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Note

Two new flavonoids from *Mosla soochouensis* Matsuda

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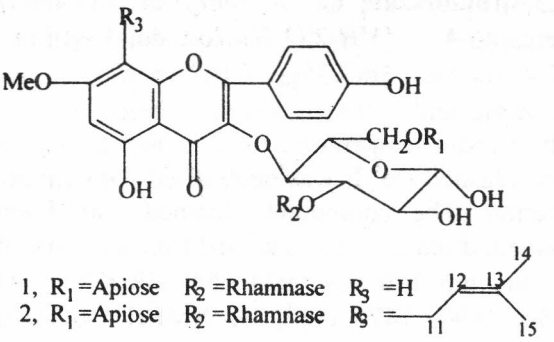
Two new flavone glucosides have been isolated from *Mosla soochouensis* Matsuda together with three known flavonoids. The structures of new flavoneglucosides have been elucidated to be rhamnocitrin-3-*O*-[α-L-rham-nopyranosyl (1→3)]-*O*-[β-D-apiofuranosyl (1→6)]-4-*O*-β-D-glucopyranoside **1** and 8-isoprenyl-rhamnocitrin-3-*O*-[α-L-rhamnopyranosyl (1→3)]-*O*-[β-D-apiofuranosyl (1→6)]-4-*O*-β-D-glucopyranoside **2**, by the methods of chemical and spectral analysis.

Mosla soochouensis Matsuda is a traditional Chinese drug growing mainly in Zhejiang, Jiangsu and Gansu provinces of China, which can cure typhoid fever, dysentery and stomach aches, etc.[1]. Its chemical constituents, however, have not been reported so far. We have made an intensive phytochemical work on this plant, and isolated five flavonoids, two of them being new flavone glycosides.

The known flavonoids, morin-7-*O*-β-D-glucoside[2], kaempferol-3-*O*-β-D-glucoside[2], and luteolin-5-*O*-β-D-glucoside[2], were identified by comparing their spectral data with those of authentic samples or with those reported in the literature. In the present note, the structural elucidation of two new flavone glucosides is reported.

Results and Discussion

Compound **1**, was obtained as yellow fragmentary crystals, m.p. 268-70°C. Both HCl-Mg and Molish tests gave positive reaction. Its spot by PLC gave a strong yellow fluorescence under UV lamp when fumigated with NH_3 vapour, indicating **1** to be a flavonoid. Its yellow colour disappeared on zirconium oxychloride-citric acid reaction, which supported the presence of hydroxyl at C-5 and not



1, R_1 =Apiose R_2 =Rhamnase R_3 =H
2, R_1 =Apiose R_2 =Rhamnase R_3 =

The structures of compounds of 1 and 2

Figure 1

at C-3. In the UV spectrum, its band I showed 24nm bathochromic shift with H_3BO_3-NaOAc, which further supported a phenolic hydroxyl at C-4′ of ring B[3]. Its IR spectrum also exhibited bands at 3380 (hydroxyl), 1660 (conjugated carboxyl), 1600, 1500 (benzene ring), and 1080, 1020 cm^{-1} (ester bond). Its ^{1}HNMR spectra showed signals at δ 7.10 and 8.19 (each 2H, d, *J*=8.0Hz) due to the A_2B_2 system of ring B substituted in the C-4′, at δ 12.45 and δ 11.9 (each 1H, s) due to two hydroxyl protons at C-5′ and C-4′, at δ 4.91 (1H, d, *J*=2.4 Hz), at δ 5.20 (1H, d, *J*=2.1 Hz) and δ 4.38 (1H, d, *J*=8.0 Hz) due to anomeric protons of three sugars, and signal at δ 3.83 (3H,s) was attributed to CH_3O-7. Irradiation of the signal of HO-5 (δ 12.45) and CH_3O-7 (δ3.83) gave 16.8% and 27.3% nOe effects at δ 6.31 (H-6), respectively. Furthermore, irradiation of the HO-4′ (δ 11.9) signal caused 12.7% and 10.8% nOe effects at δ 7.11 (H-5′) and δ 7.10 (H-3′), respectively (Table I). This clearly indicated that one methoxy and two hydroxy were at C-7, C-5 and C-4′, respectively.

Compound **1** on acid hydrolysis gave D-glucose, L-rhamnose and D-apiose, respectively. In ^{13}CNMR spectra of **1**, the downfield signals at δ 4.1 and 5.3 were assigned to C-6 and C-3 of the inner D-glucopyranoside linked to the terminal apiosyl and rhamnosyl. The signal at δ 4.94 was assigned to the C-4 of glucopyranoside which is linked to aglycone. Furthermore, the linkage between these sugars was established from the following HMBC

Table I—^{1}HNMR spectra of compounds **1** and **2**

H	1	2	J (Hz)
6	6.31d	6.30d	2.1
8	6.78d	6.76d	2.0
OMe	3.83s	3.83s	
OH	12.46s	12.42s	
2′	8.19d	8.17d	8.0
3′	7.10d	7.10d	8.0
5′	7.11d	7.10d	8.0
6′	8.19d	8.17d	8.0
OH	9.10s	9.08s	
Prenyl		1.62s	
Me		1.63s	
-C=CH		5.13t	
-CH_2		3.16d	
Glucose			
1	4.36d	4.38d	8.0
2	3.38dd	3.34dd	8.0/9.3
3	5.30t	5.28t	9.3
4	4.94t	4.91t	9.3
5	3.79	3.81	
6a	4.15-4.45	4.11-4.39	
6b	4.20-4.47	4.23-4.48	
Rhamnose			
1	5.18d	5.21d	2.1
2	3.90m*	3.93m*	
3	3.50m*	3.48m*	
4	3.28t	3.26t	9.5
5	3.55m*	3.55m*	
6	1.07d	1.07d	6.0
Apiose			
1	4.91d	4.94d	2.4
2	3.84d	3.84d	2.4
4a	3.74m*	3.74m*	
4b	3.92m*	3.90m*	
5	3.53s	3.50s	

*Interchangeable

Table II—^{13}CNMR spectra of compounds **1** and **2**

C	1	2	DEPT
2	147.0	147.2	C
3	136.0	136.1	C
4	175.7	175.5	C
5	156.0	155.9	C
6	97.0	97.2	CH
7	164.6	164.9	C
8	91.5	105.84*	CH(C)
9	160.4	160.1	C
10	103.4	103.3	C
11	31.8		CH_2
12	120.1		CH
13	134.5		C
14	17.7		CH_3
15	25.8		CH_3
1′	121.8	121.6	
2′	129.0	128.9	CH
3′	115.0	115.3	CH
4′	159.8	162.4	C
5′	115.0	115.4	CH
6′	129.0	129.0	CH
OMe	56.2		CH_3
Glucose			
1	96.6	96.9	CH
2	76.5	76.9	CH
3	80.3	80.5	CH
4	76.9	76.7	CH
5	76.3	76.1	CH
6	63.2	63.0	CH_2
Rhamnose			
1	103.4	103.9	CH
2	73.0	72.9	CH
3	72.9	73.1	CH
4	74.4	74.0	CH
5	71.2	71.5	CH
6	19.2	19.0	CH_2
Apiose			
1	108.9	109.0	CH
2	77.1	77.0	CH
3	79.8	79.4	C
4	75.8	75.9	CH_2
5	65.8	65.2	CH_2

*Interchangeable

correlations: H-1 of rhamnose with C-3 of glucose, and H-1 of apiose with C-6 of glucose. In addition, a strong correlation between H-4 of glucose and C-3 of aglycone further verified the connection of the trisaccharide chain to C-3 of the aglycone. The EI-MS spectrum supported the structure of aglycone which exhibited a prominent peaks at m/z 300,271,257,167,150,144,121. The spectral (MS,IR,UV,^{1}H and ^{13}CNMR) spectra of aglycone, were identical with authentic rhamnocitrin[4]. Hence, **1**, has been formulated as rhamnocitrin-3-*O*-[α-L-rhamno pyranosyl (1→3)]-*O*-[β-D-apiofuranosyl (1→6)]-4-*O*-β-D-glucopyranoside. Its structure was further confirmed by ^{13}C NMR spectral data (see Table II).

Though the spectral (IR, MS, UV, ^{1}H and ^{13}CNMR) data of **2**, are very similar to those of **1**, it showed slight difference in the ^{1}HNMR spectra owing to the presence of signals at δ 1.63, 1.62, 3.16 and 5.13 for isoprenyl group linked to C-8 . It was further supported by the downfield shifting of C-8 signal by 14.34 ppm in ^{13}CNMR spectra of **2**(see Table II) as compared to that of **1**[5]. The position of the linkage and configuration of the sugar moieties were established by comparing the ^{13}CNMR and ^{1}HNMR signals of **1** and **2**, together with ^{13}C-^{1}H long-range coupling correlations with ^{13}C-^{1}H long-range coupling correlations (HMBC). In addition, the characteristic chemical

reaction of **2** also indicated that it was a flavone glucoside. Therefore, the structure of **2** was characterized as 8-isoprenyl-rhamnocritrin-3-*O*-[α-L-rhamnopyranosyl (1→3)]-*O*-[β-D- apiofuranosyl) (1→6)]-4-*O*-β-D-glucopyranoside, which was confirmed by its ^{13}CNMR spectral data (see Table II).

Experimental Section

Melting points were determined with PHMK 79/2212 trace melting point apparatus (uncorrected). IR spectra in KBr disks were recorded on IR, Alpacentenr FTIR spectrometer (Japan); ^{1}HNMR spectra on a JEOL TMNGX 400NMR spectrometer (chemical shifts in δ, ppm downfield from TMS internal standard); mass spectra on MS,JEOL JMS-DS 300 mass spectrometer; and spectra UV, on UV-300 spectrometer(Japan). Silica gel (200-300 mesh, 100-200 mesh) and polyamide (120-160 mesh) were used for column chromatography.

Collection of plant material. The whole plants of *Mosla soochouensis* were collected from the south of Gansu province of China, in June 1993; Vocher deposited in the Herbarium of the Botany Department, Northwest Normal University, Lanzhou 730070, P R China.

Extraction and Isolation. The air dried plant material (10kg) was refluxed with 95% EtOH (×3, each 4h). The EtOH extract was further extracted with petrol-ether (b.p. 60-90°C), CH_2Cl_2, AcOEt and *n*-BuOH, successively. The AcOEt extract (40g) was first separated by polyamide column chromatography (100g, lower pressure) affording two fractions. A abd B, using a MeOH-H_2O gradient(7:3-3:7). Followed by rechromatography from a $CHCl_3$-MeOH gradient (10:2-2:10), Fr.A gave **2** (12mg, R_f,0.85) and Fr.B gave morin-7-*O*-β-D-glucoside (17mg, R_f,0.67). The *n*-BuOH extract (60g) was charged on polyamide column (600g), eluting with H_2O-MeOH and $CHCl_3$-MeOH-MeCOEt-Me_2CO gradients, successively, to yield kemp-ferol-3-*O*-β-D-glucoside (25 mg, R_f, 0.77) and **2** (18mg, R_f, 0.95). Another *n*-BuOH extract (40g) afforded luteolin-5-*O*-β-D-glucoside (20mg, R_f, 0.88) by CC(polyamide 300g and diatom earth 150g) using a MeOH-$CHCl_3$ gradient.

Compound 1. Yellow fragmentary crystals, m.p. 268-70°C, FAB-MS: m/z 741 (M^++1) (Calc. for $C_{33}H_{40}O_{19}$). UV (λ MeOH) (nm): 267,309, 342; IR ν(KBr) 3380, 1660, 1600, 1500, 1080, 1020cm^{-1} EI-MS(aglycone): m/z 300 (M^+,100), 299 (24), 285 (5), 282(13), 271(18), 257(10), 167(27), 151(12), 144(30), 134(18), 121(45), 93(22).

Compound 2. Yellow crystalline powder m.p. 272-73°C, FAB-MS: m/z 809 (M^++1) (Calc. for $C_{38}H_{48}O_{19}$); UV (λ MeOH) (nm): 272 (sh), 328; 339(sh); λ ($AlCl_3$) (nm): 260(sh), 278,326,384; EI-MS(aglycone): m/z 368 (M^+, 83), 313(100), 312 (60), 298 (7), 284(16), 270(11), 179(27), 134(7), 121(47), 93(22).

^{1}H and ^{13}CNMR data of **1** and **2** are listed in Tables I and II.

Acknowledgement

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References

1 Dictionary of Traditional Chinese Drugs, (Science and Technology Press, Shanghai), **1985**, p 94.
2 Zheng S Z, Li X R & Shen X W, *Acta Botanica Sinica,* 34, **1992**, 705.
3 *Identification Handbook of Flavonoids,* (Science Press, Beijing), 610, **1981**, p 399-410.
4 Cheng D L, Sun Q R, Zhu Z Q, Nin G J, *Acta Botanica Sinica*, 28, **1986**, 404.
5 Marham K R & Chai V M, *Carbon-^{13}NMR Spectroscopy of flavonoids,* in *The flavonoids Advances in Research* Isted, vol 67, edited by J B Harbone and T J Mabry, (London, New York, Chapman & Hall), **1986**, 19-51.