Chinese Chemical Letters Vol. 15, No. 2, pp 200 – 203, 2004
http://www.imm.ac.cn/journal/ccl.html

Three New C_{21} Steroidal Glycosides from the Roots of *Cynanchum komarovii* Al.Iljinski

Li Qin WANG [1], Yue Mao SHEN [1], Yu Qing WEI [2], Xing XU [2], Jun ZHOU[1] *

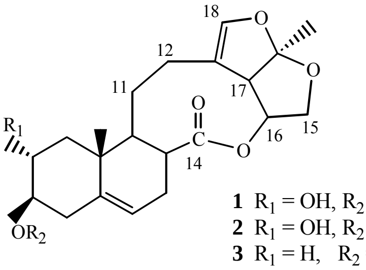
[1]State Key Laboratory of Phytochemistry and Plant Resources in West China,
Kunming Institute of Botany, Kunming 650204
[2]Ningxia Agriculture Bio-technological Key lab, Yinchuan 750002

Abstract: Three new C_{21} steroidal glycosides named komaroside A, komaroside B, komaroside C were isolated from the ethanolic extract of the roots of *Cynanchum komarovii* Al.Iljinski (Asclepiadaceae), their structures were determined by physiochemical and spectroscopic analysis.

Keywords: *Cynanchum komarovii* Al.Iljinski, Asclepiadaceae, komaroside A, B, C.

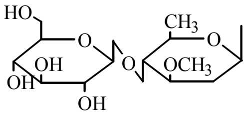
Cynanchum komarovii Al.Iljinski, is a shrub widely distributed in the northwest desert area of China. The chemical constituents of this plant have been investigated [1,2]. In order to further investigate the constituents of this plant, the roots (14.5kg) collected in *Ningxia Hui Autonomous District* were extracted with 95% EtOH. The alcoholic extract was partitioned between chloroform and water, the chloroform part was repeatedly chromatographied over silica gel, RP-18 and Sephadex LH-20 to afford three new compounds, their structures were determined by physiochemical and spectroscopic analysis, especially by 1D and 2D NMR spectroscopy.

Compound **1** was obtained as yellow amorphous, $[\alpha]_D^{18.7}$ -19.6 (c 0.404, CH_3OH), its molecular formula was determined as $C_{34}H_{50}O_{14}$ (681.3151, calcd. 681.3122) by its HRFABMS and NMR spectrum. Infrared (IR) absorptions at 3432 and 1735cm^{-1} showed the presence of hydroxyl and ester groups which were supported by ^{13}C-NMR signals at δ 69.8, δ 175.3. The ^1H-NMR spectrum of **1** showed two methyl signals of the aglycone moiety at δ_H 0.90 (s, 3H, H-19), 1.53 (s, 3H, H-21), one olefinic proton

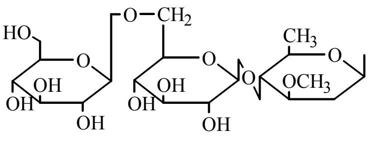


1 $R_1 = OH$, $R_2 = A$
2 $R_1 = OH$, $R_2 = B$
3 $R_1 = H$, $R_2 = B$

A=



B=



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[*] E-mail: jzhou@mail.kib.ac.cn

Table 1 The ^{1}HNMR(400 MHz) and ^{13}CNMR(100 MHz) Spectral Data of **1**, **2**, **3** (δ ppm, J Hz, in C_5D_5N)

	1(δ_H)	**1**(δ_C)	**2**(δ_H)	**2**(δ_C)	**3**(δ_H)	**3**(δ_C)	HMBC(H→C)
1α	2.42 m	44.7	2.45 m	44.8	1.79 m	36.5	2, 3, 10
1β	1.22 m		1.22 m		0.95 m		
2α		69.8		69.9	1.42 m	30.1	1, 3
2β	3.97 m		4.06 m		2.10 m		
3α	3.64 m	84.9	3.62 m	85.1	3.72 m	77.6	1′
4α	2.50 m	37.3	2.58 m	37.5	2.63 m	39.1	5
4β	2.47 m		2.44 m		2.47 m		
5	\	139.7	\	139.8	\	140.7	\
6	5.44 m	120.8	5.45 m	120.9	5.44 m	120.7.	4, 7, 10
7α	2.48 m	28.4	2.58 m	28.6	2.08 m	30.0	9
7β	2.09 m		1.96 m		1.70 m		
8	2.42 m	52.9.	2.51 m	53.1	2.50 m	53.3	10, 11, 12
9	1.23 m	40.1	1.33 m	40.3	1.24m	40.8	14
10	\	39.4	\	39.6	\	38.8	\
11α	1.33 m	23.8	1.32 m	23.9	1.42 m	24.0	9, 10, 12
11β	2.47 m		2.52 m		2.60 m		
12α	2.65 m	29.9	2.63 m	30.1	2.63 m	28.5	13
12β	2.11 m		2.17 m		2.16 m		
13	\	114.3	\	114.5	\	114.5	\
14	\	175.3	\	175.5	\	175.6	\
15α	4.25 m	67.8	4.33 m	67.8	4.28 m	67.8	17, 20
15β	3.95 m		3.95 m		3.97 m		
16	5.43 m	75.5	5.44 m	75.6	5.48 m	75.6	13, 14, 15
17	3.52 overlap	56.1	3.55 d, 8.7	56.2	3.56 d, 8.1	56.3	
18	6.49 s	143.8	6.52 s	143.9	6.49 s	143.9	13, 18, 20
19	0.90 s, 3H	18.5	0.91 s, 3H	19.1	0.85 s, 3H	18.0	1, 9, 10
20	\	118.5	\	118.6	\	118.6	
21	1.53 s, 3H	24.8	1.54 s, 3H	24.9	1.54 s, 3H	24.9	17, 20
		B-D-ole		β-D-ole		β-D-ole	
1′	4.79 d, 9.2	98.8	4.83 d, 7.4	99.2	4.81 d, 8.1	98.3	2′, 3
2′a	1.78 dd, 10.8, 10.8	37.4	1.92 dd, 9.4, 9.1	37.8	1.94 dd, 9.7, 8.9	38.0	
2′e	2.43 m		2.48 m		2.47 m		1′, 3′
3′	3.93 m	79.3	3.64 m	79.3	3.67 m	79.6	\
4′	3.73 m	82.9	3.88 m	82.9	3.85 m	83.4	\
5′	3.69 m	72.1	4.08 m	71.8	4.26 m	71.8	\
6′	1.69 d 3H, 5.3	18.5	1.68 d, 3H, 6.1	18.6	1.72 d, 3H, 6.0	18.9	4′, 5′
OMe	3.53 s, 3H	57.2	3.60 s, 3H	57.8	3.58 s, 3H	57.7	3′
		B-D-glc		β-D-glc		β-D-glc	
1″	5.08 d, 7.3	104.4	5.04 d, 7.7	104.4	5.04 d, 8.1	104.4	4′, 3″
2″	3.95 m	75.7	3.93 m	75.7	4.15 m	75.5	\
3″	4.25 m	78.1	4.10 m	77.6	4.07 m	77.6	\
4″	4.20 m	71.8	4.22 m	71.8	4.21 m	71.8	\
5″	4.53 m	78.5	4.18,m	78.7	4.22 m	78.7	\
6″	4.20 m 4.53 d, 11.3	62.9	4.38 m 4.85 d, 12.4	70.0	4.82 m 4.42 d, 12.5	70.0	1‴
				β-D-glc		β-D-glc	
1‴			5.26 d, 8.1	105.2	5.24 d, 7.7	105.2	4″
2‴			4.35 m	75.6	4.25 m	75.5	\
3‴			4.08 m	78.4	4.08 m	78.3*	\
4″			3.72 m	72.4	3.67 m	72.2	\
5‴			4.01 m	78.4	4.16 m	78.4*	\
6‴			4.55 d, 12.4 4.38 m	62.9	4.55 m 4.44 m	62.9	\

*Interchangeable

signals at δ_H 5.44 (m, 1H, 6-CH), one olefinic deshielded proton at δ_H 6.49 (s) assigned to the proton on the trisubstituted double bond, three protons adjacent to oxygen at δ_H 3.95 (m), 4.25 (m), 5.43 (m), two hydroxy-methine proton at δ_H 3.97, 3.64, all of these data were consistent with glaucogenin A[3]. And the ^{13}C-NMR spectral data were also very similar to those of glaucogenin A[3]. Two sugars of β-linkage were revealed by the coupling constants of anomeric proton signals at δ_H 5.08 (d, 1H, 7.3Hz), 4.79 (d, 1H, J=9.2Hz). The^{13}C-NMR spectrum of **1 (Table 1)** indicated the presence of oleandrose and glucose comparing with those of the methyl glycosides. The glycosidation shifts were observed at C-2 (-2.6 ppm), C-3 (+8.2 ppm), and C-4 (-2.8 ppm) in the aglycone moiety comparing with glaucogenin A [3], therefore the sugar moiety was linked to the C-3 hydroxyl group of the aglycone. The HMBC and HMQC experiments of **1** showed ^{1}H-^{13}C long-range correlation between the doublet at δ_H 4.79 (β-D-ole H-1′, δc 98.8) and C-3 (δc 84.9 ppm), between δ_H 5.08 (β-D-glc H-1″, δc 104.4) and δc 82.9 ppm (β-D-ole C–4′), so the connection between the sugars was (1→4), the terminal sugar was glucose and the inner sugar was oleandrose respectively. Thus, the structure of **1** was proposed to be glaucogenin A 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-oleandropyranoside, named komaroside A.

Compound **2** was obtained as yellow amorphous, $[\alpha]_D^{21.0}$ –6.8 (*c* 0.293, C_5H_5N), its molecular formula was determined as $C_{40}H_{60}O_{19}$ (843.3655 [M-H], calad. 843.3651) by its HRFABMS and NMR spectrum. The ^{1}H-NMR spectrum of **2** showed three anomeric proton signals at δ_H 5.26 (d, 1H, 8.1Hz), 5.04 (d, 1H, 7.7Hz), 4.83 (d, 1H, J=7.4Hz), indicating the presence of three sugars with β-linkage. The terminal β-D-glucopyranose signals were confirmed by HMBC and HMQC experiments. The NMR spectral data on the aglycone moiety of glycoside **2** were almost the same as those of **1** (**Table 1**). Therefore, **2** also consisted of glaucogenin A with sugar linkage at its C-3 hydroxyl group. The glycosidation shifts was observed at C-6 of the middle sugar β-D-glucose, to which the terminal glucose was linked. The other signals were nicely corresponded to those of **1**. The HMQC and HMBC experiments confirmed the 1→4 linkage between the inner oleandrose and the middle glucose, the 1→6 linkage between the middle glucose and the terminal glucose. Consequently the structure of **2** was deduced to be glaucogeinn A 3-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl-(1→4)-β-D-oleandropyranoside, named komaroside B.

Compound **3** was also obtained as yellow amorphous, $[\alpha]_D^{21.4}$ –28.9 (*c* 0.329, C_5H_5N), its molecular formula was determined as $C_{40}H_{60}O_{18}$ (827.3701 [M-H], calcd. 827.3695) by its HRFABMS and NMR spectrum. Comparing the ^{1}H-NMR spectrum of **3** with that of **2**, both were closely related except for the H-2 appeared as two protons at δ 1.42 and 2.10 which showed there was no hydroxyl group at C-2, and the H-1 shift slightly to high field, this fact was consistent with glaucogenin C[4]. Three sugars with β-linkage were revealed by the coupling constants of anomeric proton signals at δH 5.24 (d, 1H, 7.7Hz), 5.04 (d, 1H, 8.1Hz), 4.81 (d, 1H, 8.1Hz). The ^{13}C-NMR spectrum of **3** (**Table 1**) indicated the aglycone of **3** was very similar to those of glaucogenin C [4], and the data of sugar moieties was closely to that of **2**. The HMQC and HMBC experiments also confirmed the sugar moieties of **3** was the same as that of **2**. The glycosidation shifts were observed at C-2 (-2.3 ppm), C-3 (+7.9 ppm), and C-4 (-2.7ppm) in the aglycone moiety comparing with glaucogenin C [4], indicating that the sugar chain was linked to the C-3 hydroxyl group of the aglycone. From the above, the structure of **3** was deduced to be glaucogenin C 3-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl -(1→4)- β-D-oleandropyranoside, named komaroside C.

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Received 5 March, 2003