MINOR POLYHYDROXYSTEROIDS FROM THE STARFISH Crossaster papposus

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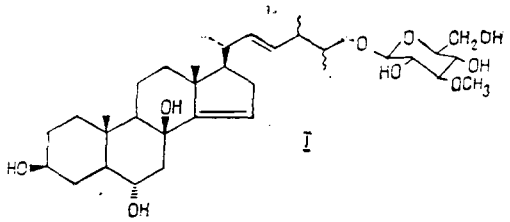
Minor polyhydroxysteroids from the starfish Crossaster papposus have been isolated and characterized: 5α-cholestane-3β,6α,8,15β,16β,26-hexanol and 24-methyl-5α-cholesta-14,22E-diene-3β,6α,8,26-tetraol 26-O-(3-O-methyl-β-D-glucopyranoside) (crossasteroside P_3). The structures of the compounds were established on the basis of spectral methods.

Continuing a study of the total polyhydroxysteroids from the starfish Crossaster papposus, we have isolated two minor components – a new glycoside which we have called crossasteroside P_3 (I), and a steroid hexaol (II). The structures of (I) and (II) have been established with the aid of spectral methods.



I

The acid hydrolysis of (I) gave a single monosaccharide, which was identified as 3-O-methyl-β-D-glucose (TLC, GLC, GLC-MS, $[\alpha]_{Hg}$). Chemical shifts at 104.9, 64.7, 88.3, 70.9, 77.9, 62.7, and 60.6 ppm in the ^{13}C NMR spectrum and the SSCCs of the $H_1' - H_6''$ protons in the ^{13}C NMR spectrum of (I) (Tables 1 and 2) agreed well with the corresponding values in the spectra of methyl 3-O-methyl-β-D-glucopyranoside (III) [1]. This indicated the β-configuration of the glycosidic bond and the size of the ring in the monosaccharide residue of glycoside (I).

The positions of the substituents in the steroid part of compound (I) were established by experiments with differential decoupling. Starting from the H-3 multiplet (3.88 ppm), the presence of hydroxy groups in the C-3, C-6, and C-8 positions was revealed as was done for asterosaponin P_1 (IV) from the starfish Patiria pectinifera [2]. The configurations of the hydroxy groups were determined from the SSCCs of the corresponding protons as 3β,6α, 8β (Table 2).

The presence of signals at 119.0, 132.6, 136.0, and 157.6 ppm in the ^{13}C NMR spectrum of (I) showed that there were two double bonds in glycoside (I).

Differential decoupling with irradiation of the vinyl proton at 5.46 ppm (H-15) converted the signals of the neighboring protons at 2.10 ppm (H-16) and 1.83 ppm (H-16') into doublets of doublets with the SSCCs 7.6 and 16.1 Hz, and 10.7 and 16.2 Hz, respectively. The recording of the Overhauser effect when H-15 was irradiated showed an enhancement of the signals at 2.7 ppm (H-7e) and 1.84 ppm (H-7a). These results indicated that one double bond was located in the 14(15) position.

The ^1H NMR spectrum of (I) lacked the multiplet signal of H-24 in the weak field that is characteristic for starfish 24-O-glycosylated polyhydroxysteroids [2]. In place of it there were two proton multiplets at 3.34 pm (H-26') and 4.03 ppm (H-26). The irradiation of the anomeric proton of the monosaccharide residue (H-1') at 4.60 ppm gave NOE signals for the multiplets at (ppm) 3.51 (H-3'), 3.67 (H-5'), and 3.34 (H-26'). Differential decoupling on the H-26 and H-26' protons established their interconnection and their

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TABLE 1. ^{13}C NMR Spectrum of Glycoside (I)* (C_5D_5N; δ, ppm; TMS = 0)

Atom	δ	Atom	δ	Atom	δ
C-1	39,0	C-13	47,5	C-25	38.5** (39,8)
C-2	31,9	C-14	157,6	C-26	14,9 (14,8)
C-3	71 2	C-15	119 0	C-27	73,5 (74,8)
C-4	33,1	C-16	36,3	C-28	19,0 (19,7)
C-5	53,4	C-17	60,0	C_1	104,9
C-6	66,5	C-18	16,5	C_2	74,7
C-7	48,8	C-19	14,0	C_3	88.3
C-8	72,4 (73.6)	C-20	39,2** (40,2)	C_4	70,9
C-9	55,9	C-21	21,1 (21,4)	C_5	77,9
C-10	37,7	C-22	136,0 (137,0)	C_6	62.7
C-11	19,0	C-23	132,6 (133,7)	OMe	60 6
C-12	44,0	C-24	38,8** (40,0)		

*The CS of the atoms of the side chain of (I) in the spectrum taken in CD_3OD are given in parentheses.
**Assignment of the signals ambiguous.

TABLE 2. ^1H NMR Spectra of Glycoside (I) (Solvent C_5D_5N–CD_3OD (4:1); TMS = 0

Proton	δ, ppm (J, Hz)	Proton	δ, ppm (J, Hz)
H-3	3,88 m	CH_3-19	1,23* s
H-4e	2,80 dm (12 5)	2H-22,23	5,17 m
H-4a	1,82 m	CH_3-21	0,94 d (6,5)
H-5	1,40 m	CH_3-27	0,87 d (6.7)
H-6	4,14 td (4,2; 11,0; 11,0)	CH_3-28	0,82 d (7,0)
H-7e	2,71 dd (4,0; 12,5)	H_1	4,60 d (8,0)
H-7a	1,84 dd (12,5; 11 0)	H_2	3,75 t (9,0)
H-15	5,46 m	H_3	3,51 t (9,0)
H-16	2,10 ddd	H_4	3,93 t (9,2)
H-16′	1,83 ddd	H_5	3,67 m
H-26	4,03 dd (5,5; 9,5)	H_6	4,10 dd (5,0; 12,0)
H-26′	3 34 dd (7,3; 9,8)	H_6	4,25 dd (2,3; 12,0)
CH_3-18	1,22* s	OMe	3,75 s

*Assignment of the signals ambiguous.

interaction with one and the same multiplet in the strong field at 1.74 ppm (H-25).

The same multiplet was obtained when the doublet of the methyl group at 0.87 ppm (CH_3-27) was irradiated. At the same time, when the CH_3-27 and CH_3-28 doublets were irradiated, no common multiplets were obtained in the strong field, which showed the absence of an isopropyl fragment in the side chain, as there is in the 24-O-glycosylated polyhydroxysteroids [2]. Irradiation of the H-22 and H-23 multiplets at 5.17 ppm gave NOE signals for all the methyl groups forming doublets. The presence of the C-20 signal at 39.2 ppm (Table 1) indicated the E-configuration of the 22(23) double bond in the side chain [3]. The structure of the side chain of (I) was also confirmed by the practically complete coincidence of the C-20–C-26 chemical shifts in the ^{13}C NMR spectrum of (I) (CD_3OD, Table 1) with the analogous values for halityloside I (V) from the starfish Halityle regularis [4].

Thus, the structure of crossasteroside P_3 has been established as 24-methyl-5α-cholesta-14,22E-diene-3β,6α,8,26-tetraol 26-O-(3-O-methyl-β-D-glucopyranoside).

The structure of steroid (II) was determined from its ^1H NMR spectrum (C_5D_5N) as 5α-cholestane-3β,6α,8,15β,16β,26-hexaol. The assignment of the signals of the protons of rings A/B and of the side chain was made by comparison with the spectrum of 5α-cholestane-3β,6α,15α,16β,26-hexaol (VI) from the starfish P. pectinifera [5]. The positions of the signals of the H-15 and H-16 protons and those of the methyl groups and the corresponding SSCCs agreed well with the similar values in the spectrum of culcitoside C_3 (VII) from the seaweed Culcita novaeguineae [6].

A steroid hexaol identical with compound (I) was recently isolated from the starfish H. regularis [4]. A structure for it was suggested on the basis of its ^{1}H NMR spectrum (CD_3OD). It has not been possible to compare the physicochemical characteristics of (II) with those of the compound isolated by the Italian authors since their paper does not give them.

EXPERIMENTAL

For general observations, see [5, 6]. The animals were collected in August, 1983, in the Sea of Okhotsk off the shores of the island of Onekotan (Kurile Islands) from a depth of 100 m.

Crossasteroside P_3 (I), $C_{35}H_{58}O_9$, amorphous $[\alpha]_{Hg}$ + 16.3° (c 0.4; methanol) was isolated with a yield of 0.004% from a lyophilizate of a methanolic extract of C. papposus by a method described previously [2].

Hydrolysis of Crossasteroside P_3. The acid hydrolysis of (I) was carried out with 2 N HCl at 100°C for 2 h. 3-O-Methyl-D-glucose was identified by TLC on silica gel and Silufol in the toluene–ethanol (9:5) system and, in the form of an aldonitrile peracetate, by GLC and GLC-MS; $[\alpha]_{Hg}$ + 29.5°, (c 0.1; water); according to the literature [7]: $[\alpha]_D$ + 31.9° (water).

5 -Cholestane-3β,6α,8,15β,16β,26-hexaol (II). $C_{27}H_{48}O_6$, mp 262-264°C, $[\alpha]_{Hg}$ + 35.4° (c 0.3; methanol) was isolated in a similar way to (I) with a yield of 0.0006%. Mass spectrum (m/z, %): 468 (1, M^+); 450(21); 432(5); 417(21); 414(20); 399(5); 331(4); 321(1); 303(15); 285(10); 259(9); 260(9); 261(9); 233(9); 232(9); 231(9); 225(10); 133(23); 123 (35); 121(31); 111(19); 109(33); 104(44); 105(21); 95(100).

^{1}H NMR spectrum (C_5D_5N, 250 MHz, δ, TMS = 0, ppm); 1.10 (d; J = 6.7 Hz; CH_3-21); 1.13 (d, J = 6.5 Hz; CH_3-27); 1.41 (s; CH_3-19); 1.65 (s; CH_3-18); 2.32 (m; H-20); 3.08 (dd; J_1 = 4.5 Hz; J_2 = 12.0 Hz; H-4e); 3.15 (dm; J = 12.0 Hz; H-4e); 3.70 (A_{dd}; J_1 = 6.5 Hz; J_2 = 10.5 Hz; H-26); 3.80 (B_{dd}; J_1 = 5.5 Hz; J_2 = 10.5 Hz; H'-26); 4.05 (m; H-3); 4.43 (td; J_1 = 4.0 Hz; J_2 = 10.5 Hz; J_3 = 10.5 Hz; H-6); 4.47 (t; J = 7.0 Hz; H-16); 4.65 (dd, J_1 = 5.2 Hz; J_2 = 7.0 Hz; H-15).

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