POLAR STEROIDAL COMPOUNDS FROM THE ANTARCTIC STARFISH *Diplasterias brucei*

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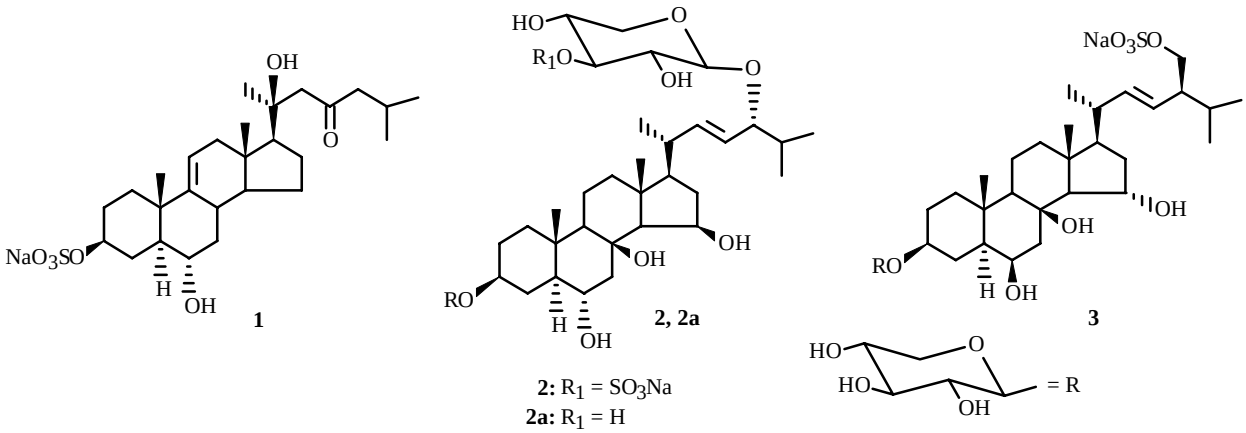
Starfish, in contrast with many other marine animals, contain highly oxidized steroids that occur in the free, sulfated, and glycosylated states [1, 2]. In continuation of our research on steroidal metabolites of starfish, we studied for the first time steroids from the Antarctic starfish *Diplasterias brucei* (Asteriidae, Forcipulatida) collected in 2000 near the shore of Ross Sea (Terra Nova Bay, Antarctica) under the auspices of the National Italian program Antarctic Research.

Starfish (460 g) was ground and extracted twice with ethanol (70%) with heating on a water bath. The solid was separated by filtration. The aqueous ethanol layer was concentrated in vacuo (35. g). Column chromatography of the dry extract over Amberlite XAD-2, Sephadex LH-20 (ethanol:water, 2:1), and silica gel ($CHCl_3$:C_2H_5OH, 8:1→1:12) and subsequent HPLC over a Zorbax ODS column [13 μm, 9.4 × 250 mm, ethanol (60% for **1**; 50%, **2** and **3**)] and rechromatography over a Diaspher-110-C18 column (5 μm, 4 × 250 mm, analogous solvents) isolated **1** (12 mg), **2** (11 mg), and **3** (1.7 mg).



PMR spectra of **1** and MALDI/TOF(-) mass spectra determined that the isolated compound was the native aglycon of asterosaponins, tornasterol A sulfate [3].

The structures of **2** and **3** were established using PMR and ^{13}C NMR spectra including 2D NMR (^1H—^1H COSY, HSQC, NOE, HMBC) and MALDI/TOF(+) and -(-) mass spectra. A comparison of our results with those in the literature found that **2** was the steroidal bioside asteriidoside H sulfated on C-3″ of β-D-xylopyranose. This was isolated previously from an Antarctic starfish of the family Asteriidae [4]. Compound **3** was asteriidoside L, a steroidal xyloside with the rare 28-sulfoxy-Δ^{22E}-24-methylcholestane side chain that was found earlier in this same starfish [4].

Tornasterol A sulfate (1), amorphous compound, $[\alpha]_D^{20}$ +2.8° (*c* 0.07, CH_3OH). MALDI/TOF(-) mass spectrum (*m*/*z*): 511 $[M_{Na} - Na]^-$, 411 $[M_{Na} - Na - 100]^-$. PMR spectrum (300 MHz, CD_3OD) was identical to that in the literature [3].

Asteriidoside H (2), amorphous compound, $[\alpha]_D^{20}$ -5.2° (*c* 0.3, CH_3OH). MALDI/TOF(+) mass spectrum (*m*/*z*): 839 $[M_{Na} + Na]^+$, MALDI/TOF(-) mass spectrum (*m*/*z*): 793 $[M - H]^-$. PMR (500 MHz, CD_3OD) and ^{13}C NMR (125.8 MHz, CD_3OD) spectra were identical to those in the literature [4].

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Desulfated 2. Compound **2** (5 mg) was heated for 2 h at 90°C in pyridine:dioxane (1:1) and purified by HPLC over a Kromasil 100A-C18 column (5 μm, 4.6 × 250 mm, ethanol 65%) to afford **2a** (3 mg), amorphous, $[\alpha]_D^{20}$ +3.25° (*c* 0.4, CH_3OH). PMR spectrum (300 MHz, CD_3OD) was identical to that reported previously for desulfated asteriidoside H [4].

Asteriidoside L (3), amorphous compound, $[\alpha]_D^{20}$ -8.2° (*c* 0.17, CH_3OH). MALDI/TOF(+) mass spectrum (*m*/*z*): 721 $[M_{Na} + Na]^+$, MALDI/TOF(-) mass spectrum (*m*/*z*): 675 $[M - H]^-$. PMR (500 MHz, CD_3OD) and ^{13}C NMR (125.8 MHz, CD_3OD) spectra were identical to those in the literature [4].

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REFERENCES

1. L. Minale, R. Riccio, and F. Zollo, in: *Progress in Chemistry of Organic Natural Products*, H. Herz, G. W. Kirby, R. E. Moore, W. Steglich, and C. Tamm, eds., Springer-Verlag, New York (1993), Vol. 62, p. 75.
2. V. A. Stonik, *Usp. Khim.*, **70**, No. 8, 673 (2001).
3. E. Finamore, F. Zollo, L. Minale, and T. Yasumoto, *J. Nat. Prod.*, **55**, 767 (1992).
4. S. De Marino, M. Iorizzi, E. Palagiano, F. Zollo, and C. Roussakis, *J. Nat. Prod.*, **61**, 1319 (1998).