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STRUCTURE OF CUCUMARIOSIDE A_2-2 — A TRITERPENE GLYCOSIDE FROM THE HOLOTHURIAN *Cucumaria japonica*

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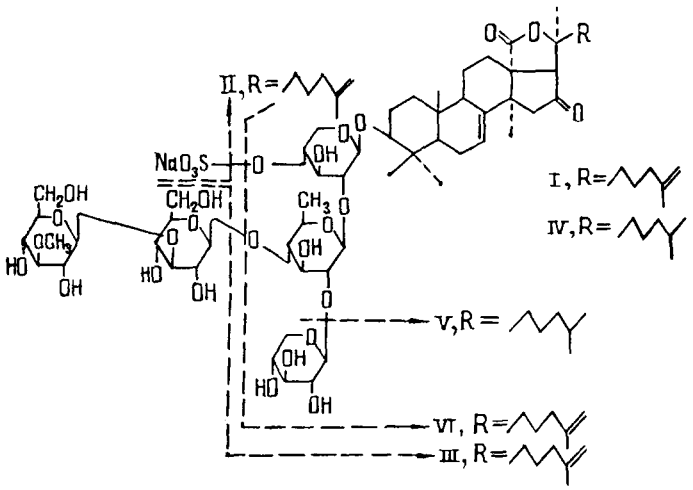
Continuing our investigation of the glycosides of the holothurian *Cucumaria japonica* Semper, we have isolated a new triperpene glycoside — cucumarioside A_2-2 (I) and have determined its structure. It had been shown previously that the native aglycone of (I) was 3β-hydroxyholosta-7,25-dien-16-one [1].

Cucumarioside A_2-2, mp 245-247°C (from ethanol), $[\alpha]_D^{20}$ −68° (c 2.0; pyridine) was isolated from a methanolic extract of the holothurian by successive chromatography on silica gel in the $CHCl_3$—C_2H_5OH—H_2O (100:100:17) system and on Polikhrom-1 (H_2O → 13% C_2H_6OH).



The acid hydrolysis of (I) gave a mixture of D-quinovose, D-xylose, 3-O-methyl-D-glucose, and D-glucose in a ratio of 1:2:1:1, and sulfuric acid. The monosaccharides were identified by GLC and by the chromato-mass-spectrometric method (GLC-MS) in the form of the peracetates of the corresponding aldononitriles. In the ^{13}C NMR spectrum of (I) signals at 105.6 (double), 105.1, 104.9, and 102.4 ppm of the anomeric carbon atoms of the carbohydrate chain showed the β-configurations of all the glycosidic bonds.

When glycoside (I) was heated in a mixture of pyridine and dioxane the desulfated derivative (II) was obtained with mp 283-285°C, $[\alpha]_D^{20}$ −76.5° (c 1.7; pyridine). The Hakomori [2] methylation of (II) followed by methanolysis and acetylation of the methanolysis products led to the formation of methyl 2-O-acetyl-3,4-di-O-methyl-α- and -β-xylopyranosides, methyl 2,3,4-tri-O-methyl-α- and -β-xylopyranosides, methyl 2,4-di-O-acetyl-3-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. The results obtained showed that the carbohydrate chain of glycoside (I) had a branched structure. The center of branching was a quinovose residue, and 3-O-methylglucose and xylose residues were terminal.

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When (I) was subjected to periodate oxidation, one of the xylose residues was split out, and the same treatment of derivative (II) led to the splitting out of both these residues, which indicated the attachment of the sulfate group to one of the xylose residues.

The enzymatic cleavage of (I) with cellulase gave the progenin (III) with mp 215-217°C, $[\alpha]_D^{20}$ −104.3° (c 1.7; pyridine). The catalytic hydrogenation of (I) in water over Adams catalyst to the corresponding dihydro derivative (IV) with mp 211-212°C, $[\alpha]_D^{20}$ −62.5° (c 1.6; pyridine) followed by Smith degradation led to the progenin (V) with mp 238-240°C, $[\alpha]_D^{20}$ −23.8° (c 1.17; pyridine). The structures of the progenins (III) and (V) were confirmed by their ^{13}C NMR spectra, by hydrolysis with the formation of a mixture of xylose and quinovose (2:1) from (III) and of xylose, quinovose, glucose, and 3-O-methylglucose (1:1:1:1) from (V), and also by the results of the methylation of the corresponding desulfated derivatives followed by methanolysis and acetylation.

The position of the sulfate group at C-4 in the xylose residue was established by comparing the ^{13}C NMR spectra of glycoside (I) and of the progenin (III) with the spectra of their desulfated derivatives. The C-5 and C-3 signals in the spectra of the sulfate-containing compounds were located 1.3 ppm upfield, and the C-4 signal 5-6 ppm downfield as compared with the spectra of (II) and (VI) [3].

On the basis of all the results obtained, the structure of cucumarioside A_2-2 has been determined unambiguously as 3β-{O-[O-(3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-O-β-D-glucopyranosyl-(1 → 4)][O-β-D-xylopyranosyl-(1 → 2)]-O-β-D-quinovopyranosyl-(1 → 2)-[4-O-(sodium sulfato)-β-D-xylopyranosyloxy]}holosta-7.25-dien-16-one.

In contrast to the glycosides isolated from homothurins known previously, glycoside (I) has an odd number of disaccharide residues.

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ALKALOIDS OF *Aconitum zeravschanicum*

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We have investigated the alkaloids of the epigeal part of *Aconitum zeravschanicum* Steinb., collected from two growth sites. The alkaloids heteratizine (zarafshanine) [1-3] and azrafshanidine [1] have previously been isolated from the epigeal part of this plant in the budding-flowering phase from Alauddinsae (Alai range).

By chloroform extraction of the epigeal part of *A. zeravschanicum* collected in the budding phase at Alauddinsae (Alai range) we obtained 0.95% of total alkaloids. Similar extraction of the epigeal part of the plant collected in the budding-flowering phase in the gorge of the R. Berksu (Trans-Alai range) gave 0.67% of combined alkaloids. By separation into phenolic and nonphenolic fractions, separation according to solubility in organic solvents and according to basicity, and the preparation of salts, and also by chromatography on columns of alumina and silica gel, from the first group of alkaloids we isolated: heteratizine (I); base (II) with the composition $C_{20}H_{27}NO$, M^+ 297.2093, mp 258-259°C (ethanol); base (III) with mp 148-150°C (acetone); base (IV) with mp 87.5-88.5°C (chloroform); base (V) with mp 130-131°C (acetone); amorphous base (VI), the hydrochloride of which had mp 296°C (ethanol, decomp.); and the amorphous base (VII).

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