STRUCTURE OF PSEUDOSTICHOPOSIDE A — THE MAIN TRITERPENE GLYCOSIDE FROM THE HOLOTHURIAN Pseudostichopus trachus

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A holostane oligoglycoside — pseudostichoposide A — has been isolated from the holothurian Pseudostichopus trachus Sluiter, collected on the oceanic side of the island of Urup (Kurile Islands). Its structure has been established with the aid of ^{13}C and ^{1}H NMR spectroscopy and partial acid hydrolysis with sulfuric acid in the presence of butanol as 3β-{O-(3-O-methyl-β-D-quinovopyranosyl-(1 → 3)-O-β-D-xylopyranosyl-(1 → 4)-O-β-D-quinovopyranosyl-(1 → 2)-[4-O-(sodium sulfato)-β-D-xylopyranosyloxy]}-holost-7-en-22-one. Its native genin, which has been called urupogenin (3β-hydroxyholost-7-en-22-one) was obtained on partial hydrolysis in the form of an individual compound. It is a new holostane derivative.

Continuing a chemical study of the holothurians of the littoral of the Kurile Islands [1-5], we have established the complete structure of pseudostichoposide A (I) as the main triterpene oligoglycoside from the holothurian Pseudostichopus trachus Sluiter (Gephirothuriidae, Aspidochirota) collected from the oceanic littoral of the island of Urup.

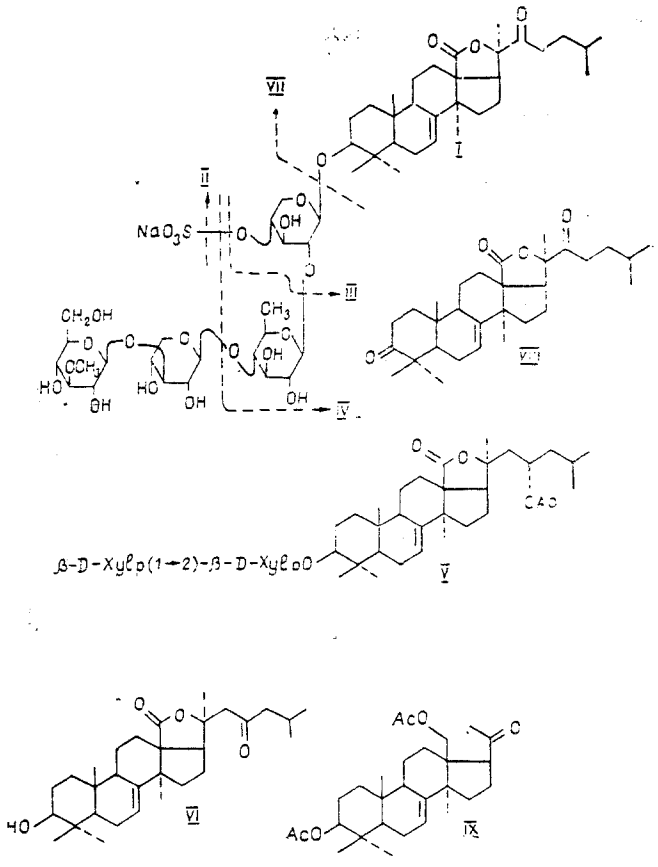

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TABLE 1. ^{13}C NMR Spectra of Glycoside (I), of the Desulfated Derivative (II), and of Progenins (III) and (IV), and also of the Aglycon Moiety of the Model Compound (V) (333 K, C_5D_5N)

Atom	I	II	III	IV	V	Atom	I	II	III	IV	V
C-1	36,2	36,2	36.2	36.4	36,1	C-27	22,2	22,4	22,4	22 4	23,2
C-2	27,0	27,1[b]	27,1[b]	27,3	27.4	C-30	17,3	17,4	17,5	17,4	17,9
C-3	89,1	89,2	89.0	89,3	89,7	C-31	28,8	28,9	28,9	28,8	28,4
C-4	39,5	39,7	39.5	39,7	39,8	C-32	30,7	30,8	30 8	30,8	30,9
C-5	48,2	48.2	47,9	48,0	48.3	C¹-1	105,1[a]	105,0[a]	107,5	105.3[a]	
C-6	23.3	23.3	23.3	23,4	22,9	C¹-2	83,0	84,0	75,2	84,0	
C-7	120,5	120.5	120,4	120,5	120,0	C¹-3	76,2	78.0	78.4	78,0	
C-8	146,1	146,1	146.1	146,1	146,5	C¹-4	75,3	70,7	71,0	70,8	
C-9	47,6	47,6	47,9	47,4	47.6	C¹-5	64,0	66,6	66,9	66,7	
C-10	35,6	35.7	36,0	35,7	35.8	C²-1	105.1[a]	105,4[a]		105,6[a]	
C-11	22,7	22,7	22,7	22.4	23.0	C²-2	76,2	76,4		76,6	
C-12	29,7	29,7	29,5	29,5	30,5	C²-3	75.3	75.6		77,7	
C-13	58,5	58.3	58.3	58,3	58,6	C²-4	74,8	74,9		77.0	
C-14	51,3	51,4	51,0	51,4	51,4	C²-5	71.6	71,7		73,4	
C-15	34,3	34,2	34,1	34,2	34,4	C²-6	17.9	18,0		18,6	
C-16	24,8	27,7[b]	27,6[b]	27,3	24,9	C³-1	105,1[a]	104,9[a]			
C-17	52,8	52.7	52.6	52.6	54.4	C³-2	73,3	73,3			
C-18	179,2	179,2	179,2	179,2	179,2	C³-3	87,6	87,6			
C-19	23,0	24,0	23,9	24,0	24.2	C³-4	69,0	69,0			
C-20	89,3	89,4	89,0	89,4	83,1	C³-5	66,3	66,4			
C-21	24,6	24,7	24,6	25,0	27,1	C⁴-1	104,8[a]	105,3[a]			
C-22	210,5	210,7	210,7	210 7	44,2	C⁴-2	74,8	74,9			
C-23	32,0	32,0	31,9	32,0	68,2	C⁴-3	87,7	87,8			
C-24	37,0	37,3	37,2	37,2	45 5	C⁴-4	70,8	70,7			
C-25	27,6	27,7	27,6	27,7	24,7	C⁴-5	78.0	78,2			
C-26	22,2	22,4	22,4	22,4	22.3	C⁴-6	62,3	62,4			
						OCH_3	60,3	60,6			

[a,b]Assignment of the signals ambiguous.

The ^{13}C NMR spectrum of the glycoside (I) showed that the aglycon of pseudostichoposide A (I) belonged to the holostane series and a single double bond occupying the 7(8) position and a keto group were detected in it (signals at 120.5 and 146.1 and at 210.5 ppm, respectively). A comparison of it with the spectrum of the model derivative (V) obtained previously in a study of stichoposide E from the holothurian Stichopus chloronotus [6] showed good agreement for the signals of the C-1–C-16 carbon atoms of the two compounds (Table 1). It followed from this that the keto group was obviously present in the side chain of the aglycon of pseudostichoposide A. A triterpene glycoside from the holothurian Synapta maculata with aglycon (VI) having a keto group in position 23 has been described in the literature [7]. However, the signals of the carbon atoms of the side chain of this aglycon, including the signal of the keto group (207.3 ppm) differed substantially from those observed in our spectrum.

As has been shown previously, characteristic for holostane compounds containing a keto group in position 23 or 16 on alkaline treatment is the opening of the lactone ring with subsequent dehydration, which leads to the formation of α,β-unsaturated ketones absorbing in the UV spectrum [8, 9]. However, the alkaline treatment of pseudostichoposide A (I) did not lead to chromophore-containing products absorbing in the ultraviolet region of the spectrum. This also excluded position 23 for the keto group in pseudostichoposide A.

At the same time, attention is attracted by the downfield shift of the C-20 signal, which is observed at 83.1 ppm in the spectrum of the 7(8)-unsaturated holostane derivative (V), to 89.3 ppm in the spectrum of (I). Correspondingly, the C-17 signal for (I) is located at 52.8 ppm, while in the model compound (V) it appears at 54.4 ppm. Such shifts could be due to the α- and β-effects of the keto group if it is assumed that it occupies position 22. On the other hand, position 24 for this function was excluded on the basis of considerations that in this case the spectrum of (I) should contain the signals of methyl groups in the 17-18 ppm region (C-26, C-27) and also a methine signal at approximately 40.0 (C-25), which were absent.

To confirm our hypothesis concerning the structure of the aglycon of pseudostichoposide A as 3β-hydroxyholost-7-en-22-one (VII), we obtained it, together with the progenins (III) and (IV), on the mild acid hydrolysis of (I) with sulfuric acid (2N) in the presence of

TABLE 2. PMR Spectra of the Genin (VII) and of Derivative (VIII) (solvent $CDCl_3$, $\delta_{TMS} = 0$)

Atom	δ(j)		Atom	δ(j)	
	VII	VIII		VII	VIII
H-3α	3,23m	—	CH_3-26	0,88 d (6,8)	0.90 (6,7)
H-7	5,57m	5,45m	CH_3-27	0,88 d (6,8)	0.90 (6,7)
H-9β	3,17dm	3,16dm	CH_3-30	0.86s	1.12 s
CH_3-19	1,05s	1,25s	CH_3-31	1,03s	1,16 s
CH_3-21	1,48s	1,48s	CH_3-32	1,10 s	1,10 s

a,bAssignment of the signals ambiguous.

butanol. The PMR spectrum of (VII) (Table 2) showed the signals of an olefinic proton at 5.57 ppm (CH-7) and of a carbonyl proton at 3.21 ppm (CH-3) connected with the 7(8)-position of the double bond and the 3β-position of the hydroxy group, respectively. The position of the 3β-hydroxy group was confirmed by comparing the PMR spectra of (VII) and of the product of its Jones oxidation (VIII). In the spectrum of (VIII) (Table 2), the signals of the C-30 and C-31 protons of the methyl groups were shifted downfield and were closer together, which is characteristic for the spectra of lanostane and holostane derivatives [10].

The ^1H NMR spectroscopic results also enabled us to exclude the 24-position of the keto group for compound (VII). In actual fact, on irradiation with a frequency corresponding to the CH_3-26 and CH_3-27 resonance a multiplet signal of H-25 at 1.55 ppm was revealed. Its strong-field position showed the absence of a carbonyl group at C-24. The mass spectrum of (VII) (M^+ 470 m/z) had as the strongest signal a peak with m/z 99, obviously formed through C-20–C-21 cleavage and quite definitely showing the presence of a keto function at C-22.

For an additional confirmation of the 22-position of the keto group we carried out the chemical degradation of the aglycon (VII). With this aim, (VII) was reduced with lithium tetrahydroaluminate. The resulting mixture of polyols was oxidized with an aqueous solution of sodium periodate in the presence of butanol. The mixture of compounds so obtained was acetylated, and the products were chromatographed on silica gel plates and were analyzed by the GLC-MS method. Among the products obtained a compound the mass spectrum of which corresponded to formula (IX) was identified. In actual fact, in the spectrum of (IX) there were peaks at m/z 398 ($M^+ - CH_3COOH$), 383 ($M^+ - CH_3COOH - CH_3$), 355 ($M^+ - CH_3COOH - CH_3CO$), 338 ($M^+ - 2CH_3COOH$), 323 ($M^+ - 2CH_3COOH - CH_3$) and 295 ($M^+ - 2CH_3COOH - CH_3CO$).

Such a considerable decrease in the molecular mass after periodate oxidation indicates the formation of polyols having an α-diol fragment on the reduction of the lactone and keto functions. This unambiguously confirms the 22-position of the keto group in (VII).

Thus, the structure of the native aglycon of pseudostichoposide A (I) was determined as (VII). We propose to call it urupogenin from the place of collection of the animals.

The acid hydrolysis of pseudostichoposide A with 2 N HCl gave xylose, quinovose, and 3-O-methylglucose in a ratio of 2:1:1, these being identified in the form of aldononitrile peracetates. The solvolytic degradation of (I) with pyridine–dioxane (1:1) led to derivative (II). When (II) was subjected to Hakomori methylation followed by methanolysis and acetylation, we obtained the methyl α- and β-glycosides of 2-O-acetyl-3,4-di-O-methylxylose, 4-O-acetyl-2,3-di-O-methylquinovose, 3-O-acetyl-2,4-di-O-methylxylose, and 2,3,4,6-tetra-O-methylglucose, which indicated the unbranched nature of the carbohydrate chain and also the terminal position of the 3-O-methylglucose residue.

According to ^{13}C NMR results and monosaccharide analysis, progenin (III) obtained on mild acid hydrolysis contained a xylose residue, while progenin (IV) contained xylose and quinovose residues. Thus, the first monosaccharide residue in the carbohydrate chain was xylose, the second quinovose, and the fourth 3-O-methylglucose. The signals of the anomeric carbon atoms at 105.1, 105.1, 105.1, and 104.8 ppm showed the β-configurations of the glycosidic bonds [11]. The position of the sulfate group at C-4 of the first xylose residue was determined by comparing the ^{13}C NMR spectra of pseudostichoposide A and its desulfated derivative (II).

The C-5 signal of this residue shifted on desulfation from 64.0 ppm to 66.6 ppm, which is characteristic for the β-effect of a sulfate group [11]. The C-3 and C-4 signals under-

went corresponding shifts (+1.8 and −4.6 ppm, respectively). The counter-ion in the sulfate group was determined as sodium with the aid of atomic absorption spectroscopy.

Thus, the complete structure of pseudostichoposide A has been established as (I). Triterpene glycosides from representatives of the family Gephirothuriidae have not been studied previously.

Recently, French workers isolated from the tropical holothurian Neothyonidium magnum (Phyllophoridae, Dendrochirota) a glycoside differing substantially from pseudostichoposide A in the structure of the aglycon but having an identical carbohydrate chain [12]. The coincidence of the structures of the carbohydrate chains from representatives of taxons remote from one another we regard as the result of the action of the law of homologous series in hereditary variability established by Vavilov, i.e., as arising in parallel and independently on a similar genetic basis [13].

EXPERIMENTAL

Melting points were determined on a Boetius stage. Specific rotations were measured on a Perkin-Elmer 141 polarimeter in pyridine solutions at room temperature. Atomic absorption spectral analysis for metals was carried out on a AA-780 instrument. UV absorption was determined on a Specord UV-VIS instrument.

^{13}C NMR spectra were obtained on Bruker HX-90E and WM-250 spectrometers. PMR spectra were recorded at 250 MHz on a Bruker WM-250 instrument. The signals in the NMR spectra are given on the δ-scale.

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

The chromato-mass spectrometric analysis of the products of the degradation of the aglycon was carried out on a LKB-2091 instrument coupled with a Packard 438A chromatograph with an injector of the "falling needle" type at a temperature of the injector of 260°C, of the ion source of 270°C, and of the molecular separator of 265°C, with a 25-m capillary quartz column containing the phase SE-54 at a column temperature of 200-260°C (1°C/min) using helium as the carrier gas (1 ml/min) and an ionizing energy of 20 eV.

The animals were collected in the oceanic littoral of the island of Urup (Kurile Islands) from a depth of 100-160 m by beam trawl in July, 1986, during the second voyage of the Scientific Research Vessel "Akademik Oparin;" the holothurians were determined by A. V. Smirnov.

The isolation of pseudostichoposide A (I) was carried out by a procedure described previously [1]. Glycoside (I) was obtained with mp 200-202°C, $[\alpha]_D^{20}$ −23° (c 0.1; pyridine).

Desulfation of Pseudostichoposide A. Glycoside (I) (39 mg) was boiled in pyridine–dioxane (1:1) for 1 h and the product was chromatographed on silica gel in the chloroform–methanol–water (75:25:1) system. This gave 32 mg of the desulfated derivative (II) with mp 249-252°C, $[\alpha]_D^{20}$ −33° (c 0.1; pyridine).

Methylation of the Desulfated Derivative (II). A solution of 15 mg of (II) in 2 ml of dry dimethyl sulfoxide (DMSO) was added to a solution of methylsulfinyl anion (prepared from 100 mg of NaH and 2 ml of DMSO), and the mixture was stirred at 50°C in an atmosphere of argon for 1 h. The reaction mixture was treated with 1 ml of CH_3I and was then left at room temperature for 2 h, after which it was diluted with water (10 ml) and was 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 residue obtained was boiled with 1 ml of HCl-saturated anhydrous methanol for 2 h. The solution was evaporated, the residue was covered with a mixture of pyridine and acetic anhydride, this mixture was heated at 100°C for 1 h and was evaporated, and the residue was analyzed by GLC-MS in order to identify the methyl glycosides produced.

Partial Acid Hydrolysis of Pseudostichoposide A (I). A solution of 300 mg of pseudostichoposide A (I) in a mixture of 20 ml of butanol and 20 ml of 2 N sulfuric acid 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) system. This gave 10 mg of crude aglycon, 20 mg of progenin (III) with mp 269-272°C, $[\alpha]_D^{20}$ −4° (c 0.1; pyridine), and 31 mg of progenin (IV) with mp 260-263°C, $[\alpha]_D^{20}$ −6° (c 0.1; pyridine). The aglycon was further purified by chromatography on silica gel in the benzene–ethyl acetate (85:15) system, which gave 6 mg of (VII) mp 220-222°C, $[\alpha]_D^{20}$ +34° (c 0.1; pyridine); mass spectrum: M^+ 470 m/z.

Determination of the Monosaccharide Composition of Glycoside (I) and of Progenins (III) and (IV). The glycoside or progenin (4 mg) 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 filtered off 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, after the addition of 5 mg of hydroxylamine hydrochloride, the mixture was heated at 100°C for 1 h. Then 1 ml of acetic anhydride was added and the resulting mixture was heated at 100°C for another 1 h. It was then evaporated and the residue was analyzed by GLC. For (I), xylose, quinovose, and 3-O-methylglucose were identified in a ratio of (2:1:1); for (III), xylose; and for (IV), xylose and quinovose (1:1).

Jones Oxidation of Urupogenin (VII). A solution of 3 mg of (VII) in 5 ml of acetone was treated with 0.2 ml of the Jones reagent, and the mixture was stirred for 10 min. Then 1 ml of isopropanol was added and it was stirred for another 15 min, after which it was diluted with 50 ml of water and was extracted with ethyl acetate (2 × 5 ml). The ethyl acetate layers were combined and washed with water (2 × 2 ml) and were then evaporated. The dried residue was chromatographed on silica gel in the benzene–ethyl acetate (6:1) system. This gave 2 mg of derivative (VIII), amorphous $[\alpha]_D^{20}$ +20° (c 0.1; pyridine); mass spectrum: M^+ 468 m/z.

Alkaline Treatment of Pseudostichoposide A (I). A solution of 4 mg of (I) in 1 ml of 0.1 N KOH solution was heated in the boiling water bath for 1 h. After the solution had been cooled, no absorption was detected in the UV spectrum.

Degradation of the Aglycon (VII). A solution of 3 mg of (VII) in 5 ml of dry diethyl ether was treated with 100 mg of lithium tetrahydroaluminate, and the reaction mixture was stirred for 10 h. The excess of tetrahydroaluminate was carefully decomposed with 5 ml of water, and then 1 ml of concentrated hydrochloric acid was added to the reaction mixture. The ethereal layer was separated off and the aqueous layer was twice extracted with ether. The combined ethereal layers were washed with water (2 × 5 ml) and evaporated. The dry residue was dissolved in 5 ml of butanol, and to this solution were added 5 ml of water and 50 mg of sodium periodate. The reaction mixture was stirred for a week, and then the butanol layer was separated off, washed with water (2 × 5 ml), and evaporated to dryness, and the residue was treated with 2 ml of pyridine–acetic anhydride (1:1) and the resulting mixture was heated at 100°C for 1 h. After the solution so obtained had been evaporated to dryness, the residue was separated by preparative TLC on silica gel in the hexane–ethyl acetate (4:1) system and the fraction obtained was analyzed by the GLC-MS method. Substance (IX) was identified: mass spectrum, m/z: 398 ($M^+ - CH_3COOH$), 383 ($M^+ - CH_3COOH - CH_3$), 355 ($M^+ - CH_3COOH - CH_3CO$), 338 ($M^+ - 2CH_3COOH$), 323 ($M^+ - 2CH_3COOH - CH_3$), 295 ($M^+ - 2CH_3COOH - CH_3CO$).

SUMMARY

It has been shown that pseudostichoposide A from Pseudostichopus trachus Sluiter is 3β-{O-(3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-O-β-D-xylopyranosyl-(1 → 4)-O-β-D-quinovopyranosyl-(1 → 2)-[4-O-(sodium sulfato)-β-D-xylopyranosyloxy]}-holost-7-en-22-one.

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SYNTHESIS OF THE N-TERMINAL TRIPEPTIDE SEQUENCE OF OXYTOCIN WITH VARIOUS PROTECTIVE GROUPS FOR THE CYSTEINE RESIDUE

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The influence of the nature of the protective groups at the sulfur and nitrogen atoms in the cysteine molecule on the reactivity of this amino acid in the peptide condensation reaction has been investigated. The synthesis of the N-terminal tripeptide sequence of oxytocin was selected as a model reaction. For identifying the compounds synthesized and checking their purity, in addition to traditional physicochemical methods (TLC, melting points, angles of optical rotation), wide use has been made of the ^{13}C NMR method.

The successful synthesis of oxytocin depends to a considerable degree on the appropriate choice of protective group for the thiol function of cysteine. In spite of the fact that at the present time more than 70 such groups are known, the optimum protection of the mercapto group of cysteine has not been found [1]. This is due to the fact that demands are placed on these protections, on the one hand, for the stable blocking of the mercapto function under the conditions of synthesis and of eliminating the temporary protective grouping (BOC, Z, Trit, OR, etc.) and, on the other hand, for ready elimination under mild conditions excluding the racemization, degradation, or oligomerization of the nonapeptide.

The presence of electron-active groups in the cysteine molecule (—SR', —NR") must have a substantial influence on the properties of the carboxy function of the molecule. It is difficult to predict the combination of the effects of the introduced protections of the thiol function (R') and of the amino function (R") on these properties. It is all the more difficult to predict the reactivities of various cysteine derivatives. And while, as before, great attention is being devoted to the search for new protective groups for the thiol function of cysteine in the literature, there are practically no reports on the comparative characteristics and influence of these groups on the completeness of the creation of the peptide bond [2].

In view of this, it appeared to us to be of interest to elucidate the influence of various readily available protective groups of the thiol function of cysteine on the reactivity of cysteine derivatives, using as an example the synthesis of the N-terminal tripeptide se-

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