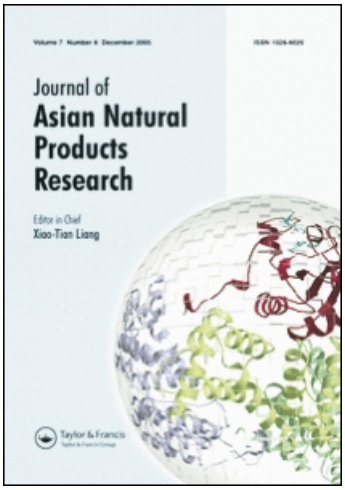

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A new triterpene glycoside from *Asterias rollentoni*

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A new triterpene glycoside, rollentoside A, has been isolated from *Asterias rollentoni* Bell and identified as 3β-*O*-{3-*O*-methyl-β-D-xylopyranosyl-(1 → 3)-*O*-β-D-glucopyranosyl-(1 → 4)-*O*-β-D-quinopyranosyl-(1 → 2)-*O*-β-D-xylopyranosyl}-16-β-acetoxy-23*S*-acetoxy-holost-7-ene (**1**), together with a new natural product, rollentoside B (**2**). The structures of compounds **1** and **2** were elucidated by extensive 1D and 2D NMR investigation (^{1}H–^{1}H COSY, TOCSY, HSQC, HMBC, NOESY).

Keywords: *Asterias rollentoni*; Triterpene saponin; Rollentoide A

1. Introduction

The starfish (Asterias) has received attention from organic chemists, biochemists and pharmacologists as an interesting source of bioactive marine nature products, and various secondary metabolites, including glycosides, sterols, anthranquinones and alkaloids, have been reported [1,2]. There are only a few reports on the chemical constituents of *Asterias rollentoni* Bell [3]. In this paper, we describe the isolation and structure elucidation of one new triterpene glycoside (figure 1) from the ethanol extract of *Asterias rollentoni* Bell.

2. Results and discussion

Compound **1** was isolated as a white amorphous powder with no UV absorption band above 210 nm. The IR (KBr) absorption bands at 3419, 1720, and 1627 cm^{-1} were due to hydroxyl and carbonyl functions. HR-FABMS (positive) showed a $[M + Na]^+$ peak at *m/z* 1181.5730 consistent with the molecular formula $C_{57}H_{90}O_{24}$. ESIMS (positive) gave a $[M + Na]^+$ peak at *m/z* 1181, together with other major fragments at *m/z* 1034 $[M - 147 + Na]^+$ and 1017 $[M - 164 + Na]^+$, corresponding to the sequential loss of *O*-methyl-pentose units.

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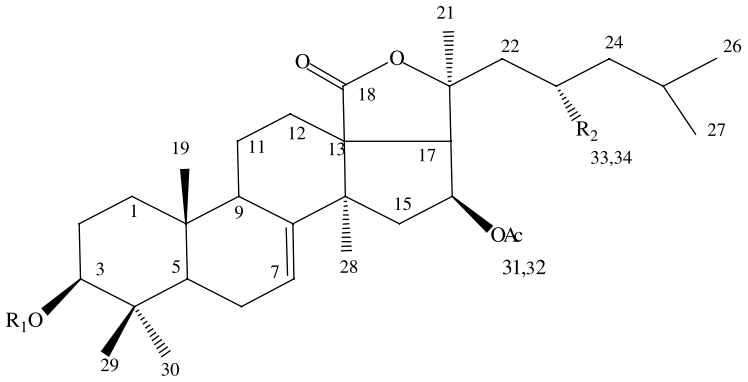

R_1 = 3-*O*-methyl-β-D-xyl- (1→3)-*O*-β-D-glu- (1→4)-*O*-β-D-qui- (1→2)-*O*-β-D-xyl

1 R_2 = OAc

2 R_2 = H

Figure 1. The structures of compounds **1** and **2**.

The ^{1}H-NMR spectrum of **1** (table 1) shows 11 methyl signals at δ 0.85 (d, 3H, $J = 6.6$ Hz), 0.94 (d, 3H, $J = 6.6$ Hz), 1.05 (s, 3H), 1.18 (s, 3H), 1.24 (s, 3H), 1.34 (s, 3H), 1.60 (s, 3H), 1.70 (d, 1H, $J = 5.8$ Hz), 2.05 (s, 3H), 2.17 (s, 3H) and 3.85 (s, 3H), one olefinic proton at δ 5.63 (brs, 1H) and four anomeric signals at δ 5.24 (d, 1H, $J = 7.3$ Hz), 5.17 (d, 1H, $J = 7.6$ Hz), 4.98 (d, 1H, $J = 7.8$ Hz) and 4.82 (d, 1H, $J = 7.4$ Hz). The large J values of the anomeric protons suggest that the four sugar units are all β oriented. Complete analysis of the ^{13}C-NMR and 2D NMR spectra revealed that 30 resonance signals could be assigned to the aglycone, 22 to the oligosaccharide, four to the acetyl and one to the methoxyl. The spectral features of aglycone are very similar to those of holosta-7-ene-3β-ol [4] with two acetoxy groups.

The presence of an acetoxy group at C-16 was deduced from the chemical shift of H-16 (δ 5.96), which showed coupling to the signals at δ 2.74 (H-17), 2.64 (Hα-15) and 1.74 (Hβ-15) in the ^{1}H–^{1}H COSY spectrum, and this correlated with the signal δ 169.79 (OAc) in the HMBC spectrum. Inspection of the NOESY spectrum revealed δ 5.96 (H-16) had a strong NOE effect with δ 2.74 (H-17), 2.64 (Hα-15) and 1.05 (H-28), which showed H-16 is α, leading to a β configuration for the acetoxy group at C-16 (figure 2).

Detailed analysis of the ^{1}H-, ^{13}C- and 2D-NMR spectra determined the position of an acetoxy group at C-23. In the ^{1}H–^{1}H COSY spectrum, the chemical shift of H-23 (δ 5.53) was found to be coupled to the signals at δ 2.44, 2.50 (H-22), and 1.65, 1.18 (H-24), and was correlated with the signal at δ 171.1 (OAc) in the HMBC spectrum. According to the reported value [4], the acetoxy group at C-23 is in the *S* configuration.

Combined analysis of the HMBC, HSQC and ^{1}H–^{1}H COSY spectra, and especially the TOCSY spectrum, clarified that their were sugars present. In the HMBC spectrum, the signal at δ 4.82 (xyl-H-1) was correlated with δ 89.32 (C-3). The position of attachment of the sugar chain, and the $^3J_{C-H}$ correlations between the anomeric protons (δ 5.17, 4.98, 5.24) and the corresponding carbons (δ 84.54, 87.66, 87.16) were observed in the HMBC spectrum, revealing the sugar sequence (table 1).

Table 1. ^{1}H- and ^{13}C-NMR data for **1** and **2** in C_5D_5N.

	1		***2***	
	^{13}C	^{1}H	^{13}C	^{1}H
1	36.3 t	1.50	36.3	
2	27.7 t	2.03, 2.20	27.4	
3	89.3 d	3.35	89.4	3.35
4	39.7 s		39.8	
5	47.9 d	1.03	47.6	
6	23.4 t	2.04	23.4	
7	120.6 d	5.63	120.5	5.67
8	145.7 s		145.8	
9	47.2 d	3.41	47.2	
10	35.7 s		35.7	
11	22.7 t	1.76, 1.48	22.7	
12	31.3 t	1.88, 1.97	31.5	
13	59.0 s		59.4	
14	47.6 s		47.6	
15	43.9 t	2.64, 1.74	43.7	
16	75.7 d	5.96	75.0	5.96
17	56.1 d	2.74	54.7	
18	179.4 s		179.6	
19	24.1 q	1.24	24.1	1.24
20	83.9 s		85.2	
21	28.9 q	1.60	28.4	1.60
22	43.9 t	2.44, 2.50	39.3	
23	68.8 d	5.53	22.9	
24	45.6 t	1.65, 1.18	39.8	
25	24.6 d	1.58	28.3	
26	21.8 q	0.94	22.4	0.84
27	23.6 q	0.85	22.9	0.84
28	32.5 q	1.05	33.3	1.06
29	17.4 q	1.18	17.4	1.18
30	28.8 q	1.34	28.8	1.35
31	169.8 s		169.8	
32	21.4 q	2.05	21.4	2.05
33	171.6 s			
34	21.6 q	2.17		
Xyl				
1	105.7 d	4.80	105.7	4.82
2	84.5 d	4.06	84.5	
3	78.4 d	4.22	78.3	
4	70.9 d	4.20	70.8	
5	66.9 t	4.33, 3.69	66.9	
Qui				
1	105.8 d	5.17	105.8	5.17
2	76.5 d	4.09	76.5	
3	76.1 d	4.12	76.1	
4	87.7 d	3.69	87.7	
5	71.7 d	3.82	71.7	
6	18.3 q	1.76	18.3	
Glc				
1	105.1 d	4.98	105.2	4.98
2	74.1 d	4.04	74.0	
3	87.2 d	4.24	87.1	
4	70.2 d	4.08	70.2	
5	78.2 d	4.05	78.2	
6	62.4 t	4.53, 4.22	62.4	
Xyl				
1	106.2 d	5.24	106.2	5.26
2	74.9 d	3.92	74.8	
3	87.9 d	3.66	87.9	
4	69.7 d	4.05	69.6	
5	67.2 t	4.21	67.2	

Table 1 – *continued*

	1		***2***	
	^{13}C	^{1}H	^{13}C	^{1}H
OCH_3	60.8 q	3.85	60.8	3.85

Chemical shifts are relative to internal TMS.

Based on the above analysis and comparison of the spectral data with those of known compounds [5–7], compound **1** was elucidated as 3β-*O*-{3-*O*-methyl-β-D-xylopyranosyl-(1 → 3)-*O*-β-D-glucopyranosyl-(1 → 4)-*O*-β-D-quinopyranosyl-(1 → 2)-*O*-β-D-xylopyranosyl}-16-β-acetoxy-23*S*-acetoxy-holost-7-ene, which we called rollentoside A.

Compound **2** was identified as 3β-*O*-{3-*O*-methyl-β-D-xylopyranosyl-(1 → 3)-*O*-β-D-glucopyranosyl-(1 → 4)-*O*-β-D-quinopyranosyl-(1 → 2)-*O*-β-D-xylopyranosyl}-16-β-acetoxy-holost-7-ene, which we named rollentoside B [8].

3. Experimental

3.1 General experimental procedures

Melting points were measured on a Yanaco micro-hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin IFS-55 spectrophotometer. NMR spectra were recorded on a Bruker-ARX-600 spectrometer (^{1}H at 300 MHz and ^{13}C at 75 MHz) with TMS as internal standard. The HR-FABMS spectra were determined by

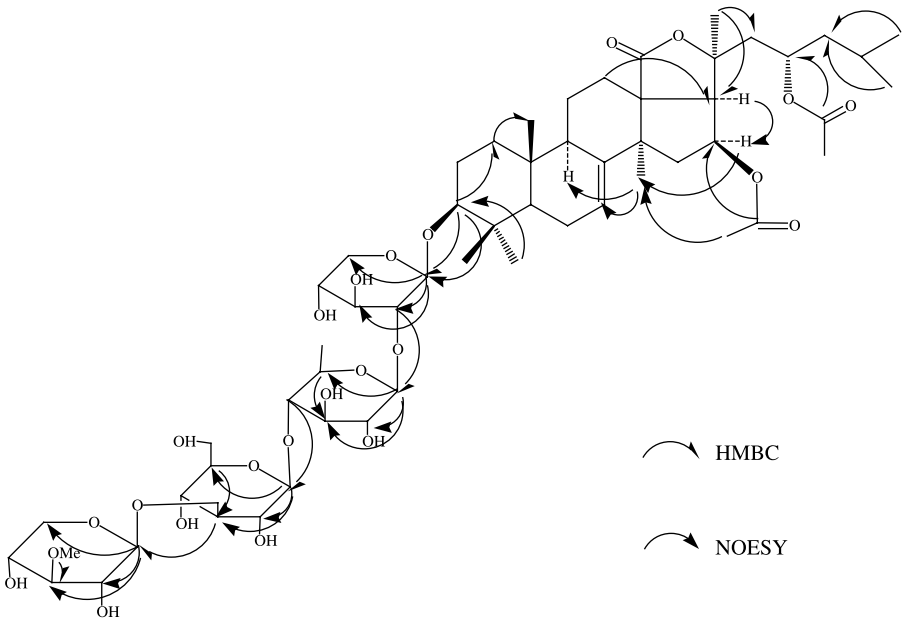

Figure 2. The key HMBC and NOESY correlations of **1**.

a MAT-95 mass spectrometer. ESIMS spectra were recorded on an LC-MSD-Trap-SL (Agilent). HPLC was performed using a Shimadzu LC-8A on a Shimadzu PRC ODS. Column chromatography was performed using silica gel G (200–300 mesh, Qingdao Haiyang Chemical Factory).

3.2 Animal material

Dry bodies of *Asterias rollentoni* Bell were collected from Lianyungang, Jiangsu, China, and identified by Professor Guo You Wu. A voucher specimen has been deposited at the School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University.

3.3 Extraction and isolation

The dry bodies of *Asterias rollentoni* Bell (5 kg) were extracted repeatedly with 70% EtOH (50 l × 3). The EtOH solution was concentrated *in vacuo* to give a reside (480 g), which was dissolved in water and further fractionated with petroleum ether (60–90%), EtOAc and *n*-butanol, respectively. The EtOAc fraction (11.5 g) was chromatographed on a silica gel column, and eluted with $CHCl_3$–MeOH (100:0 to 50:100, v/v, each 1000 ml) mixtures of increasing polarity to yield eight fractions. Fraction 7 (100 mg) was further purified by HPLC (ODS, 10 μm, 20 mm × 250 mm, MeOH–H_2O = 7:3) to afford rollentoside A (10 mg) and rollentoside B (5 mg).

3.3.1 Rollentoside A. White amorphous powder; mp 213–215°C ($CHCl_3$–MeOH = 1:1); $[\alpha]_D^{25}$ −6.3 (*c* 0.1, $CHCl_3$–MeOH = 1:1); HR-FAB-MS *m/z*: 1181.5730 (calcd for $C_{57}H_{90}O_{24}Na$, 1181.5719); ESIMS (positive) *m/z*: 1181, 1034, 1017; ESIMS (negative) *m/z*: 1194, 1157, 1115; ^{1}H- and ^{13}C-NMR see table 1.

3.3.2 Rollentoside B. White amorphous powder; mp 209–212°C ($CHCl_3$–MeOH = 1:1); $[\alpha]_D^{25}$ −6.2 (*c* 0.01, $CHCl_3$–MeOH = 1:1); HR-FAB-MS *m/z*: 1123.5728 (calcd for $C_{55}H_{88}O_{22}Na$, 1123.5664); ESIMS (positive) *m/z*: 1123; ESIMS (negative) *m/z*: 1135, 1099; ^{1}H- and ^{13}C-NMR see table 1.

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