,9	55,7	55,9	55,9	55,8	C_2^3	72,6	72,3	73,6			75,0
C_{14}	41,6	41,4	42,1	42,2	42,2	42,2	42,2	C_3^3	86,2[c]	87,6	88,3			78,4[c]
C_{15}	51,7	51,5	52,0	52,0	52,1	52,1	52,1	C_4^3	68,5	68,6	69,9			71,8
C_{16}	213,7	213,0	212,6	212,9	212,5	212,7	212,9	C_5^3	74,4	76,6	77,8			78,4[c]
C_{17}	60,2	60,2	61,5	61,4	61,7	61,7	61,6	C_6^3	65,8[d]	60,9	62,4			62,8
C_{18}	176,0	176,0	175,7	175,9	175,8	175,8	175,8	C_1^4	103,9[a]	104,0[a]	105,4			
C_{19}	21,7	21,6	22,0	22,2	22,2	22,2	22,2	C_2^4	73,7	73,5	74,8			
C_{20}	83,0	82,9	83,0	83,2	83,1	83,0	83,2	C_3^4	86,2[c]	86,0[a]	87,7			
C_{21}	26,6	26,5	26,9	26,8	27,1	27,0	27,0	C_4^4	69,3	69,4	70,7			
C_{22}	37,8	37,7	38,4	39,1	39,2	39,2	39,2	C_5^4	75,1	76,9	78,1			
C_{23}	21,7	21,6	22,0	22,2	22,1	22,2	22,2	C_6^4	66,0[d]	60,9	62,4			
C_{24}	37,6	37,4	38,1	39,4	39,5	39,4	39,5	OMe	60,2	59,9	60,4			
C_{25}	145,3	145,2	145,5	28,0	28,0	28,0	28,0							
C_{26}	110,3	110,4	110,6	22,6	22,6	22,6	22,7							
C_{27}	22,3	22,1	22,4	22,6	22,6	22,6	22,7							
C_{30}	16,3	16,2	16,6	16,5	16,9	16,8	16,8							
C_{31}	27,6	27,5	28,2	28,8	28,6	28,7	28,7							
C_{32}	20,5	20,4	20,5	20,7	20,6	20,7	20,7							

*Signals overlapping with the signals of the solvent; a, b, c, and d — assignment of the signals ambiguous.

The ^{13}C NMR spectra of psoluthurin A (VIII) and its desulfated derivative (IX) given by these authors basically agree with the corresponding characteristics for psolusoside A and the product of its desulfation. The physical constants of (IX) and (II) were close, but the constants of (I) and (VIII) differed somewhat, which may be connected with difficulties in purifying polar glycosides.

The structure of (VIII) given by the Canadian authors differs from the structure of (I) that we have found by the position of the quinovose and glucose residues. The sequence of monosaccharide residues in the carbohydrate chain of psoluthurin A was established on the basis of physical methods of investigation, mainly with the aid of mass spectroscopy.

TABLE 2. ^{1}H NMR Spectra of the Genin (IV) and of the Progenins (V), (VI), and (VII); solvent C_5D_5N, δ, TMS – 0

Atom	IV	V	VI	VII	Atom	IV	V	VI	VII
H-3	3,50 dd	3,32dd	3,35 dd	3,30dd	CH_3–26	0,84d	0,83d	0,84d	0,85d
H-8	3,28m	3,26m	3,30 m	3,00m	CH_3–27	0,85d	0,85d	0,85d	0,84d
H-11	5,37m	5 35m	5.36 m	5,35m	CH_3–30	1,11s	1,07s	1,22s	1,16s
2H-12	2,52m	2,50m	2,51 m	2,51 m	CH_3–31	1,26 s	1,35s	1,45s[a]	1,44s[a]
H-15α	2,40d	2,40d	2,40d	2,42d	CH_3–32	0,9ls	0,91s	0,92s	0,93s
H-15β	2,28 d	2,27d	2,28d	2,28 d	H-1′		4,88d	4,87 d	4,85d
H-17	2.82s	2.81s	2 82s	2,84s	H-1″			5,28 d	5,23 d
CH_3-19	1,43s	1,38s	1,38s	1,36s	CH_3-6″			1,72 d	1,80d
CH_3-21	1,41s	1,40s	1,41s[a]	1,41s[a]	H-1‴				5,03d

a – assignment of the signal ambiguous.

According to the results of investigations that we have carried out in recent years, the structures of the glycosides of taxonomically close holothurians do not depend on the gathering site [7, 8] but form a reliable chemosystematic characteristic [9]. It is therefore most probable that the Canadian workers permitted an error in the interpretation of the mass spectra as a result of which the sequence of the monosaccharides in the carbohydrate chain of the main component of the glycosidic fraction of *Psolus fabricii* was determined incorrectly.

At the present time, the complete structures of more than a score of glycosides of holothurians of the order *Aspidochirota* have been established. The carbohydrate chains of these glycosides contain even numbers of monosaccharide residues and are constructed on the block principle from biosidic components linked to one another by (1 → 4)-bonds. Such glycosides either contain a single sulfate group in the C-4 position of a xylose residue or they contain no sulfate group [10]. All these glycosides belong to the holostane series.

The order *Dendrochirota* has been less well studied chemically. Psolusoside A is only the third glycoside of representatives of *Dendrochirota* for which the complete structure has been established, following cucumarioside G_1 from *Cucumaria fraudatix* [11] and cucumarioside A_2^2 from *Cucumaria japonica*. Structural features essentially distinguishing them from glycosides of representatives of *Aspidochirota* are characteristic for all three glycosides. Cucumarioside A_2^2 contains an odd number of monosaccharide residues, cucumarioside G_1 the residue of a sugar that is unusual for holothurian glycosides – 3-O-methylxylose, and psolusoside A two sulfate groups, attached, moreover, to the C-6 positions of glucose and 3-O-methyl glycose residues. Furthermore, kurilogenin – an artefactual triterpene aglycone of unusual structure that is not a derivative of the holostane series – has recently been isolated from glycosides of the holothurian *Duasmodactyla kurilensis* Levin (*Phyllophoridae*, *Dendrochirota*) [2].

The complex of paleontological and morphological facts indicates that *Dendrochirota* are closer to the ancestral forms of holothurians than *Aspirochirota*. The order *Aspirochirota* has a smaller phylogenetic age [12].

Consequently, the structural features of the glycosides of *Dendrochirota* show that it is precisely in the process of evolutionary develcpment of the holothurians that the principles of the biosynthesis of their triterpene glycosides were developed.

EXPERIMENTAL

Melting points were determined on a Boëtius stage. Specific rotations were measured on a Perkin-Elmer 141 polarimeter in pyridine solutions at room temperature. Atomic absorption analysis for metals was performed on an AA-780 instrument.

^{13}C NMR spectra were obtained on Bruker HX-90E and WM-250 instruments. PMR spectra were recorded at 250 MHz on the Bruker WM-250. The signals in the NMR spectra are given on the δ scale. The signals of the methyl groups in the PMR spectrum of the genin (IV) were assigned by recording the NOE on irradiation of H-17 (CH_3-21,32) and H-8 (CH_3-19). On double resonance with irradiation of CH_3-32, the lines of the H-15β proton underwent contraction. The assignment of the signals in the ^{13}C NMR spectrum of this genin to a definite type of carbon atoms was carried out with the use of the SEFT method [13]. The signals of the methyl groups were assigned with selective decoupling from protons and by comparison with literature information [14]. The distinction between the C-22 and C-24 signals was made on the basis of an evaluation of their relaxation times starting from the assumption that C-24 should relax more slow-

ly. The sequence of the C-22–C-24 signals was made similarly in the case of a side chain with a 25,26- double bond.

GLC analysis was performed on a Tsvet-110 chromatograph using 0.3 × 150 cm glass columns with 3% of QF-1 on Chromaton N-HMDS at temperatures of 110-222°C, 5 deg/min, with argon as the carrier gas (60 ml/min). Chromato-mass spectrometric analysis was performed on an LKB-9000S mass spectrometer using 0.3 × 300 cm columns containing 1.5% of QF-1 on Chromaton N-HMDS with helium as the carrier gas (30 ml/min). Analysis was performed under the following conditions; temperature of the evaporator 275°C, of the column 110-220°C (5 deg/min), of the molecular separator 265°C, and of the ion source 255°C, ionizing voltage 70 eV.

The animals were collected in Sea of Okhotsk in the littoral of the island of Onekotan (Kurile islands) from a depth of 100 m with a comb-type dredge in August-September, 1982. The holothurians were determined by V. S. Levin.

The psolusoside A (I) was isolated as described previously [1]. Mp 208-211°C, $[\alpha]_D^{25}$ − 73° (c 0.1; pyridine).

Desulfation of Psolusoside A. A solution of 90 mg of the glycoside in 10 ml of pyridine–dioxane (1:1) was boiled for 1 h. Then the reaction mixture was evaporated to dryness, and the residue was additionally purified by column chromatography on silica gel in the chloroform–methanol (6:1) system. This gave 40 mg of the desulfated derivative (II) with mp 293-296°C, $[\alpha]_D^{25}$ − 78° (c 0.1; pyridine).

Hydrogenation of the Desulfated Derivative (II). With heating, 100 mg of (II) was dissolved in 50 ml of butanol, and then 20 mg of hydrogenated Adams catalyst in 10 ml of butanol was added and hydrogenation was carried out at 50°C with vigorous stirring for a day. The reaction mixture was filtered, the spent catalyst was washed on the filter with chloroform–methanol (6:1) and the combined filtrate was evaporated. This gave 95 mg of the hydrogenated desulfated compound (III) with mp 295-298°C, $[\alpha]_D^{25}$ − 75° (0.1; pyridine).

Methylation of the Desulfated Derivative (II). A solution of 10 mg of (II) in 2 ml of dry dimethyl sulfoxide (DMSO) was added to a solution of the methylsulfinyl anion (prepared from 100 mg of NaH and 2 ml of DMSO), and the mixture was stirred in an atmosphere of argon at 50°C for 1 h. Then 1 ml of CH_3I was added to the reaction mixture and it was left at room temperature for 2 h. The reaction mixture was diluted with water (10 ml) and extracted with chloroform (3 × 2 ml). The extract was washed with 2 ml of saturated sodium thiosulfate solution and with 2 ml of water and was evaporated. The resulting residue was boiled with 1 ml of anhydrous methanol saturated with HCl for 2 h. The solution was evaporated and the residue was covered with a mixture of pyridine and acetic anhydride; the reaction mixture was heated at 100°C for 1 h and was evaporated, and the product was analyzed by GLC-MS to identity the methyl glycosides.

Periodate Oxidation of Psolusoside A. A solution of 4 mg of (I) in 2 ml of water was treated with 30 ml of sodium periodate and the mixture was left at +5°C for 2 weeks. Then the reaction product was extracted with butanol (3 × 2 ml) and the butanol layer was washed with water and evaporated. The residue was heated with 0.5 ml of 12% HCl at 90-100°C for 2 h. The reaction mixture was extracted with chloroform and the aqueous layer was neutralized with Dowex anion-exchange resin (HCO_3^-). The resin was separated off by filtration and was washed with water. The aqueous layer and the wash-waters were combined and concentrated in vacuum to dryness. The residue was dissolved in 1 ml of dry pyridine, and then 5 mg of hydroxylamine hydrochloride was added and the mixture was heated at 100°C for 1 h. Then 1 ml of acetic anhydride was added to it and it was heated at 100°C for another 1 h. After this, it was evaporated and analyzed by GLC. The peracetates of the aldononitriles of glucose and of 3-O-methylglucose were identified (1:1).

Partial Acid Hydrolysis of the Hydrogenated Desulfated Derivative (III). A mixture of 200 mg of (III), 20 ml of butanol, and 20 ml of 2 N H_2SO_4 was heated in the boiling water bath with vigorous stirring for 1 h. The butanol layer was separated off and was washed with water (5 ml), with 1% $NaHCO_3$ solution (5 × 2 ml) and again with water (5 × 2 ml), and was then evaporated. The dry residue was chromatographed on silica gel in the chloroform–methanol (6:1) and chloroform–methanol (10:1) systems. This gave 39 mg of the aglycone (IV), 10 mg of the progenin (V) with mp 296-298°C, $[\alpha]_D^{25}$ − 85° (c 0.1; pyridine), 9 mg of the progenin (VI), mp 325-328°C, $[\alpha]_D^{25}$ − 112° (c 0.1; pyridine), 15 mg of the progenin (VII) with mp 278 280°C, $[\alpha]_D^{25}$ − 65° (c 0.1; pyridine), and 26 mg of the initial substance (III).

Determination of the Monosaccharide Compositions of the Progenins (V), (VI), and (VII). Each progenin (4 mg) was hydrolzyed with 2 N HCl (100°C, 2 h) and the monosaccharides obtained were analyzed as described above, in the form of the aldononitrile peracetates. On hydrolysis, progenin (V) gave xylose, progenin (VI) xylose and quinovose (1:1) and progenin (VII) xylose, quinovose, and glucose (1:1:1).

Methylation of the Progenin (VII). The progenin (VII) (7 mg) was methylated, and the product was subjected to methanolysis and acetylation as described above. The methyl glycosides obtained were analyzed by GLC-MS.

SUMMARY

It has been shown that psolusoside A from the holothurian *Psolus fabricii* is 3β-[0-(3-0-methyl-6-0-sulfato-β-D-glucopyranosyl-(1 → 3)-0-(6-0-sulfato-β-D-glucopyranosyl)-(1 → 4)-0-β-D-quinovopyranosyl-(1 → 2)-β-D-xylopyranosyloxy]-holosta-9(11),25-dien-16-one.

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