Indian Journal of Chemistry
Vol. 41B, June 2002, pp. 1319-1320

Note

The flavonoids from *Polygonum aviculare*

Liping Sun*, Shangzhen Zheng, Jinxin Wang & Xuwei Shen

Department of Chemistry, Northwest Normal University, Lanzhou 730070, P. R. China

and

Xudong Zheng

Department of Chemistry, Qingyang Teachers' College, Qingyang, 745000, P. R. China

Received 11 February 2000; accepted (revised) 8 June 2001

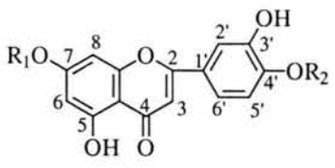
A new flavonoid, 5, 3′-dihydroxy-4′-*O*-angeloxyflavone –7-*O*-β-D-glucopyranoside **1** has been isolated from *Polygonum aviculare*, together with quercetin –3-*O*-α-L-arabifuranoside (**2**, avicularin), luteolin-7-*O*-β-D-glucopyranoside **3**, luteolin-5-*O*-β-D-glucopyranoside **4**, quercetin-3-*O*-β-D-glucopyranoside **5** and vitexin **6** and their structures have been established by spectroscopic methods and chemical reactions.

Polygonum aviculare is a traditional Chinese drug, which cures jaundice, roundworms and piles[1]. To our knowledge, flavonoids, stilbenes and terpenoids have been isolated from the species of south China[2, 3]. We report here the isolation and structure elucidation of a novel flavonoid along with five known flavonoids from this species collected in Qingyang county of Gansu province in Northwest of China.

Results and Discussion

Flavonoids were isolated from the ethanol extract of the whole plant of *Polygonum aviculare* L. Compound **1** was isolated along with the known flavonoids, quercetin –3-*O*-α-L-arabifuranoside (**2**, avicularin), luteolin-7-*O*-β-D-glucopyranoside **3**, luteolin-5-*O*-β-D-glucopyranoside **4**, quercetin-3-*O*-β-D-glucopyranoside **5** and vitexin **6** by comparison of their ^{1}HNMR and ^{13}CNMR data with reported data[4, 5].

Compound **1**, was obtained as yellow crystals, mp 253-54°C. Both HCl-Mg and Molish tests gave positive reaction, which indicated **1** to be a flavone glycoside. The UV spectrum of **1** showed a maxima at 256, 294, 356nm, which was typical for flavones and the 5-OH was identified by the bathochromic shift (40nm) observed after addition of $AlCl_3$/HCl to a methanolic solution of **1**. The FAB-MS gave a pseudomolecular ion at m/z 531 (M^++H). In the ^{1}HNMR spectrum, two doublets at δ 6. 76 and 6. 84 with a coupling constant of 2. 2Hz typical of two *meta* coupled protons, were assigned to H-6 and H-8, respectively. Its ^{1}H NMR spectra also showed signals at δ 12. 57 (5-OH), 9. 45 (1H, s, 3′-OH), 6. 95 (1H, d, *J*=8.0 Hz, 5′-H), 7. 46 (1H, dd, 2′, 6′-H) and 5. 08 (1H, *J*=7. 2Hz, due to anomeric proton of sugar). Acid hydrolysis of **1** released a glucose identified by TLC comparison with an authentic sample. The connecting position of the sugar was established using HMBC technique. A correlation was observed between the anomeric proton signal of glucose (δ5. 08, 1H, *J*=7. 2Hz) and the C-7 (δ164. 9), which indicated that glucosyl group was at C-7.



3 R_1= glc, R_2= H

1 R_1= glc, R_2= ang

Figure 1. The structures of compounds **1** and **3**

Comparison of ^{1}HNMR data of **1** with luteolin-7-*O*-β-D-glucopyranoside **3** showed that **1** and **3** were similar except for the presence of a angeloxy group of signals at δ 6. 10 (d, *J* =7Hz, 3‴-H), 1. 94 (3H, d, *J*=1. 5Hz, 4‴-CH_3), 1. 82 (3H, d, *J*=1. 5Hz, 5‴-CH_3), which was proved by the ion at m/z 83 ($C_5H_7O^+$) and ^{13}CNMR signal at δ169.8. The connecting position of the angeloxy group was established using HMBC technique. A correlation was observed between the carboxyl (δ169.8) and 5′-H (δ6.95), which indicated that angeloxy group was at C-4′. Thus, **1** was formulated as 5, 3′-dihydroxy-4′-*O*-angeloxyflavone-7-*O*-β-D-glucopyranoside.

Experimental Section

Melting points were determined with PHMK 79/2212 trace melting point apparatus and are uncorrected. IR spectra as KBr disks were recorded on FTIR spectrophotometer (Japan); ^{1}HNMR and ^{13}CNMR, DEPT spectra in DMSO-d_6 on a JEOL TMNG×400 Spectrometer using TMS as internal standard; and UV Spectra on a UV-300 Spectrometer. Silica gel (200-300 mesh, 100-160 mesh) was used for column chromatography.

Table I — ^{13}C NMR chemical shifts of **1** and **3**

C	3(DEPT)	1(DEPT)	HMBC
2	164.6(CH)	164.3(C)	2′,6′-H
3	103.2(CH)	103.0(CH)	2′,6′-H
4	181.6(C)	181.5(C)	
5	161.0(C)	161.1(C)	6,8-H,5-OH
6	99.5(CH)	99.7(CH)	5-OH,8-H
7	162.9(C)	164.9(C)	6-H,1″-H
8	94.9(CH)	94.9(CH)	
9	156.7(C)	156.9(C)	8-H
10	105.4(C)	105.5(C)	5-OH,8-H
1′	121.6(C)	121.4(C)	5′-H,6′-H
2′	113.8(CH)	113.8(CH)	5′-H
3′	145.7(C)	145.7(C)	5′-H
4′	149.7(C)	149.5(C)	6′-H
5′	116.1(CH)	116.0(CH)	2′-H
6′	119.0(CH)	119.0(CH)	2′-H
Glc			
1″	99.9(CH)	99.8(CH)	
2″	70.9(CH)	71.2(CH)	
3″	73.1(CH)	73.1(CH)	
4″	69.5(CH)	69.5(CH)	
5″	77.1(CH)	77.1(CH)	
6″	60.6(CH_2)	60.5(CH_2)	
		ang	
		169.8(C)	5′-H
		127.3(C)	
		137.6(CH)	
		15.9(CH_3)	
		20.1(CH_3)	

Collection of plant material

The whole plant of *Polygonum aviculare* L. was collected from Qingyang district of Gansu province of China in July 1997; a voucher specimen is deposited at Botany Department of Northwest Normal University, Lanzhou, P. R. China.

The whole plant material (4kg) was refluxed with 95% EtOH (×3, each 4hr). The EtOH extract was further extracted successively with petrol-ether (b.p. 60-90°C), $CHCl_3$, EtOAc and *n*-BuOH. Silica gel column chromatography of $CHCl_3$ extract (60g) (EtOEt-EtOAc=90:1-1:90) gave **1** (40mg), **2** (25mg), and **3** (31mg). Polyamide column chromatography of the EtOAc extract (H_2O-MeOH gradients) gave **4** (20mg), **5** (30mg) and **6** (25mg).

Compound **1**. yellow crystals, mp 253-54°C. FAB-MS :m/z 531 (M^++1), 447 (M^+-83), 286 (M^+-162-83+1); UV (MeOH) (nm):256, 294, 356. (λ+MeOH+HCl/$AlCl_3$) (nm):274, 358, 396. ^1H NMR (DMSO-d_6, TMS):δ 12. 57 (1H, s, 5-OH), 9. 45 (1H, s, 3′-OH), 6. 95 (1H, *J*=8. 0Hz, 5′-H), 7. 46 (2H, dd, *J*=2.0 Hz, 8. 0 Hz, 2′, 6′-H), 6. 76 (1H, dd, *J*=1. 5Hz, 6-H), 6. 84 (1H, d, *J*=1. 5Hz, 8-H), 6. 50 (1H, s, 3-H), 5. 08 (1H, d, *J*=7. 0 Hz, anomeric 1″-OH), 6. 10 (1H, d, *J*=7. 0Hz, 3‴-H) ^{13}C NMR data of **1** **(see Table I)**.

Acknowledgement

This work was supported by Natural Science Foundation of Gansu Province, China.

References

1 *Dictionary of Traditional Chinese Drug*, (Science and Technology Press, Shanghai), **1985**, 2329.

2 Xu L X & Liu A R, *Acta Pharm Sin*, 18, **1983**, 700.

3 Kim H J, *J Nat Prod*, 57, **1994**, 581.

4 Panosyan A G, *Khim Farm Zh*, 20, **1986**, 190.

5 Markham K R, Ternai Giger H & Mabry T J, *Tetrahedron*, 34, **1978**, 1389.