A NEW AGLYCONE FROM THE ASTEROSAPONINS OF THE STARFISH *Asterias amurensis*

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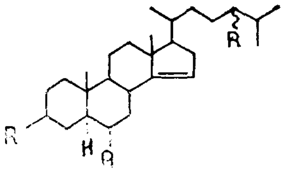
Continuing investigations of the asterosaponins, from an ethanolic extract of the digestive organs of *Asterias amurensis* we have isolated the total glycosides, have hydrolyzed them, and have separated the resulting mixture of aglycones on columns with silica gel as described previously [1]. Mass spectrum of the minor genin (I), m/z: 418 (M^+), 400, 382, 289, 271, 253, 159, 129, 111, 99, 97, 96, 95, 81.



I. R = OH

II. R = OAc

Details of the ^1H NMR spectrum of compound (I) (Bruker WH-250) are given in Table 1. It can be seen from a comparison of the values given with the analogous values of 3β,6α-dihydroxy-5α-cholestane (III) (Table 1) that two hydroxy groups in (I) occupy the 3β and 6α positions.

When the protons giving the multiplet at 3.60 ppm were irradiated, the multiplet at 1.87 ppm collapsed. The same multiplet was obtained by differential decoupling, starting from the signals of the 26,27-methyl groups. It followed from this that the third OH group was located at C-24.

TABLE 1. NMR Spectra of Compounds (I), (II), and (III) (δ´ TMS = 0)*

Atom	I (C_5D_5N)	II ($CDCl_3$)	III (C_5D_5N)
H-3	3,93 m	4,70 m	3,94 m
H-4e	3,08(12,5) dm		3,07(12,6) dm
H-4a	1,72(11,0; 12,4; 12,4) td		1,72(10,8; 12,6; 12,6)td
H-5	1,38(10,3; 12,7; 2,9) ddd		1,38(9,9; 12,6; 2,7) ddd
H-6	3,78 td	4,70 m	3,73 td
H-7e	2,52(3,8; 3,8; 12,0) dt		2,29(3,8; 3,8; 11,8) dt
H-7a	1,62(11,8) q		1,24(10,7; 11,8; 11,8) td
H-15	5,28	5,13 m	
H-16	2,40 m		
H-16′	2,03 m		
H-17	1,66 m		
H-24	3,60 m		
H-25	1,87 m		
3H-18	0,96m	0,91† s (0,90)	0,78s
3H-19	0,91 s	0,88† s (0,87)	1,01 s
3H-21	1,03(6,2) d	0,93(6,1) d	1,08(6,3)d
3H-26,27	1,15; 1,13(6,7) d	0,99(6,1) d	1,00(6,3) d
OAc-6H		2,06 s	
OAc-3H		2,04 s	

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*The magnitudes of the splitting of the multiplets (in parentheses) are given in hertz.

†Assignment of the signals ambiguous.

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By irradiating the multiplet at 5.28 ppm we obtained the signals of one-proton multiplets at 2.20 and 2.40 ppm and of a multiplet at 2.03 ppm. Signals at the position of the 2.20-ppm multiplet were also obtained when H-7e was irradiated; consequently, they related to H-8. It followed from this that the double bond could be present in one of two positions: 9(11) or 14(15). The $\Delta^{9(11)}$ position, was excluded, since double resonance of the protons at C-15 converted the multiplet at 2.40 ppm into a doublet of doublets of doublets with first-order constants of 1.2, 7.3, and 15.0 Hz. If the latter are regarded as geminal, the other two agree only with the 14(15) position of the double bond.

The acetylation of (I) gave (II). Making use of information in the literature [2-4], we calculated the chemical shifts for 3H-18 and 3H-19 in (II) (Table 1, in parentheses). For a compound with a 9(11) double bond, calculation gave values of 0.60 and 0.96 ppm, respectively (0.74 and 0.99 ppm in the spectrum of 3β,6α-diacetoxy-20-hydroxycholest-9(11)-en-23-one [5]).

Thus, it has been shown that the new minor aglycone from A. amurensis is 5α-cholest-14-ene-3β,6α,24ξ-triol.

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