The filtrate was boiled for 1 h. The cooled solution was neutralized with type ARA-8p anion-exchange resin. The residue after the elimination of the resin and the evaporation of the water was chromatographed on a column with elution by system 7. This led to the isolation of 10 mg of a syrupy mass which consisted of a tri-O-methyl derivative of D-apiose. On GLC [4], this compound had two peaks with relative retention times (T_{rel}) of 0.42 and 0.53. The chemical shifts of the carbon atoms of the D-apiose residue in the ^{13}C NMR spectrum of glycoside (I) (Table 1) determined the methylated monosaccharide under consideration as 2,3,5-tri-O-methyl-D-apio-D-furanose.

On continuing the elution of the column with the same system, we obtained 6 mg of a methylated D-glucose. To 2 mg of the latter in 0.2 ml of methanol was added 8 mg of sodium periodate in 0.2 ml of water, and the mixture was left at room temperature for 30 min. TLC in system 7 showed that the partially methylated D-glucose had been oxidized. By GLC [4], the methylated monosaccharide under consideration was identified as 3,4,6-tri-O-methyl-D-glucopyranose (T_{rel} 1.28). After the silylation of the methyl glycoside of this monosaccharide, two peaks appeared on GLC with relative retention times (T_{rel}) of 2.06 and 2.24.

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STRUCTURES OF FOUR NEW TRITERPENE GLYCOSIDES FROM THE HOLOTHURIAN Cucumaria japonica

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Four new triterpene glycosides of the holostane series have been isolated from an alcoholic extract of the economically important Pacific Ocean holothurian Cucumaria japonica: cucumariosides A_1-2 (I), A_2-3 (II), A_2-4 (III), and A_4-2 (IV). The structures of these substances have been established by the methods of carbohydrate chemistry and ^{13}C NMR spectroscopy.

We have previously [1] reported the structure of a new triterpene glycoside from the holothurian Cucumaria japonica – cucumarioside A_2-2 (I). Continuing our investigations, with the aid of reversed-phase chromatography we have isolated another three new glycosides from this holothurian: cucumariosides A_2-3 (II), A_2-4 (III), and A_4-2 (IV). In the present paper we describe the determination of the structures of these substances (I–IV).

Analysis of the ^{13}C NMR spectra (Table 1) showed that cucumarioside A_2-2 had as the native aglycon 3β-hydroxyholosta-7,25-dien-16-one [2, 3], which had been obtained previously from the total glycosides of this holothurian.

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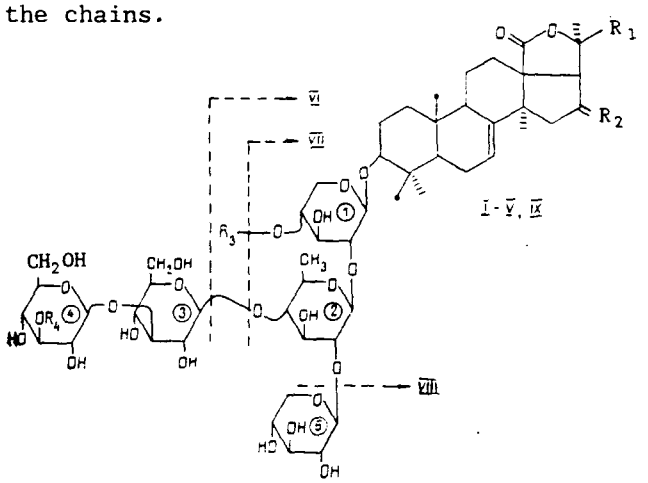
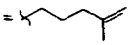
TABLE 1. Aglycon Sections of the ^{13}C NMR Spectra of Glycosides (I-IV) (δ_{TMS} = 0, pyridine)

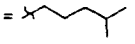
Atom	I	II	III	IV	Atom	I	II	III	IV
C-1	36,0	36,0	36,4	35,9	C-16	213,2	212,5	24,6	212,6
C-2	27,1	27,1	27,1	27,0	C-17	63,7	63,6	53,4	63,6
C-3	89,1	89,0	89,3	89,0	C-18	178,8	178,3	179,6	178,3
C-4	39,7	39,3	39,7	39,6	C-19	24,1	24,1	24,1	24,1
C-5	48,5	48,4	48,4	48,4	C-20	83,5	83,3	84,0	83,2
C-6	23,3	23,5	23,5	23,4	C-21	26,3	26,3	26,3	26,3
C-7	121,9	121,8	119,8	121,7	C-22	38,5	39,0	39,0	38,4
C-8	144,2	143,9	145,6	143,9	C-23	22,6	22,4	22,4	22,5
C-9	47,2	47,1	47,5	47,1	C-24	28,1	39,6	28,2	38,0
C-10	35,9	35,8	35,8	35,8	C-25	145,7	28,0	145,1	145,5
C-11	22,6	22,7	23,1	22,5	C-26	110,4	22,7	110,7	110,4
C-12	29,8	29,8	30,6	29,7	C-27	22,3	22,7	22,3	22,3
C-13	56,8	56,7	58,8	55,6	C-30	17,5	17,6	17,6	17,5
C-14	45,8	45,7	51,5	45,7	C-31	28,9	28,8	29,0	28,8
C-15	52,1	52,0	54,5	52,0	C-32	32,0	31,9	31,0	31,9

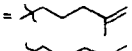
The acid hydrolysis of (I) gave a mixture of D-xylose, D-quinovose, D-glucose, and 3-O-methyl-D-glucose in a ratio of 2:1:1:1, these sugars being identified by GLC-MS in the form of aldononitrile peracetates. The assignment of these monosaccharides to the D-series was made after a determination of the specific rotation of the monosaccharide mixture obtained. The presence of five carbohydrate residues linked with one another and with the aglycon by β-glycosidic bonds was confirmed by the ^{13}C NMR spectrum (Table 2), in which there are five signals of the C-1 atoms of monosaccharides in the 102.3-105.9 ppm region [4].

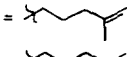
The solvolytic desulfation of (I) on heating in a mixture of pyridine and dioxane led to the desulfated derivative (V). The Hakomori methylation of (V), followed by methanolysis and acetylation of the methanolysis products gave the methyl α- and β-glycosides of 2-O-acetyl-3,4-di-O-methylxylopyranose, of 2,4-di-O-acetyl-3-O-methylquinovopyranose, of 3-O-acetyl-2,4,6-tri-O-methylglucopyranose, of 2,3,4,6-tetra-O-methylglucopyranose, and of 2,3,4,-tri-O-methylxylopyranose, which were identified by the GLC–MS method. It followed from the results of methylation that the carbohydrate moiety of glycoside (I) had a branched structure. The center of branching was the quinovose residue, while the xylose and 3-O-methylglycose residue were located at the ends of the chains.

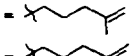


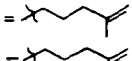
I. R_1 =  ; R_2 = O; R_3 = SO_3Na; R_4 = CH_3

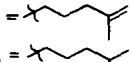
II. R_1 =  ; R_2 = O; R_3 = SO_3Na; R_4 = CH_3

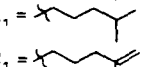
III. R_1 =  ; R_2 = ; R_3 = SO_3Na; R_4 = CH_3

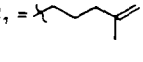
IV. R_1 =  ; R_2 = O; R_3 = SO_3Na; R_4 = H

V. R_1 =  ; R_2 = O; R_3 = H; R_4 = CH_3

VI. R_1 =  ; R_2 = O; R_3 = SO_3Na;

VII. R_1 =  ; R_2 = O; R_3 = H;

VIII. R_1 =  ; R_2 = O; R_3 = SO_3Na; R_4 = CH_2

IX. R_1 =  ; R_2 = O; R_3 = H; R_4 = H

The enzymatic cleavage of (I) with the addition of cellulase led to progenin (VI), the desulfation of which gave the derivatives (VII). The acid hydrolysis of (VI) produced a mixture of xylose and quinovose in a ratio of 2:1. The Hakomori methylation of (VII) followed by methanolysis and acetylation of the resulting products gave a mixture of the methyl α- and β-glycosides of 2-O-acetyl-3,4-di-O-methyl-xylopyranose, of 2-O-acetyl-3,4-tri-O-methylquinovopyranose, and of 2,3,4-tri-O-methylxylopyranose. It followed from this progenin (VI) had a linear carbohydrate chain with a xylose residue at the end. Furthermore, a comparision of the results of the methylation of (V) and (VII) showed that the biosidic block 3-O-methylglucose-(1 → 3)-glucose was attached to C-4 of the quinovose residue in derivative (V).

It remained to determine the sequence of arrangement in the carbohydrate chain of the quinovose residue and the second xylose residue and also where the sulfate group was located.

The position of the sulfate group at C-4 in the xylose residue was established by comparing the ^{13}C NMR spectra of (I) and (VI) with the spectra of their desulfated derivatives (V) and (VII) [4, 5]. Furthermore, on the periodate oxidation of glycoside (I) followed by acid hydrolysis, one of the xylose residues was split out, while on the periodate oxidation of the desulfated derivative (V) both xylose residues were plit out, which also indicated the presence of a sulfated group in one of the xylose residues.

The catalytic hydrogenation of (I) over Adams catalyst led to derivative (II). The subsequent Smith degradation of (II) gave the progenin (VIII). According to ^{13}C NMR results, it had a known carbohydrate chain – the same as in holothurin A [6]. In actual fact, acid hydrolysis of (VIII) gave a mixture of xylose, quinovose, glucose, and 3-methylglucose in a ratio of 1:1:1:1, and desulfation followed by Hakomori degradation, methanolysis, and acetylation of the products obtained led to the formation of a mixture of the methyl α- and β-glycosides of 2-O-acetyl-3,4-di-O-methylxylopyranose, of 4-O-acetyl-2,3-di-O-methyl-quinovopyranose, of 3-O-acetyl-2,4,6-tri-O-methylglucopyranose, and of 2,3,4,6-tetra-O-methylglucopyranose. It followed from the results of the methylation of (V) and the desulfation of (VIII) that on Smith degradation the terminal xylose residue, attached by a (1 → 2)-bond to the quinovose residue, was split out.

The combination of all these facts permitted the conclusion that a xylose residue sulfated in the fourth position was present in the position of attachment of the carbohydrate chain to the aglycon, and to this was attached by a (1 → 2)-bond a quinovose residue substituted in the second and fourth positions. Thus cucumarioside A_2-2 can unambiguously be assigned formula (I).

A comparison of the NMR spectra of (I) and of the minor cucumarioside A_2-3 (II) showed their considerable similarity. The differences consisted mainly in the positions of the signals of the carbon atoms of the side chain of the aglycon. In (II), in contrast to (I), the signal of a 25 (26)-double bond was absent. Furthermore, the physical constants and the spectra of cucumarioside A_2-3 coincided completely with those for the product of the catalytic hydrogenation of cucumarioside A_2-2, which showed their identity.

A comparison of the ^{13}C NMR spectra of the minor cuccumarioside A_2-4 (III) with the spectra of (I) showed a coincidence of the signals of the carbon atoms in the carbohydrate moiety (Table 2), which indicated the complete identity of their carbohydrate components [6]. Furthermore, to confirm this conclusion concerning the structure of the carbohydrate chain in glycoside (III), double Smith degradation was performed at the analytical level under conditions analogous to those for the degradation of A_2-2. As the result of the first oxidation (20 mg), a progenin (12 mg) was obtained the hydrolysis of which (4 mg) gave a mixture of xylose, quinovose, glucose, and 3-O-methylglucose in a ratio of 1:1:1:1. As a result of the second oxidation, the aqueous eluate from chromatography on Polikhrom was found to contain a bioside derivative after the hydrolysis of which we identified glucose and 3-O-methylglucose. Subsequent elution of the column with 50% ethanol led to a progenin containing in the carbohydrate moiety only a sulfated xylose residue, which was confirmed by desulfation and acid hydrolysis.

The signals of the carbon atoms of aglycons (I) and (III) in the ^{13}C NMR spectra were close to or coincided with those for C-1–C-15 and C-18–C-32, while the C-16 signal was shifted upfield from 213.2 to 24.6 ppm, which showed the absence of a keto group at C-16 in (III). On the basis of these facts it was possible to conclude that the aglycon in (II) was holosta-7,25-dien-3β-ol, isolated previously from the triterpene glycosides of the holothurian Cucumaria japonica, the structure of which was established with the aid of mass and ^1H NMR spectra [3]. The structure of cucumarioside A_2-4 is described by formula (III).

TABLE 2. Carbohydrate Parts of the ^{13}C NMR Spectra of Glycosides (I-IV) and Their Derivatives (δ_{TMS} = 0, pyridine)

Атом	I	II	III	IV	V	VI	VII	VIII	IX
C_1^1	104,9[a]	104,6	104,8[a]	104,8	105,1[a]	104,9	105,1	105,6	105,1
C_2^1	81,8	82,0	82,	81,7	83,0	81,9	82,8	84,0	82,8
C_3^1	76,0	75,6	75,7	75,9	77,5	75,7	77,6	77,9	77,8
C_4^1	76,3	75 8	76,1	76,4	70,6	76,1	70,4	71 0	70,4
C_5^1	64,6	64,3	64,4	64,4	66,4	64,4	66,2	66,5	66,4
C_1^2	102,4	102,5	102,4	102,3	103,1	102 7	103,3	105 6	103,0
C_2^2	82,4	82,6	82,4	82,3	83,0	84,2	84,7	76,4[a]	83,2
C_3^2	76,0	75,6	75,7	75,6	76,0	77,5	77,3	76,1[a]	75,8
C_4^2	87,0	86,7	86,8	86,7	86,6	76,5	76,5	87,2	86,7
C_5^2	71,2	71,0	71,1	71,0	71,3	72,7	72,8	71,8	71,1
C_6^2	18,1	18,2	18,1	18,0	18,2	18,3	18,3	18,1	18,1
C_1^3	105 1[a]	104,6	104,7[a]	104,6	104,7[a]			104,7	104,6
C_2^3	73,8	73,5	73,6	73,6	73,8			73,8	73,7
C_3^3	88,0	87,8	88,0[b]	88,0	88,4			88,4	88,4
C_4^3	69,8	69,6	69,8	69,6	70,1			70,1	69,8
C_5^3	77,9	77,7	77,7	77,7	77,9			77,9	77,7
C_6^3	62,1[b]	61,9	62,1	61,9	62,6			62,6	62,2
C_1^4	105,6	105 5	105,6[c]	105,4	105,6			105,6	105,6
C_2^4	75,1	74,8	75,0	75,4	75,0			75,0	75,4
C_3^4	88,0	87,8	88,2[b]	78,5	87,9			87,9	78,5
C_4^4	70,7	70,4	70,7[d]	71,5	71,0			71,0	71,7
C_5^4	78,4	78,2	78,3	78,1	78,2			78,3	78,1
C_6^4	62,3[b]	62,1	62,3	62,3	62,6			62,6	62,5
O—CH_3	60,	60,7	60,8		60,5			60,5	
C_1^5	105,6	105,5	105,4[c]	105,9	106,0	105,9	106,3		105,9
C_2^5	75,1	74,8	75,0	75,6	75,5	75,2	75,6		75,1
C_3^5	76,7	76,4	76,5	75,9	77,1	77,1	77,6		77,0
C_4^5	70,7	70,6	70,5[d]	70,4	70,6	70,5	70,6		70,6
C_5^5	66,6	66,5	66,5	66,4	66,9	66,8	67,2		66,9

*a, b, c, d – Ambiguous assignment of the signals.

One of the main components of the triterpeneglycosides of the holothurian Cucumaria japonica [cucumarioside A_4-2 (IV)] has as its aglycon, 3β-hydroxyholosta-7,25-dien-16-one, just like glycoside (I) (analysis of ^1H and ^{13}C NMR spectra).

A comparison of the ^{13}C NMR spectra of (I) and (IV), and also their desulfated derivatives (V) and (IX) showed a considerable similarity of these compounds. The difference consisted in the fact that in the spectra of (IV) and (IX) the signals of the carbon atoms of a terminal unmethylated glucose appeared in place of the signals of the terminal 3-O-methylglucose residue in the spectra of (I) and (V). Furthermore, in agreement with this observation, the acid hydrolysis of (IV) gave a mixture of xylose, quinovose, and glucose in a ratio of 2:1:2. When glycoside (IV) was treated with cellulase, a biosidic fragment (glucose—glucose) was split out and the progenin (VI) described previously, was formed. On the periodate oxidation of (IV), one of the xylose and one of the glucose residues decomposed, and on the periodate oxidation of the desulfated derivative of this glycoside (IX), both the xylose residues and the glucose residue decomposed. The Hakomori methylation of derivative (IX), followed by treatment with CH_3OH/HCl and Ac_2O/C_5H_5N, gave the same set of monosaccharide derivatives as was obtained from desulfated (I).

All these facts showed that (IV) differed from (I) only by the fact that in (IV) the biosidic block glucose-(1 → 3)-glucose is attached to C-4 of the quinovose residue in place of the block 3-O-methylglucose-(1 → 3)-glucose (I). Thus, the structure of cucumarioside A_4-2 is described by formula (IV).

EXPERIMENTAL

The spectral analyses and GLC-MS analyses were performed under the conditions described in [5]. Atomic-absorption spectral analysis for metals was performed on an AA-780 spectrometer.

The animals were collected in Posyet Bay in September, 1981, by means of an industrial bottom trawl a depth of 30-120 m.

The isolation of the triterpene glycosides has been described in [7].

Isolation of the Individual Glycosides (I), (II), (III), and (IV). Glycoside (I) was isolated by chromatography on columns of silica gel in the chloroform–ethanol–water (100:100:17) system (system 1) and of Polikhrom-1 (water → 13% ethanol). Glycosides (II), (III), and (IV) were isolated by column chromatography on silica gel in system 1 and by the HPLC method on a Du Pont 8800 chromatograph with a Zorbax C-8 column (4.6 × 250 mm). For (II) and (III) the mobile phase was 32% ethanol (1.3 ml/min), and for (IV) 30% ethanol (1 ml/min). Cucumarioside A_2-2, mp 245–247°, $[\alpha]_D^{20}$ –68° (*c* 0.2; pyridine), cucumarioside A_2-3, mp 211–212°, $[\alpha]_D^{20}$ – 62.5° (*c* 0.16; pyridine), cucumarioside A_2-4, mp 203–205°, $[\alpha]_D^{20}$ – 53° (*c* 0.1; pyridine), cucumarioside A_4-2, mp 205–207°, $[\alpha]_D^{20}$ – 91° (*c* 0.1; pyridine).

The acid hydrolysis of the glycosides, the progenins, and the desulfated derivatives and the analysis of the monosaccharide mixtures produced, in the form of aldononitrile peracetates, were carried out as described in [5].

Desulfation. A solution of 25 mg of a glycoside or progenin in 10 ml of pyridine–dioxane (1:1) was boiled for 1 h. After this, the reaction mixture was evaporated to dryness, and the residue was chromatographed on silica gel in the chloroform–ethanol-water (100:50:4) system 2). This gave derivative V, mp 283–285°, $[\alpha]_D^{20}$ – 76.5° (*c* 0.17; pyridine), derivative VII, mp 251–253°, $[\alpha]_D^{20}$ – 112° (*c* 0.1; pyridine), dertivative IX, mp 210–212°, $[\alpha]_D^{20}$ – 80.9° (*c* 0.1; pyridine).

Periodate Oxidation. A solution of 5 mg of a glycoside (or of a desulfated derivative) in 5 ml of water (or 4 ml of water and 1 ml of butanol in the case of the desulfated derivatives) was treated with 30 mg of sodium periodate, and the mixture was stirred vigorously at 20°C for three days. The excess of periodate was decomposed by the addition of 50 μl of ethylene glycol (20°C, 3 h). The reaction mixture was extracted with butanol (3 × 2 ml). The butanolic extracts were combined, washed with water, 2 × 2 ml), and then evaporated in vacuum. The residue was dissolved in 1.5 ml of 2 N HCl, and hydrolysis was carried out at 100°C for 2 h, after which the monosaccharides obtained were analyzed as described above [5].

Enzymatic Hydrolysis of (I) and (IV). A solution of 100 mg of the glycosides in 50 ml of water was treated with 10 mg of cellulase. The mixture was thermostated at 37°C for four days. After this, the solution was evaporated in vacuum, and the residue was chromatographed on a column of silica gel in system 1. This gave progenin (VI), mp 215-217°C, $[\alpha]_D^{20}$–104.3° (c 0.17; pyridine).

Hydrogenation of (I). A solution of 110 mg of (I) in 25 ml of water was added to a suspension of 10 mg of hydrogenated Adams catalyst in 25 ml of water, and hydrogenation was carried out at 25°C with vigorous stirring for 24 h. The solution was filtered to eliminate the catalyst, the filtrate was evaporated to dryness, and the residue was chromatographed on silica gel in system 1. This gave 105 mg of (II) with mp 212-213°C, $[\alpha]_D^{20}$–63° (c 0.16; pyridine).

Smith Degradation of (II). A solution of 100 mg of (II) in 50 ml of water was treated with 100 mg of sodium periodate, and the mixture was left at 20°C for 4 days. Then it was deposited on a column of Polikhrom in water, and the salts were washed out with water. The oxidized glycoside was eluted from the column with 50% ethanol and the eluate was evaporated to dryness. The residue was dissolved in 20 ml of absolute ethanol, and to this solution was added 15 mg of sodium tetrahydroborate in the form of a suspension in absolute ethanol

(5 ml). The reaction mixture was stirred vigorously for 8 min, acidified with acid to pH 5.0, and concentrated in vacuum, and then methanol was added to the residue in portions and the boric acid was evaporated off in vacuum in the form of methyl borates. The residue was dissolved in 20 ml of 0.5 N hydrochloric acid and, after 20 min, it was passed through a column of Polikhrom as described above. The progenin (VIII) that was eluted with 50% ethanol was chromatographed on a column of silica gel in system 1. This gave 23 mg of (VIII), mp 238-240°C, $[\alpha]_D^{20}$ −23.8° (c 0.12; pyridine).

Methylation. A solution of 20 mg of a desulfated glycoside or progenin in 1 ml of dry dimethyl sulfoxide (DMSO) was added to a solution of the methylsulfinyl anion (prepared from 300 mg of sodium hydride and 7 ml of DMSO), and the mixture was stirred at 60°C in an atmosphere of dry argon for 2 h. Then, at 0°C, 2 ml of methyl iodide to the reaction mixture and it was left at room temperature for 2 h and was then diluted with water (10 ml) and extracted with CH_3I (2 × 2 ml). The extract was washed with 2 ml of a saturated solution of sodium thiosulfate and with 2 ml of water and was evaporated in vacuum. The residue so obtained was boiled in 2 ml of anhydrous methanol saturated with hydrogen chloride for 2 h, the solvent was driven off in vacuum, and the residue was dissolved in 2 ml of pyridine–acetic anhydride (1:1) to give a reaction mixture which was heated at 100°C for 1 h. The mixture of derivatives of methyl α- and β-glycosides obtained was analyzed by GLC and by GLC-MS.

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CONFORMATIONAL FEATURES OF PEPTIDE FRAGMENTS OF THE C-END OF HISTONE H1

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The conformational possibilities of four synthesized oligopeptides with the amino acid sequences 165–172, 173–184, 152–172, and 152–184 of the C-end of histone H1 of calf thymus above been studied in solution under various conditions by the method of circular dichroism.

Histone H1 is ascribed a particularly important role in the structure of chromatin [1, 2]. This fraction, bound with the linker section of DNA, is responsible for maintaining the higher levels of its structural organization and it also, apparently, participates in the processes of compactization–decompactization of chromatin during its functioning. The elucidation of the structural possibilities of the polypeptide chain of this histone is extremely important for understanding the mechanism of such processes.

Histone H1 has a three-domain organization [3, 4]. The N-terminal domain from the 1st to the 35th amino acid residue is the most variable and is highly charged, and in it are con-

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