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GLYCOSIDES OF MARINE INVERTEGRATES.

XI. TWO NEW TRITERPENE GLYCOSIDES FROM HOLOTHURIANS OF THE FAMILY *Stichopadidae*

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By repeated column chromatography on silica gel new glycosides have been isolated from the holothurians *Astichopus multifidus* and *Stichopus chloronotus* — astichoposide C and stichoposide C (I and II, respectively). Their structures have been studied with the aid of chemical and physicochemical methods. The complete structures of the glycosides have been established as 23(S)-acetoxy-3β-{4'-O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-β-D-glucopyranosyl]-2'-O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-O-β-D-xylopyranosyl-(1→4)-β-D-quinovopyranosyl]-β-D-xylopyranosyloxy}holosta-7,25-diene and -holost-7-ene.

Continuing a study of the triterpene glycosides from *Stichopodidae* [1], we have determined the complete structure of astichoposide C from the holothurian *Astichopus multifidus* and of stichoposide C from the holothurian *Stichopus chloronotus*.

Acid hydrolysis of astichopososide C (I), isolated from an ethanolic extract of *A. multifidus*, gave a mixture of sapogenins and the monosaccharides D-glucose, D-xylose, D-quinovose, and 3-O-methyl-D-glucose in a ratio of 1:2:1:2, these being identified by GLC in the form of the acetates of the corresponding aldononitriles [2].

The repeated chromatography of the sapogenins on columns of silica gel gave the native sapogenin (II).

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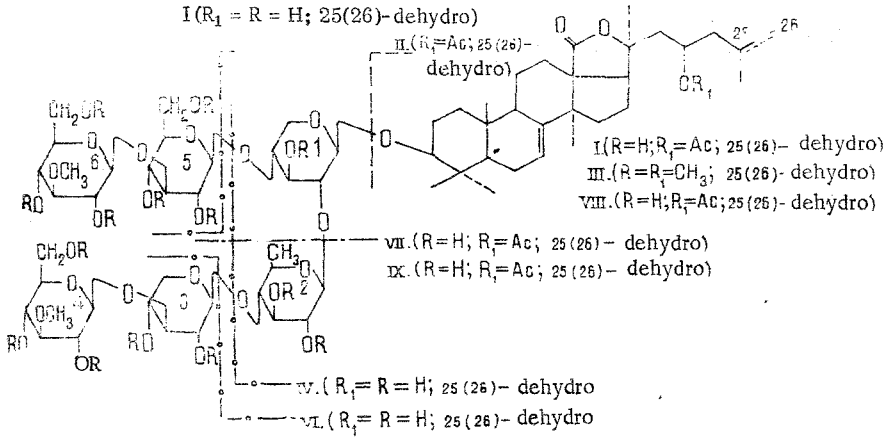
In order to establish the structure of the oligosaccharide moiety of (I), we used enzymatic cleavage, methylation, and periodate oxidation.



Periodate oxidation followed by acid hydrolysis of the glycoside led to the isolation of all the monosaccharides apart from the quinovose. The cleavage of only the quinovose showed that the hydroxy groups in positions 3 of the glucose and xylose residue were substituted or that the monosaccharides were present in positions of the branching of the carbohydrate chain.

The methylation of (I) under the conditions of the Hakomori reaction [3] led to the per-O-methyl derivative (III), the IR spectrum of which showed the absence of free hydroxy groups. The methanolysis of (III) followed by acetylation gave a mixture of methyl 2,3,4,6-tetra-O-methyl-α- and -β-glucopyranosides, methyl 3-O-acetyl-2,4-di-O-methyl-α-xylopyranoside, methyl 4-O-acetyl-2,3-di-O-methyl-α- and -β-quinovopyranosides, methyl 2,4-di-O-acetyl-3-O-methyl-α-xylopyranoside, and methyl 3-O-acetyl-2,4,6-tri-O-methyl-α- and -β-glucopyranosides, which were identified by GLC and by chromato-mass spectrometry. The results obtained show that the oligosaccharide moiety in glycoside (I) is branched at the xylose residue, while the 3-O-methylglucoside residues occupy terminal positions. Correspondingly, the signals from the carbon atoms in ^{13}C spectrum of the glycoside have a doubled intensity (Table 1).

The further hydrolysis of glycoside (I) with cellulase gave the progenins (IV)VI), and the Smith cleavage of (I) [4] gave the progenin (VII).

The least polar progenin (IV) contained one residue each of quinovose and xylose. After methylation followed by methanolysis and acetylation, it gave methyl 2-O-acetyl-3,4-di-O-methyl-α-xylopyranoside and methyl 2,3,4-tri-O-methyl-α- and -β-quinovopyranosides. The ^{13}C NMR spectrum of the carbohydrate moiety of the progenin coincided with that of the carbohydrate moiety of desulfated holothurin B [5]. Signals at 106.0 and 105.5 ppm from the anomeric carbon atoms showed that β configurations of the glycosidic bonds [6]. Thus, xylose is present at the position of attachment of the carbohydrate chain to the aglycone.

Another progenin (V) contained residues of quinovose, 3-O-methylglucose, and xylose in a ratio of 1:1:2. The periodate oxidation of (V) followed by acid hydrolysis gave only xylose and 3-O-methylglucose (1:1). The values of the chemical shifts of the anomeric carbon atoms at 105.3 (C-3) and 105.0 ppm in the ^{13}C PMR spectrum of progenin (V) showed the β configurations of the glycosidic bonds. The assignment of the other signals in the spectrum was carried out with the aid of literature information [7, 8]. The shift of the C-4 signal in the quinovose residue from 76.0 to 85.9 ppm showed the attachment to this atom of a xylose-3-O-methylglucose bioside fragment. The presence of a 1→3 bond between these monosaccharides followed from the stability of the xylose to periodate oxidation and from the results of the methylation of (I).

Monosaccharide analysis of the progenin (VI) showed that it contained residues of xylose, glucose, and 3-O-methylglucose in a ratio of 1:1:1:1. In the periodate oxidation of (VI), only the quinovose residue was destroyed. The ^{13}C NMR spectrum of the carbohydrate moiety of (VI) had C-1 signals at 106.0, 103.0, 105.6, and 105.2 ppm. The signal of the xylose C-4 was shifted in comparison with (IV) from 70.8 to 77.8 ppm through the attachment of a glucose-3-O-methylglucose fragment at this position. The presence of the signal of anomeric carbon atom at 103.0 ppm for C-1 of the glucose residue did not make it possible to choose unambiguously between the α and β configurations for the glycosidic bond between the glucose

TABLE 1. ^{13}C NMR Spectra of the Carbohydrate Moieties of Glycoside (I) and of the Progenins (IV-VII) (C_5D_5N), 60°C, TMS = 0

C	I	IV	V	VI	VII	C	I	IV	V	VI
C_1^1	105,4	106,0	105 3	106,0	106,9	C_1^2	105.4	105,5	105,3	105,25
C_2^1	83,15	83,6	83 95	83,2	75,1	C_2^2	76,4	76,7	76,4	76,65
C_3^1	75 45	77,85	77,9	75,7	76,2	C_3^2	76,45	77,85	75,6	77,8
C_4^1	78 05	70,8	70 85	77,8	78,2	C_4^2	85,8	76,9	85,9	76,9
C_5^1	64 0	66,5	66,5	64,0	64,4	C_5^2	71,7	73,4	71,75	73,4
C_1^5	102,8	—	—	103,0	103,1	C_6^2	18,0	18,4	18,1	18,5
C_2^5	72,9	—	—	73,1	73,2	C_1^3	105.4	—	105,0	—
C_3^5	88,1	—	—	88,3	88,1	C_2^3	73,2	—	73,4	—
C_4^5	69,9	—	—	70,0	70,0	C_3^3	87,7	—	87,7	—
C_5^5	78,05	—	—	78,15[a]	78,2	C_4^3	69,0	—	69,1	—
C_6^5	62,4	—	—	62,4	62,45	C_5^3	66,4	—	66,5	—
C_1^6	105.4	—	—	105,6	105.5	C_1^4	105 4	—	105.3	—
C_2^6	74,9	—	—	75,1	75,1	C_2^4	74,9	—	74,9	—
C_3^6	87,7	—	—	87,8	87,8	C_3^4	87,7	—	87,7	—
C_4^6	70,8	—	—	70,8	70,8	C_4^4	70,8	—	70,85	—
C_5^6	78,05	—	—	78 15	78.2	C_5^4	78,05	—	78,1	—
C_6^6	62.4	—	—	62,4	62,45	C_6^4	62,4	—	62,45	—
OCH_3	60,6	—	—	60,5	60,6	OCH_3	60,4	—	60,7	—

[a]Ambiguous assignment of the signals.

and the xylose residues [6]. Calculation by Klyne's rule [9] showed that the difference in the molecular rotations of the progenin (VI) and the progenin (IV) amounted to −200.1° (calculated for the β configuration −110° and for the α configuration +640°), which agrees well with the β configuration of this glycosidic bond.

The Smith cleavage of the glycoside (I) gave the progenin (VII) having one residue each of xylose, glucose, and 3-O methylglucose. The IR spectrum of (VII) had the absorption bands of γ-lactone and acetate carbonyls at 1760 and 1735 cm^{-1}, which showed the absence of the saponification of these functional groups in the cleavage of the initial glucoside. After (VII) had been subjected to methylation, methanolysis, and subsequent acetylation, methyl 2,3,4,6-tetra-O-methyl-α- and -β-glucopyranosides, methyl 3-O-acetyl-2,4,6-tri-O-methyl-α- and -β-glucopyranosides, and methyl 4-O-acetyl-2,3-di-O-methyl-α-xylopyranoside were identified. A second Smith cleavage of (VII) led to the genin (II). The results obtained, and also the ^{13}C NMR spectrum of (VII) (see Table 1) show that this progenin has a linear carbohydrate chain with a 3-O-methylglucose residue at its end, and the xylose residue is attached to the aglycone. The glucose residue present in the middle of the chain is attached to the terminal sugar residue by a 1→3 bond.

The addition of the oligosaccharide moiety to the hydroxy group at C-3 in the native aglycone followed from a comparison of the ^{13}C NMR spectra of the aglycone (II) and the glycoside (I) (the C-3 signal is shifted downfield by 9.2 ppm in the spectrum of (I) as compared with that of (II) [6]), and, from the fact that the genin (II) formed in the hydrolysis of the glycoside has a single free hydroxy group in position 3.

The facts given above enabled us to determine the complete structure of astichoposide C, which is represented by formula (I).

Similarly from an ethanolic extract of the holothurian *S. choloronotus*, we have obtained a new triterpene glycoside which we have called stichoposide C. A comparison of the

^{13}C spectra of glycoside (I) and of stichoposide C (VIII) showed a considerable similarity. The differences consisted mainly in the positions of the signals from the C-25 and C-26 atoms of the aglycone, which were shifted downfield in the spectrum of (VIII) as compared with that of (I) (the C-25 signal to 23.4 ppm from 141.6 ppm, and the C-26 signal to 23.1 ppm from 140.3 ppm). It might be assumed that (VII) was the 25,26-dihydro derivative of (I). In actual fact, after the catalytic hydrogenation of (I) we obtained a glycoside which was identical with glycoside (VIII) according to a comparison of the ^{13}C spectra and their constants, and also from the absence of a depression in a mixed melting point. On being subjected to Smith degradation, glycoside (VIII) yielded a progenin (IX), identical with the product of the hydrogenation of the progenin (VII) (comparison of ^{13}C NMR spectra and constants, mixed melting point).

From an ethanolic extract of the holothurian *Stichopus variegatus* we obtained a mixture of glycosides (I) and (VIII) which was difficult to separate but which on catalytic hydrogenation was converted into glycoside (VIII).

EXPERIMENTAL

Melting points were determined on a Boëtius block. Optical rotations were measured on a Perkin-Elmer 141 polarimeter in pyridine solutions at room temperature. IR spectra were recorded on a Specord IR-75 spectrophotometer in chloroform solution. ^{13}C NMR spectra were determined on a Bruker HX-90e spectrometer in pyridine solution. The figures in Table 1 are given in the δ system relative to TMS. GLC analysis was performed on a Tsvet-110 chromatograph using 15 × 0.3 cm glass columns containing 3% of QF-1 on Chromaton N-HMDS with argon as the carrier gas (80 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 300 × 0.3 cm column 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 240°C, of the molecular separator 265°C, and of the ion source 255°C; ionizing voltage 70 V.

The animals were collected in the following regions: *A. multifidus* Isla de Pinos, Cuba, May, 1979: *S. chloronotus* and *S. variegatus* — Great Barrier Reef (Australia), January, 1980.

Isolation of Astichoposide C. Freshly-trapped holothurians (crude weight 1 kg) were ground and extracted with 70% ethanol at room temperature. After two days, the extract was poured off and the residual tissue was covered with a new portion of ethanol and after another two days the extracts were combined. Concentration in vacuum of the total ethanolic extract was carried out with the periodic addition of butyl alcohol to the solution. After concentration of the extract to a volume of 100 ml, the suspension formed was left overnight at 5°C. The precipitate of glycosides was separated off by centrifugation and was washed with water and ethyl acetate. This gave about 6 g of crude glycosidic fraction, which was dissolved in 30 ml of water at 100°C, and after the solution had been filtered 4 ml of butanol was added to it with vigorous stirring and the resulting mixture was cooled at 5°C for 12 h. The crystalline precipitate of astichoposide C that has formed was filtered off and was recrystallized from butanol-saturated water to give 1.05 g of crude astichoposide C. The glycoside was freed from traces of other glycosides accompanying it by column chromatography on silica gel using the $CHCl_3$-MeOH-H_2O (75:25:1) system. Astichoposide C: mp 248-250°C $[\alpha]_D^{20}$ −45.7° (c 0.45; pyridine). Stichoposide C was obtained similarly, the yield on the crude weight of holothurian being 0.1%; mp 260°C, $[\alpha]_D^{20}$ −40.8° (c 0.45; pyridine).

Hydrolysis of Astichoposide C. Astichoposide C (2 mg) was heated under reflux with 0.5 ml of 12% HCl at 90-100°C for 2 h. Then the reaction mixture was extracted with chloroform, and the aqueous layer was neutralized with Dowex 1 × 10 (HCO_3^-). After neutralization, the resin was separated off by centrifugation and washed with water. The wash-waters and the aqueous layer were combined and concentrated in vacuum to dryness. The residue was dissolved in 1 ml of dry pyridine, and then 5 mg of $NH_2OH \cdot HCl$ was added and the mixture was heated to 100°C for 1 h, after which 1 ml of acetic anhydride was added to the reaction mixture and it was heated at 100°C for another 1 h. The resulting solution was concentrated in vacuum to dryness. The residue was analyzed by GLC. The peracetates of the aldononitrile derivatives of xylose, glucose, quinovose, and 3-O-methylglucose were identified in a ratio of 2:1:1:2. The quantitative monosaccharide compositions of stichoposide C and of the progenins were determined similarly.

Periodate Oxidation of Astichoposide C and its Progenins. The glycoside (5 mg) was dissolved in 3 ml of water, and then 10 mg of $NaIO_4$ was added to the solution and the mixture

was left at 5°C for 12 h. The excess of periodate was decomposed by the addition of 5 µl of ethylene glycol (20°C, 1 h). The reaction products were extracted with butanol (3 × 0.5 ml), and the butanolic extracts were combined and were washed with 0.5 ml of saturated $Na_2S_2O_3$ solution and with 0.5 ml of water. The residue after vacuum concentration was hydrolyzed and worked up as described above for the analysis of the monosaccharides in the form of the peracetates of the aldononitriles.

Methylation of Astichoposide C and the Progenins. A solution of the glycoside or a progenin (10 mg) in 2 ml of a solution of methylsulfinyl anion (prepared from 350 mg of NaH and 15 ml of DMSO) was stirred at 50°C in an atmosphere of argon for 1 h. Then 1 ml of CH_3I was added to the reaction mixture and it was left at 20°C for 12 h. After this, it was diluted with water and was extracted with CH_3I (3 × 2 ml). The extract was washed with 2 ml of saturated $Na_2S_2O_3$ solution and 2 ml of water and was concentrated in vacuum to dryness. The methylation product was purified by column chromatography of silica gel L (40-100 µ) in the hexane–ethyl acetate (3:1) system.

The methanolysis of the methylated products obtained (3.3 mg) was carried out by boiling them under reflux with, in each case, 1 ml of anhydrous methanol saturated with HCl (10% HCl). The solvent was evaporated off in vacuum, the residue was treated with pyridine–acetic anhydride (1:1), and the reaction mixture was kept at room temperature for 12 h and was then concentrated in vacuum and the mixture was analyzed by GLC-MS to identify the methyl glucosides.

Enzymatic Hydrolysis of Astichoposide C. The astichoposide (170 mg) was dissolved in 50 ml of hot water, the solution was cooled, 50 mg of the cellulase was added, and the mixture was thermostated at 37°C for 168 h. The precipitate was separated off by centrifugation, dried in vacuum, and extracted with $CHCl_3$–MeOH (1:1) (3 × 10 ml). The supernatant was extracted with butanol (3 × 10 ml), and the extracts were combined and concentrated in vacuum. The mixture was separated on a column of silica gel L (40-100 µ) in the $CHCl_3$-MeOH-H_2O (75:25:1) system. This gave 12 mg of the progenin (VI), 24 mg of the progenin (V), and 8 mg of the progenin (IV).

The progenin (IV), mp 263°C, $[\alpha]_D^{20}$ −47.4° (c 0.45; pyridine). After acid hydrolysis, quinovose and xylose were identified in a ratio of 1:1. The ^{13}C NMR spectra for the carbohydrate chain of this and the other progenins are given in Table 1.

The progenin (V), mp 275-277°C, $[\alpha]_D^{20}$ −43.1° (c 0.44; pyridine). After acid hydrolysis, quinovose, xylose, and 3-O-methylglucose were identified in a ratio of 1:2:1.

The progenin (VI), mp 284-286°C, $[\alpha]_D^{20}$ −50.5° (c 0.45; pyridine). After acid hydrolysis, quinovose, xylose, and glucose, and 3-O-methylglucose were identified in a ratio of 1:1:1:1.

Cleavage of Astichoposide C by Smith's Method. Astichoposide C (230 mg) was dissolved in 50 ml of water at 5°C and the solution was filtered through 10 g of acidic alumina to eliminate iodate and periodate ions. The eluate was concentrated in vacuum, the residue was dissolved in 50 ml of 50% ethanol, this solution was added to a solution of 500 mg of KBH_4, and the resulting mixture was left at 20°C for 2 h. Then it was acidified to pH 4.5-5.0 and was concentrated in vacuum, and the boric acid was eliminated in the form of methyl borates by adding methanol in portions and eliminating it under vacuum. The residue was dissolved in 50 ml of water and the solution was treated with 4 ml of concentrated HCl, and after 20 min the resulting precipitate of the progenin (VII) was filtered off. The progenin obtained was washed on the filter with water and was then dissolved in 30 ml of $CHCl_3$-MeOH (1:1). The solution was concentrated in vacuum. The residue (120 mg) was purified on a column of silica gel L (40-100 µ) in the $CHCl_3$-MeOH-H_2O (75:25:1) system, which gave 110 mg of the progenin (VII).

The progenin (VII), mp 254-256°C, $[\alpha]_D^{20}$ −37.4° (c 0.40; pyridine). After acid hydrolysis, xylose, glucose, and 3-O-methylglucose were identified in a ratio of 1:1:1.

Periodate Oxidation of the Progenin (VII). A mixture of 5 mg of the progenin, 2 ml of water, and 2 ml of butanol was treated with 10 mg of $NaIO_4$ and the mixture was stirred at this temperature for 24 h. The butanol layer was separated off, washed with water (2 × 1 ml), and evaporated to dryness in vacuum, and the residue was hydrolyzed, as described above, to obtain the peracetates of the aldonitriles. The corresponding derivatives of glucose and 3-O-methylglucose were identified in the hydrolysate obtained.

Hydrogenation of Astichoposide C. The hydrogenation of 100 mg of astichoposide C in 50 ml of water over 10 mg of Adams catalyst at room temperature for 20 h gave stichoposide C.

CONCLUSION

The structures of two new triterpenehexaosides have been established: astichoposide C from the holothurian *A. multifidus* as 23(S)-acetoxy-3β-{4'-O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-β-D-glucopyranosyl]-2'-O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-O-β-D-xylopyranosyl-(1→4)-β-D-quinovopyranosyl]-β-D-xylopyranosyloxy}holosta-4,25-diene (I) and stichoposide C from the holothurian *S. chloronotus* as 23(S)-acetoxy-3β-{4'-O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-β-D-glucopyranosyl]-2'-O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-O-β-D-xylopyranosyl-(1→4)-β-D-quinovopyranosyl]-β-D-xylopyranosyloxy}holost-7-ene (VIII).

It has been shown that glycosides of these holothurians collected in various regions of the world oceans have identical carbohydrate chains and differ from one another only by details of the structures of the side chains in the aglycone.

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GLYCOSIDES OF MARINE INVERTEBRATES.

XII. STRUCTURE OF A NEW TRITERPENE OLIGOGLYCOSIDE FROM HOLOTHURIANS OF FAMILY *Stichopodidae*

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From an ethanolic extract of the holothurians *Stichopus chloronotus* by column chromatography on silica gel a new triterpene oligoside has been isolated the structure of which has been established as 23(S)-acetoxy-3β-{4'-O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-β-D-glucopyranosyl]-2'-O-[O-(3-O-methyl-β-D-glucopyranosyl(-(1→3)-O-β-D-xylopyranosyl-(1→4)-β-D-glucopyranosyl]-β-D-xylopyranosyloxy}holost-7-ene. A hypothesis has been put forward concerning the biosynthesis of the carbohydrate chains in the glycosides of holothurians of the order *Aspidochirota* from bioside blocks.

Continuing an investigation of the structure of glycosides from holothurians [1], we have isolated a new triterpene glycoside, stichoposide D (I) from ethanolic extracts of the holothurians *Stichopus chloronotus* and *S. variegatus* and have made a structural study of it.

We have shown previously that the native genin of the stichoposides from *S. chloronotus* is 23(S)-acetoxyholost-7-en-3β-ol (II) [2]. The acid hydrolysis of glycoside (I) gave, in addition to (II) and artefactual sapogenins, D-glucose, D-xylose, and 3-O-methyl-D-glucose in a ratio of 2:2:2.

A comparison of the ^{13}C NMR spectra of (I) and the genin (II) [3] showed that the carbohydrate chain in the glycoside was attached to the C-3 atom of the native genin. In ac-

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