spectrum (in ethanol): $\lambda_{max}$, 232 nm (ε 28,000); according to the literature [2]: mp 118°C, $[\alpha]_D$ + 51°. This acetate, like the free alcohol, was isolated by Bohlmann [2] from the epigeal part of *Palafoxia rosea* (Bush.) Cory (family Compositae).

The reduction with lithium tetrahydroaluminate in diethyl ether of the acetate obtained gave free 3β-hydroxy-trans-biformene in the form of an unstable oil the PMR spectrum of which (in deuterochloroform) corresponded to that given in the literature [2]. It must be mentioned that in Bohlmann's publication [2] inaccuracies have been admitted in the drawing up of Table 1 with details of the PMR spectra of his substances (I) and (II). Thus, the assignments of the 3β-H and 3α-H signals in the column must change places, since in a labdane compound with a 3β-hydroxy group the $H_3$ proton should appear in the form of a doublet of doublets and not as a singlet. In the PMR spectrum of a model compound — labda-8(17),13E-diene-3β,15-diol [3] — the $H_3$ signal coincides in form and position with that for 3β-hydroxy-trans-biformene (doublet of doublets at 3.23 ppm, J = 11.0 and 4.7 Hz).

By the GLC method with the addition of authentic samples, in the ester fraction from the shoots under investigation we established the presence of the native acetate of 3β-hydroxy-trans-biformene (0.2% of the fraction) and of geranylgeraniol acetate. This is the first time that 3β-hydroxy-trans-biformene and its acetate have been detected in a coniferous plant. The other labdane diterpenoids with oxygen-containing functional groups at $C_3$ have been found previously in the oleoresin of the Japanese stone pine [4].

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# HOLOTHURIN A — THE MAIN TRITERPENE GLYCOSIDE OF THE CUVIERIAN ORGANS OF THE HOLOTHURIAN *Bohadschia graeffei*. THE STRUCTURES OF THE NATIVE AGLYCONE AND OF PROGENINS.


N. S. Ivanova and T. A. Kuznetsova



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It has been shown previously that the glycosides of *Bohadschia graeffei* (Semper.) differ in their chromatographic behavior and structure from the glycosides of other holothurians of this genus [1, 2]. Recently, Levin et al., on the basis of an analysis of a complex of biochemical morphological, and ecological features of *B. graeffei*, have separated out the species into the newly established genus *Pearsonothuria* Levin [3].

We have studied the glycoside fraction obtained from the Cuvierian organs of this holothurian. The animals were collected in February 1982 on the coast of North Vietnam during the expedition cruise of the Scientific-Research ship "Professor Bogorov." The isolated Cuvierian organs were extracted with 70% ethanol, and the dry extract was dissolved in water and extracted with butanol. Then the butanolic extract (1 g) was separated on Polikhrom (250 g) in the water—ethanol (100:20) system. The main glycoside, with mp 228-230°C, was identified from its $^{13}C$ spectrum as holothurin A, isolated previously from the holothurians *Holothuria leucospilota* [4] and *Actinopyga agassizi* [5]. Then holothurin A was incubated with glycosidases from the snail *Eulota maackii* (100 mg, 38°C, 4 days), which gave combined genins and progenins. Column chromatography on silica gel in the hexane—ethyl acetate (3:1) system


Pacific Ocean Institute of Bioorganic Chemistry, Far-Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok.


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led to the isolation of the minor native aglycone (3 mg) with mp 274-275°C, the structure of which was established by mass and $^1$H NMR spectroscopy as 22,25-epoxyholost-9(11)-ene-3β,12α,17α-triol. Mass spectrum, m/z: 502 ($M^+$), 484, 451, 283, 99 (100%). $^1$H NMR ($CDCl_3$, δ, ppm): 5.38 (q, 1 H, C-11, $J_{11,12}$ = 5.75 Hz), 4.58 (d, 1 H, C-12); 3.25 (m, 1 H, C-3).

Column chromatography on silica gel in the chloroform—ethanol—water (75:25:0.5) system yielded progenins 1 and 2, and the chloroform—methanol—water (60:30:4) system gave progenin 3. The main progenin, 1, mp 290-292°C $[\alpha]_D^{20}$ −5° (MeOH) was identified from its constants and $^{13}$C spectrum as the known 3β-D-xylopyranosyloxy-22,25-epoxyholost-9(11)-12α,17α-diol [5, 6]. The hydrolysis of the minor progenin 2 with mp 280-282°C gave the monosaccharides D-xylose and D-quinovose, and the $^{13}$C NMR spectrum enabled its structure to be established as 3-[O-β-quinovopyranosyl-(1 → 2)-β-xylopyranosyloxy]-22,25-epoxyholost-9(11)-ene-12α,17α-diol. From its $^{13}$C NMR spectrum, progenin 3 was identified as the known 3-(4-O-sulfato-β-xylopyranosyloxy)-22,25-epoxyholost-9(11)-ene-12α,17α-diol [6].

Thus, the main glycoside of the Cuvierian organs of *Bohadschia graeffei* is holothurin A. A preparation of snail enzymes cleaves the sulfate containing carbohydrate chain of holothurin A with the formation of three progenins and the native aglycone.

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