GLYCOSIDES AND THYMIDINE FROM THE MOLLUSK *Cryptochiton stelleri*

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In continuation of the search for biologically active compounds in marine organisms [1-3], we investigated the extract of the mollusk *Cryptochiton stelleri*.

Mollusks were collected using a small trawl in September 1995 in the Sea of Japan near Tumannyi Cape (42° 58.90′ N, 134° 06.60′ E) at a depth of about 140 m. The ground specimens were extracted with ethanol. The alcohol was evaporated. The aqueous solution was extracted with petroleum ether to remove nonpolar substances and left in a refrigerator overnight. The precipitated salt was filtered off. The supernatant was concentrated in vacuum to give a polar fraction that was separated over a column of silica gel L (40/100 μ, Czech Rep.) using a $CHCl_3$:ethanol gradient (50:1 → 5:1). The two most polar fractions were purified over a column of Sephadex LH-20 using $CHCl_3$:ethanol (10:1) and then twice over silica gel with elution by ethylacetate:hexane (2:1 → 3.5:1) and (2:1 → 5:1). HPLC over a reversed-phase column (YMC-Pack ODS-A, 250 × 10 mm, 1.5 mL/min) using ethanol (60%) isolated three pure compounds (**1-3**).

***n*-Butyl-α-D-glucopyranoside (1).** Yield 4.2×10^{-3}% of the dry animal mass, R_f 0.20 ($CHCl_3$:ethanol:water, 11:3.5:0.2).

Ethyl-α-D-glucopyranoside (2). Yield 1.2×10^{-3}% of the dry animal mass, R_f 0.47 ($CHCl_3$:ethanol:water, 11:3.5:0.2).

The acetates of **1** and **2** (**1a** and **2a**, respectively) were prepared by treating weighed portions of these compounds with pyridine:acetic anhydride (1:1) for 1 d at room temperature. The solutions were evaporated to dryness with added benzene.

The structures of **1** and **2** were established using the modern NMR spectroscopy methods DEPT, COSY, and HMBC. The proton spectra were interpreted using COSY experiments for **1a** and **2a** (Table 1). Signals for C atoms in ^{13}C NMR spectra of the sugars of **1** and **2** were assigned by comparing them with those in spectra of α-D-glucopyranoside [4]. Signals for C atoms of the carbohydrates of **1a** and **2a** agree well with the corresponding values for the model acetate of α-D-glucopyranoside [5]. Therefore, both glycosides have the identical structure in the carbohydrate parts. Signals for C-2′, C-3′, and C-4′ of the aglycon in the ^{13}C NMR spectrum of **1** are similar to the corresponding signals of *n*-butanol [6].

Thymidine (3). Yield 1.5×10^{-4}% of the dry animal mass. UV, PMR, and ^{13}C NMR spectra of **3** agree with those of standard thymidine and thymidine isolated by us previously from the sea pen *Pavonaria finmarchica* [3].

The chemical composition of the mollusk *Cryptochiton stelleri* has not previously been studied.

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TABLE 1. PMR and ^{13}C NMR Data for **1**, **2**, **1a**, and **2a** (δ, ppm, J/Hz, 0 = TMS)

Compounds					
1 (MeOD)		**1a** ($CDCl_3$)			
C atom	^{13}C	DEPT		H atom	^{1}H
1	100.7	CH	95.7	1	5.07 d (J = 3.8)
2	74.2	CH	71.0	2	4.85 dd (J = 3.8; 10.3)
3	75.7	CH	70.3	3	5.48 t (J = 9.7)
4	72.5	CH	68.7	4	5.05 t (J = 9.6)
5	74.2	CH	67.2	5	4.02 ddd (J = 2.4; 4.6; 10.0)
6	63.4	CH_2	62.0	6	4.09 dd (J = 2.4; 12.2)
1′	69.4	CH_2	68.5	6′	4.25 dd (J = 12.2; 4.6)
2′	33.5	CH_2	31.3	1′	3.69 dt (J = 9.9; 6.4)
3′	21.0	CH_2	19.2	$2H_2'$, $2H_3'$	3.44 dt (J = 9.9; 6.4)
4′	14.8	CH_3	13.7	$3H_4'$	1.58 m (2H); 1.40 m (2H)
AcO			169.6; 170.1; 170.2; 170.7; 20.6; 20.7		0.93 t (J = 7.5) 2.01; 2.03; 2.06; 2.09

Compounds					
1 (MeOD)		**1a** ($CDCl_3$)			
C atom	^{13}C	DEPT		H atom	^{1}H
1	100.3	CH	95.5	1	5.07 d (J = 4.0)
2	74.1	CH	70.9	2	4.84 dd (J = 3.7; 10.3)
3	75.7	CH	70.3	3	5.47 t (J = 9.7)
4	72.3	CH	68.7	4	5.04 t (J = 9.7)
5	74.0	CH	67.2	5	4.03 ddd (J = 2.4; 4.7; 10.0)
6	63.2	CH_2	62.0	6	4.09 dd (J = 2.4; 12.2)
1′	65.0	CH_2	64.2	6′	4.25 dd (J = 12.2; 4.7)
2′	15.9	CH_2	14.9	$2H_1'$	3.72 m; 3.52 m
				$3H_2'$	1.22 t (J = 6.9)
AcO			170.1; 170.2; 170.7; 16.96; 20.6; 20.7; 20.9		

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