

The hydrolysis of the methylated fatsiasides followed by reduction and acetylation led to 1,5-di-O-acetyl-2,3,4-tri-O-methylarabitol identified by GLC, for both glycosides A₁ and B₁. For fatsiasides C₁ and D₁, 1,5-di-O-acetyl-2,3,4,6-tetra-O-methylsorbitol and 1,2,5-tri-O-acetyl-3,4-di-O-methylarabitol were found in a ratio of 1:1, which shows the sequence of the structure of the carbohydrate chain.

A summation of the results obtained and a comparison of them with literature information [3-6] permits the following structures to be suggested for them for the fatsiasides: A₁ [4] - oleanolic acid 3-O- α -L-arabinopyranoside; B₁ (corresponding to leontoside A) [5] - hederagenin 3-O- α -L-arabinopyranoside; C₁ [6] - oleanolic acid 3-O-[O- β -D-glucopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside]; and D₁ [6] hederagenin 3-O-[O- β -D-glucopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranoside].

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GLYCOSIDES OF THE HOLOTHURIAN *Bohadschia graeffei*

V. I. Kalinin and V. A. Stonik

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It has been shown previously that the chromatographic behavior of the glycosides of *Bohadschia graeffei* (Semper) does not coincide with that of the glycosides of other holothurians of this genus [1].

Continuing an investigation of the triterpene glycosides of holothurians, we have studied the glycoside fraction from *B. graeffei*. The animals were collected in July-August, 1974, on the coast of the Maldives islands. Glycoside (I) was isolated by a method described [2].

Glycoside (I) had mp 242-244°C (from ethanol), $[\alpha]_D^{25} -12.4^\circ$ (c 0.01; pyridine). The acid hydrolysis of 45 mg of the glycoside (2 N HCl, 90°C, 2 h) yielded the sum of the artefact aglycones, from which, by column chromatography on silica gel in the benzene-ethyl acetate (8.5:1) system was isolated 16 mg of genin (II) [mp 280-282°C (from ethanol); UV spectrum, nm, $\lambda_{C_2H_5OH}^{max}$: 234, 243, 253 (log ϵ 4.21); mass spectrum (M^+ 170)] which was found to be identical with a known sample of holosta-7,9(11)-diene-3 β ,17 α -diol by comparison of constants and mass spectra [3], together with a mixture of monosaccharides. With the aid of GLC, the monosaccharides, in the form of the aldonitrile acetates, were identified as quinovose, glucose, 3-O-methylglucose, and xylose (1:1:1:1). The hydrolysate gave a positive test with BaCl₂.

When the glycoside (I) was subjected to periodate oxidation followed by acid hydrolysis the quinovose residue was destroyed. The Smith degradation of glycoside (I) followed by desulfation performed by a method described previously [4] yielded a progenin (III) with mp 298-301°C (from methanol), $[\alpha]_D^{25} -9^\circ$ (c 0.01; pyridine). The acid hydrolysis of (III) gave xylose. From its physical constants and the results of acid hydrolysis, (III) was identified as the known 3-O- β -D-xylopyranosylholost-9(11)-ene-3 β ,12 α ,17 α -triol [4].

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The ^{13}C NMR spectrum of glycoside (I) coincides with the spectrum of the known holothurin A₂, isolated previously from the holothurians *Holothuria edulus* [2, 4] and *Holothuria floridana* [15].

On this basis, glycoside (I) was identified as 3-O-{2-O-[3-O-methyl- β -D-glucopyranosyl-(1 \rightarrow 3)-O- β -D-glucopyranosyl-(1 \rightarrow 4)-O- β -D-quinovopyranosyl]-4-O-sulfato- β -D-xylopyranosyl} holost-9(11)-ene-3 β ,12 α ,17 α -triol.

The results that we have obtained show that the glycosides of *B. graeffei* have structural differences from the glycosides of other holothurians of the genus [6] and are similar to the glycosides of holothurians of the genera *Holothuria* [4, 5] and *Actinopyga* [7].

Thus, the main component of the glycosidic fraction of *B. graeffei* is holothurin A₂.

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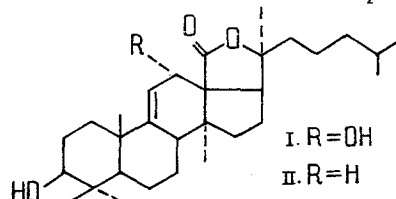
NATIVE AGLYCONES OF TRITERPENE GLYCOSIDES OF THE HOLOTHURIAN *Bohadschia argus*

V. A. Stonik, V. F. Sharypov,
T. A. Kuznetsova, and A. I. Kalinovskii

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The native aglycosides of holothurians of the family Holothuriidae, as a rule, contain a 12 α -hydroxy-9(11)-ene fragment in the holostane nucleus [1-3]. Under the conditions of acid cleavage of the glycosidic bonds, they are unstable and are transformed into artefactual genins with a 7,9(11)-diene grouping or with a 12 α -hydroxy-9(11)-ene fragment [1, 2]. For this reason, the acid hydrolysis of genins forms artefactual genins as the main products, and conclusions concerning the structures of the native aglycones are made mainly on the basis of the spectral study of the glycosides themselves [3-5]. Having analyzed the structures of the carbohydrate chains of holothurins and glycosides from holothurians of the genus *Bohadschia*, we observed that the Smith degradation of such compounds should give progenins with a 2,3-diol grouping in the monosaccharide attached to the aglycone. A repeat cleavage of the genins by the same method opens up the possibility of obtaining the native aglycones.

On applying such a two-stage degradation to the combined glycosides from *Bohadschia argus* [6], we isolated two native aglycones (I) and (II). Aglycone (I) was a 12-hydroxy-9(11)-ene-containing compound and has not been obtained previously.



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