The ^{13}C NMR spectrum of glycoside (I) coincides with the spectrum of the known holothurin A_2, 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 → 3)-O-β-D-glucopyranosyl-(1 → 4)-O-β-D-quinovopyranosyl]-4-O-sulfato-β-D-xylopyranosyl} holost-9(11)-ene-3β,12α,17α-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 A_2.

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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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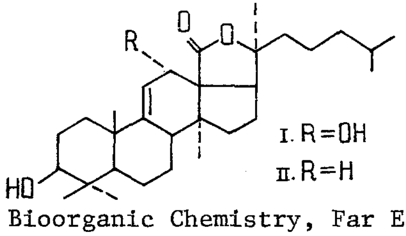
The native aglycosides of holothurians of the family Holothuriidae, as a rule, contain a 12α-hydroxy-9(11)-ene fragment in the holostane nucleus [1-3]. Under the conditions of acid cleavage of the glycosidic bonds, they are unstable and are transformed into artefactual genins with a 7,9(11)-diene grouping or with a 12α-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.



I. R=OH
II. R=H

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center,

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The Smith cleavage was carried out under conditions described previously [7] with treatment of the periodate-oxidized and (sodium tetrahydroborate)-reduced glycosides or progenins with 0.5% hydrochloric acid at 20°C for 2 h. Aglycones (I) and (II) were separated by column chromatography on silica gel in the hexane–ethyl acetate (3:1) system.

Holost-9(11)-ene-3β,12α-diol (I), mp 248–250°C, $[\alpha]_D^{20}$ +20° (c 1.0; $CHCl_3$). MS: M^+ 472 m/z. PMR ($CDCl_3$, ppm): 5.47 (C-11, q, 1 H, $J_{11,8}$ = 1.7 Hz, $J_{11,12}$ = 5.6 Hz); 4.21 (C-12, d, 1 H); 3.18 (C-3, m, 1 H); 2.96 (C-8, m, 1 H); 1.46 (C-21, s, 3 H); 1.17 (C-19, s, 3 H); 1.00 (C-32, s, 3 H); 0.89 (C-26, C-27, d, 6 H). The spin–spin coupling constant of the protons $J_{11,12}$ = 5.6 Hz indicates the α-OH configuration at C-12. ^{13}C NMR ($CDCl_3$, ppm): 153.3 (C-9); 116.1 (C-11); 68.2 (C-12).

Holost-9(11)-en-3β-ol (II), mp 233–235°C, $[\alpha]_D^{20}$ –23° (c 0.8, $CHCl_3$). According to the literature: mp 231-233°C, $[\alpha]_D^{20}$ –16° [3]. Mass spectrum: 456 m/z. PMR ($CDCl_3$, ppm): 5.20 (C-11, m, 1 H); 3.24 (C-3, m, 1 H); 3.04 (C-8, m, 1 H); 1.38 (C-21, s, 3 H); 1.16 (C-19, s, 3 H); 0.99 (C-32, s, 3 H); 0.92, 0.84 (C-30, C-31, 2 s, 3 H, 3 H); 0.89 (C-26, C-27, d, 6 H). ^{13}C NMR ($CDCl_3$, ppm): 151.1 (C-9); 111.4 (C-11); 33.5 (C-12).

The absence of artefactual genins among the products of two-stage Smith degradation shows the great possibilities of this method obtaining the native aglycones from holothurian glycosides.

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