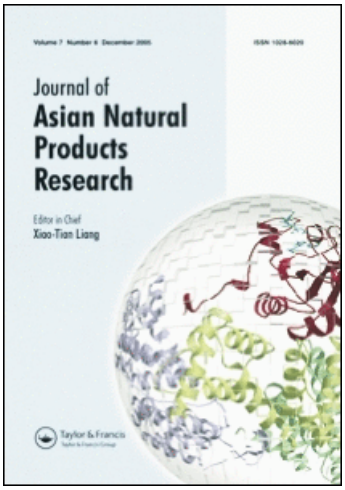

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Two new flavonoid alkaloids from *Senecio argunensis*

Ning Li[a]; Li Shao[a]; Chao-Feng Zhang[a]; Mian Zhang[a]
[a] Key Laboratory of Modern Chinese Medicines, Ministry of Education, Research Department of Pharmacognosy, China Pharmaceutical University, Nanjing, China

To cite this Article Li, Ning , Shao, Li , Zhang, Chao-Feng and Zhang, Mian(2008) 'Two new flavonoid alkaloids from *Senecio argunensis*', Journal of Asian Natural Products Research, 10: 12, 1143 — 1146
To link to this Article: DOI: 10.1080/10286020802361198
URL: http://dx.doi.org/10.1080/10286020802361198

Journal of Asian Natural Products Research
Vol. 10, No. 12, December 2008, 1143–1146

Two new flavonoid alkaloids from *Senecio argunensis*

Ning Li, Li Shao, Chao-Feng Zhang* and Mian Zhang

Key Laboratory of Modern Chinese Medicines, Ministry of Education,
Research Department of Pharmacognosy, China Pharmaceutical University, Nanjing, China

(*Received 28 February 2008; final version received 14 June 2008*)

Two new flavonoid alkaloids, 8-(2″-pyrrolidinone-5″-yl)-quercetin (**1**) and 8-(2″-pyrrolidinone-5″-yl)-isorhamnetin (**2**), were isolated from the herb of *Senecio argunensis*. Their structures were elucidated by spectral analysis.

Keywords: *Senecio argunensis*; flavonoid alkaloid; 8-(2″-pyrrolidinone-5″-yl)-quercetin; 8-(2″-pyrrolidinone-5″-yl)-isorhamnetin

1. Introduction

Senecio, belonging to the family Compositae, is a large genus consisting of 1000 species or more. There are about 63 species distributed in China [1] and many of them are used as folk medicines. *Senecio argunensis* Turcz. is a perennial herb mainly growing in northeast and northwest China and is often used for the treatment of sore throat, dysentery, snake bite, etc. [2]. As a part of systematic research on *Senecio* plants, the chemical investigation on *S. argunensis* has been carried out and a new biflavonoid has been isolated in our earlier work [3]. This paper describes the isolation and structural elucidation of two new flavonoid derivatives with a γ-lactam group, 8-(2″-pyrrolidinone-5″-yl)-quercetin (**1**) and 8-(2″-pyrrolidinone-5″-yl)-isorhamnetin (**2**) (Figure 1).

2. Results and discussion

Compound **1**, obtained as a yellow amorphous powder, showed a negative Dragendorff's reaction but positive ferric chloride and aluminum chloride reactions. The molecular formula was determined to be $C_{19}H_{15}NO_8$ by HRESIMS with a quasi-molecular ion $[M + H]^+$ at *m/z* 386.0882. The IR spectrum indicated that compound **1** possessed hydroxyl groups (3370 cm^{-1}), a carbonyl group (1640 cm^{-1}), and aromatic rings (1603, 1555, 1525, and 1436 cm^{-1}). The ^1H and ^{13}C NMR spectral data of compound **1** (Table 1) were similar to those of quercetin [4], except for the disappearance of a proton signal in ring A and the appearance of new signals assigned to $CHCH_2CH_2$ and a carbonyl group. A detailed analysis of the ^1H–^1H COSY and HMQC spectra led to consider that compound **1** might be a quercetin derivative with a 2″-pyrrolidinone-5″-yl group at C-6 or C-8 position. The HMBC spectrum (Figure 2) unambiguously confirmed that the pyrrolidinone group was connected with quercetin at C-8 position due to the long-range correlations of H-5″ (δ 5.39) with C-7, C-8, and C-9. Therefore, the structure of compound **1** was elucidated as 8-(2″-pyrrolidinone-5″-yl)-quercetin.

The molecular formula of compound **2** was determined to be $C_{20}H_{17}NO_8$ by HRESIMS with a quasi-molecular ion $[M + H]^+$ at *m/z* 400.1036. Its ^1H and ^{13}C NMR spectra

*Corresponding author. Email: njchaofeng@126.com

ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020802361198
http://www.informaworld.com

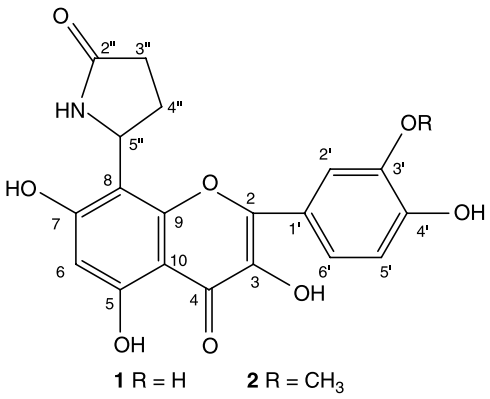

Figure 1. Structures of compounds **1** and **2**.

(Table 1) closely resembled those of compound **1**, except for the disappearance of a hydroxyl group and the appearance of a methoxyl signal. Further spectral comparison indicated that the methoxyl group was connected to C-3′, and the flavonoid part was isorhamnetin [5]. Thus, the structure of compound **2** was elucidated as 8-(2″-pyrrolidinone-5″-yl)-isorhamnetin.

To date, only two flavan-3-ol derivatives with the 2-pyrrolidinone-5-yl group at C-8 have been isolated from a Korean folk medicine *Davallia mariesii* Moore [6].

3. Experimental

3.1 General experimental procedures

Optical rotations were measured with a JASCO P-1020 digital automatic polarimeter. The UV spectra were recorded on a Shimadzu UV-2501 spectrometer (Kyoto, Japan). The IR spectra were taken on a Nicolet Impact 410 infrared spectrophotometer (Madison, WI, USA). HRESIMS were obtained on an Agilent G3250AA LC/MSD TOF mass spectrometer (Santa Clara, CA, USA).

Table 1. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectral data of compounds **1** and **2** (DMSO-d_6).

Position	**1**		**2**	
	δ_H (multiplicity, *J*)	δ_C	δ_H (multiplicity, *J*)	δ_C
2		147.2		147.4
3		135.6		135.7
4		176.2		176.2
5		159.7		159.7
6	6.28 (s)	98.3	6.29 (s)	98.3
7		162.2		162.2
8		106.4		106.4
9		153.9		154.1
10		103.2		103.3
1′		122.1		122.1
2′	7.68 (d, 2.1)	115.4	7.72 (d, 2.0)	112.5
3′		145.1		149.1
4′		147.8		147.3
5′	6.87 (d, 8.5)	115.8	6.93 (d, 8.5)	115.7
6′	7.50 (dd, 2.1, 8.5)	120.1	7.56 (dd, 2.0, 8.5)	121.8
2″		176.9		176.7
3″	2.33 (m)	31.0	2.32 (m)	31.0
4″	2.38 (m); 2.19 (m)	26.0	2.38 (m); 2.19 (m)	26.0
5″	5.39 (t, 7.3)	47.4	5.36 (t, 7.4)	47.5
NH	7.75 (br s)		7.72 (br s)	
3-OH	9.57 (br s)		9.74 (br s)	
5-OH	12.68 (br s)		12.68 (br s)	
7-OH	10.95 (br s)		10.98 (br s)	
3′-OH	9.20 (br s)			
4′-OH	9.36 (br s)		9.41 (br s)	
O-CH_3			3.83 (s)	56.0

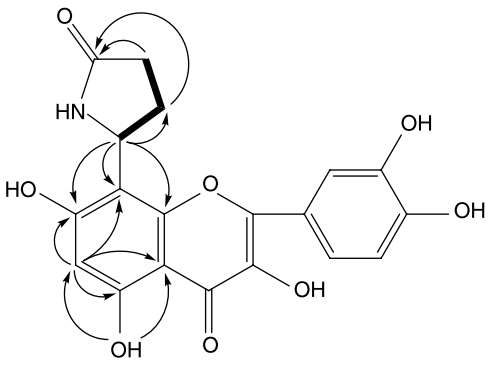

Figure 2. $^{1}H-^{1}H$ COSY (▬) and key HMBC correlations (H → C) of compound **1**.

The NMR experiments were performed on a Bruker AV-300 spectrometer (Fällanden, Switzerland) with TMS as an internal standard. Silica gel (200–300 mesh for column chromatography and GF254 for TLC) was obtained from Qingdao Marine Chemical Company, Qingdao, China. Sephadex LH-20 was purchased from Amersham BioSciences, Uppsala, Sweden.

3.2 Plant material

The herbs of *S. argunensis* Turcz. were collected from Tonghua, Jilin province, China, in 2005 and authenticated by Dr Mian Zhang. A voucher specimen (SA-2005-07) has been deposited in the Research Department of Pharmacognosy, China Pharmaceutical University.

3.3 Extraction and isolation

The air-dried herbs of *S. argunensis* (25.0 kg) were extracted with 90% ethanol under reflux and evaporated *in vacuo* to yield a syrupy residue (3000 g). The residue was suspended in water (3000 ml) and partitioned with petroleum ether (3000 ml × 3), $CHCl_3$ (3000 ml × 5), EtOAc (3000 ml × 5), and *n*-BuOH (3000 ml × 3) successively and evaporated *in vacuo* respectively, to yield the corresponding fractions (400, 250, 120, and 200 g). The EtOAc extract (100 g) was subjected to column chromatography on silica gel and gradiently eluted with $CHCl_3$–MeOH to yield seven fractions (fraction 1–fraction 7). Fraction 4 (17.0 g) was chromatographed on silica gel with a $CHCl_3$–MeOH gradient system (20:1 to 2:1) to yield seven sub-fractions (fraction 4A–fraction 4G). Fraction 4F (2.0 g) was subjected to repeated column chromatography on Sephadex LH-20 with MeOH as an eluent to afford compound **1** (5 mg). Fraction 2 (4.0 g) was chromatographed on Sephadex LH-20 eluting with MeOH to yield compound **2** (3 mg).

3.3.1 8-(2″-Pyrrolidinone-5″-yl)-quercetin (*1*)

A yellow amorphous powder; $[\alpha]_{20}^{D}$ 0 (*c* 0.50, pyridine); UV (MeOH) λ_{max} (nm) (log ϵ): 258 (4.82), 374 (4.77); IR (KBr) υ_{max} (cm^{-1}): 3470, 1640, 1603, 1555, 1525, 1436, 1352; ^{1}H and ^{13}C NMR spectral data are listed in Table 1; HRESIMS: *m/z* 386.0882 $[M + H]^{+}$ (calcd for $C_{19}H_{16}NO_8$, 386.0870).

3.3.2 8-(2″-Pyrrolidinone-5″-yl)-isorhamnetin (*2*)

A yellow amorphous powder; $[\alpha]_{20}^{D}$ 0 (*c* 0.50, pyridine); UV (MeOH) λ_{max} (nm) (log ϵ): 258 (3.9), 373 (3.65); IR (KBr) λ_{max} (cm^{-1}): 3423, 2919, 1646, 1600, 1555, 1515, 1422, 1384; ^{1}H and ^{13}C NMR spectral data are listed in Table 1; HRESIMS: *m/z* 400.1036 $[M + H]^{+}$ (calcd for $C_{20}H_{18}NO_8$, 400.1026).

Acknowledgements

This work was partly supported by a grant from the National High Technology Research and Development Program of PR China (863 Program; No. 2004AA2Z3730-15).

References

[1] Y.L. Chen, *Flora Reipublicae Popularis Sinicae*, 77, (Science Press, Beijing, 1999).
[2] State Administration of Medicine and Drug of PRC (Compilation Committee of Zhonghua Bencao), *Zhonghua Bencao*, Zhonghua Bencao. (Shanghai Scientific and Technical Publishers,

Shanghai, (Shanghai Scientific and Technical Publishers, Shanghai, 1999).
[3] N. Li, C.F. Zhang, and M. Zhang, *J. Chin. Pharm. Univ*. **39**(1), 20 (2008).
[4] C.F. Zhang, Q.S. Sun, Y.Y. Zhang, and Z.T. Wang, *Chin. J. Med. Chem.* **11**(5), 274 (2001).
[5] J.B. Harborne and T.J. Mabry, *The Flavonoids: Advances in Research*, (Chapman and Hall, New York, 1982).
[6] C.B. Cui, Y. Tezukay, T. Kikuchi, H. Nakano, and J.H. Park, *Chem. Pharm. Bull.* **38**, 2620 (1990).