## POLYHYDROXYSTEROIDS AND THYMIDINE

## FROM THE SEA PEN Pavonaria finmarchica

I. I. Kapustina, T. N. Makar'eva, A. I. Kalinovskii, and V. A. Stonik UDC 547.925:593.6

Marine organisms are a rich source of a variety of biologically active compounds [1]. In continuation of a search for such compounds [2], we investigated the composition of the sea pen *Pavonaria finmarchica* (Coelenterata, Anthozoa, Pennatulacea). Several new diterpenoids [3-5] and steroids [6, 7] were isolated earlier from related Coelenterata.

Sea pens were collected in August 2001 in the Okhotsk Sea near Cape Aniva ( $46^{\circ}00.9 \text{ N}$ ,  $143^{\circ}49.7 \text{ E}$ ) at a depth of 213 m. The ground animals were extracted with ethanol. The evaporated extract was dissolved in CHCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH (1:1) and was separated as a concentrated solution over silica gel using a CHCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH gradient (100:0-90:10). Two of the resulting fractions were separated individually over columns packed with Sephadex LH-20 in ethanol and over silica gel in hexane:ethylacetate (70:30-50:50 and 50:50-25:75) in addition to double HPLC (YMC-Pack ODS-A,  $250\times10$  mm, 1.5 mL/min) in 90 and 70% ethanol. Compounds 1, 2, and 3 were isolated.

**24-Norcholesta-7,22***E***-dien-3** $\beta$ **,5** $\alpha$ **,6** $\beta$ **-triol (1).** Yield 8×10<sup>-5</sup>% of animal wet mass,  $R_f$  0.78 (CHCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O, 11:3.5:0.2).

PMR spectrum (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm, J/Hz, 0 = TMS): 0.60 (CH<sub>3</sub>-18, s), 0.95 (CH<sub>3</sub>-26,27, d, J = 6.6), 1.01 (CH<sub>3</sub>-21, d, J = 6.7), 1.09 (CH<sub>3</sub>-19, s), 3.72 (H-6, m), 4.09 (H-3, m), 5.17 (H-22, dd, J = 8.4 and 15.3), 5.29 (H-23, dd, J = 6.4, J = 15.3), 5.36 (H-7, m). Mass spectrum (direct probe), m/z; 384 [M - H<sub>2</sub>O]<sup>+</sup>, 369 [M - H<sub>2</sub>O - CH<sub>3</sub>]<sup>+</sup>, 366 [M - 2H<sub>2</sub>O]<sup>+</sup>, 351 [M - 2H<sub>2</sub>O - CH<sub>3</sub>]<sup>+</sup>, 287 [M - side chain - H<sub>2</sub>O]<sup>+</sup>, 269 [M - side chain - 2H<sub>2</sub>O]<sup>+</sup>, 251 [M - side chain - 3H<sub>2</sub>O]<sup>+</sup>, 97 (side chain).

**Cholesta-7,22***E***-dien-3** $\beta$ **,5** $\alpha$ **,6** $\beta$ **-triol (2).** Yield  $7 \times 10^{-5}$  %,  $R_f 0.78$  (CHCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O, 11:3.5:0.2).

PMR spectrum (300 MHz,  $CDCl_3$ ,  $\delta$ , ppm, J/Hz, 0 = TMS): 0.60 ( $CH_3$ -18, s), 0.87 ( $CH_3$ -26,27, d, J = 6.6), 1.02 ( $CH_3$ -21, d, J = 6.6), 1.09 ( $CH_3$ -19, s), 2.12 (H-4, dd, J = 12.8, J = 12.8), 3.62 (H-6, m), 4.08 (H-3, m), 5.18 (H-22 or H-23, m), 5.26 (H-22 or H-23, m), 5.36 (H-7, d, J = 4.9).

24-Norcholesta-7,22*E*-dien-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol and cholesta-7,22*E*-dien-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol were isolated for the first time from sponges [8, 9] and later from sea lily [10]. The spectral properties of steroids **1** and **2** agree with those published [8, 10]. They have not previously been found in Coelenterata.

Thymidine (3). Yield  $6.4\times10^{-4}\%$ ,  $R_f$  0.53 (CHCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O, 11:3.5:0.2), UV spectrum (EtOH,  $\lambda_{max}$ , nm): 264. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD:C<sub>6</sub>D<sub>6</sub> 1:1, δ, ppm, 0 = TMS): 151.4 (C-2, s), 165.4 (C-4, s), 110.7 (C-5, s), 137.2 (C-6, d), 85.7 (C-1', d), 40.6 (C-2', t), 71.3 (C-3', d), 88.0 (C-4', d), 62.0 (C-5', t), 12.0 (CH<sub>3</sub>, q).

A comparison of the  $^{13}$ C NMR spectrum of 3 with those in the literature [11] and the PMR spectrum of 3 with standard spectra identified 3 as thymidine. Thymidine is a common metabolite. However, its isolation from representatives of the Pennatulacea order has not been reported.

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Pacific Institute of Bioorganic Chemistry, Far-East Division of the Russian Academy of Sciences, 690022, Vladivostok, pr. 100-Years to Vladivostok, 159, fax (74232) 31 40 50, e-mail: piboc@stl.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 1, p. 44, January-February, 2003. Original article submitted January 8, 2003.

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