# GLYCOSIDES OF MARINE INVERTEBRATES.

# XVIII. HOLOTHURIN $A_2$ FROM THE CARIBBEAN HOLOTHURIAN *Holothuria floridana*

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We have previously established that the polar glycosidic fraction from the holothurian *H. floridana* contains two triterpene glycosides — holothurin $A_1$ and holothurin $A_2$ [1]. In the present communication we consider the determination of the complete structure of holothurin $A_2$ (I).

Holothurin $A_2$ was isolated from an ethanolic extract of the holothurians by reversed-phase chromatography on polytetrafluoroethylene (Polikhrom-1). By recrystallization from ethanol, the glycoside (I) was obtained in the form of colorless needles with mp 246–248°C, $[\alpha]_D^{20}$ −11.05° (c 0.026; $C_2H_5OH$). $\nu_{max}^{KBr}$ ($cm^{-1}$): 1750 (C=O), 1230, 830 (sulfate group). $^1H$ NMR spectrum of (I) (δ, pyridine, ppm): 0.86 d (C-26,27); 1.04 s, 1.23 s (C-30,31); 1.36 s (C-19); 1.70 s (C-32); 1.86 s (C-21); 4.62 m (CH—O); 5.51 (=C—H).

The $^{13}C$ NMR spectrum of holothurin $A_2$ (δ, pyridine, ppm) — 174.87 (C-18), 153.95 (C-9), 115.54 (C-11), 89.36 (C-17), 87.21 (C-20), 71.43 (C-12) confirms the structure of the native glycone as holost-9(11)-ene-3β,12α,17α-triol (see below) [2, 3]. The IR spectrum of (I) and the result of the solvolytic cleavage of its pyridinium salt [4] showed that the glycoside has a sulfate group.

The methylation of holothurin $A_2$, followed by the methanolysis of the completely methylated product, the periodate oxidation of glycoside (I) and of its desulfated derivative, and Smith degradation have shown the carbohydrate chain of glycoside (I) is identical with that of holothurin $A_1$, which has been described previously [1].

We give the characteristics of the $^{13}C$ NMR spectrum of holothurin $A_2$ (pyridine);

| C-atom | δ, ppm | C-atom | δ, ppm | C-atom | δ, ppm | C-atom | δ, ppm |
|---|---|---|---|---|---|---|---|
| $C_1$ | 36.6 | $C_{15}$ | 38.93 | $C_{31}$ | 28.00 | $C_2^3$ | 73.9 |
| $C_2$ | 27.1 | $C_{16}$ | 36.0 | $C_{32}$ | 20.1 | $C_3^3$ | 88.2 |
| $C_3$ | 88.64 | $C_{17}$ | 89.36 | $C_1^1$ | 105.1 | $C_4^3$ | 69.9 |
| $C_4$ | 40.03 | $C_{18}$ | 174.87 | $C_2^1$ | 83.0 | $C_5^3$ | 77.7 |
| $C_5$ | 52.70 | $C_{19}$ | 22.5 | $C_3^1$ | 76.2 | $C_6^3$ | 62.4 |
| $C_6$ | 21.2 | $C_{20}$ | 87.21 | $C_4^1$ | 75.42 | $C_1^4$ | 105.4 |
| $C_7$ | 28.0 | $C_{21}$ | 23.00 | $C_5^1$ | 63.9 | $C_2^4$ | 74.9 |
| $C_8$ | 40.08 | $C_{22}$ | 36.6 | $C_1^2$ | 105.1 | $C_3^4$ | 87.7 |
| $C_9$ | 153.95 | $C_{23}$ | 22.29 | $C_2^2$ | 76.2 | $C_4^4$ | 70.8 |
| $C_{10}$ | 39.71 | $C_{24}$ | 39.71 | $C_3^2$ | 75.6 | $C_5^4$ | 78.0 |
| $C_{11}$ | 115.54 | $C_{25}$ | 28.00 | $C_4^2$ | 87.0 | $C_6^4$ | 62.4 |
| $C_{12}$ | 71.49 | $C_{26}$ | 22.61 | $C_5^2$ | 71.7 | OMe | 60.4 |
| $C_{13}$ | 58.61 | $C_{27}$ | 22.67 | $C_6^2$ | 18.1 | | |
| $C_{14}$ | 46.40 | $C_{30}$ | 16.7 | $C_1^3$ | 104.6 | | |

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Thus, holothurin $A_2$ is 3β-[O-(3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-O-β-D-glucopyranosyl-(1 → 4)-O-β-D-quinovopyranosyl-(1 → 2)-{4-(sodium sulfato)-β-D-xylopyranosyloxy}]holost-9(11)-ene-12α,17α-diol.

The determination of the complete structures of two glycosides of the holothurian *H. floridana* — holothurin $A_1$ [1] and holothurian $A_2$ — has shown that the holothurians of one species may contain triterpene oligosides with different aglycones but having carbohydrate chains of the same structure.

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# ALKALOIDS OF *Petilium raddeanum*.

## III. STRUCTURE OF PETISIDINE


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We have continued the separation of the combined alkaloids of the epigeal part and bulbs of *Petilium raddeanum* (Rgl) Vved. [1, 2]. The fraction with pH 4.99 obtained from the epigeal part [1] was separated according to solubilities into ethereal and chloroform fractions. The chromatographic separation of the ethereal fraction on a column of silica gel with elution by chloroform–methanol (9:1) led to the isolation of base with mp 236–239°C (acetone), $[\alpha]_D$ +17° (c 0.50; chloroform), $C_{27}H_{45}NO_3$ (I), $M^+$ 431.

The physicochemical properties of (I) (melting point, IR, mass, and NMR spectra) coincided with those of isodihydroimperialine [3]. A direct comparison of (I) with an authentic sample of isodihydroimperialine showed their identity.

The material from the mother liquor after the isolation of the alkaloids mentioned in our previous paper [2] was dissolved in benzene, and the bases remaining in it were extracted with 3% acetic acid and then with 5% sulfuric acid. The benzene solution was made alkaline and the solvent was distilled off. The residue was chromatographed on a column of silica gel and, on elution with benzene–acetone (8:2), the initial fractions yielded a base with mp 150–152°C, $C_{27}H_{41}NO_3$, $M^+$ 427, identical with the petisidine (II) isolated previously from the epigeal part of this plant [1].

The UV spectrum of (II): $\lambda_{max}$ 285 nm (log ε 2.65). IR spectrum ($cm^{-1}$): 3380, 1065 (OH), 1691 (C=O), 1615 (N=C).

The mass spectrum of (II) is characterized by the ions with m/z 97 (28%), 110 (19%), 111 (28%), 121 (7%), 124 (9%), 129 (9%), 139 (33%), 140 (100%), 149 (14%), 150 (9%), 164 (9%), 256 (7%), 412 $(M - 15)^+$ (7%), 427 $M^+$ (33%).

The mass-spectrometric fragmentation of petisidine in the region of low masses was similar to that of tomatillidine [4–6], which permits (II) to be assigned to the steroid alkaloids of the verazine group [3].

The NMR spectrum of (II) shows two singlets at 0.57 ppm, (3 H, 19-$CH_3$) and 0.66 ppm (3 H, 18-$CH_3$), and two doublets from secondary methyl groups at 0.99 ppm (J = 6 Hz) and 1.06 ppm (J = 7 Hz).


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