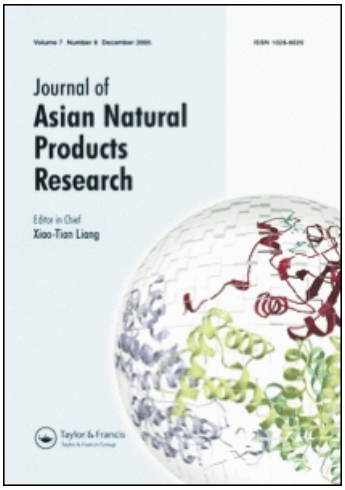


Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Studies on chemical constituents of *Polygonum perforliatum* L.

T. Shen[a]; Z. -J. Jia[a]; S. -Z. Zheng[b]
[a] National Laboratory of Applied Organic Chemistry, Institute of Organic Chemistry, Lanzhou University, Lanzhou, China [b] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, China

To cite this Article Shen, T. , Jia, Z. -J. and Zheng, S. -Z.(2007) 'Studies on chemical constituents of *Polygonum perforliatum* L.', Journal of Asian Natural Products Research, 9: 2, 129 — 133
To link to this Article: DOI: 10.1080/10286020420003248 44
URL: http://dx.doi.org/10.1080/10286020420003248 44

Journal of Asian Natural Products Research, Vol. 9, No. 2, March 2007, 129–133

Studies on chemical constituents of *Polygonum perforliatum* L.

T. SHEN†, Z.-J. JIA†¶ and S.-Z. ZHENG‡*

†National Laboratory of Applied Organic Chemistry, Institute of Organic Chemistry, Lanzhou University, Lanzhou 730000, China
‡College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

(Received 2 March 2004; revised 2 July 2004; in final form 30 August 2004)

Two new apianen lactones, named as guanyeliaoine I (**1**) and guanyeliaoine II (**2**), have been isolated along with seven known compounds from *Polygonum perforliatum* L. (Chinese name "Guanyeliao", Berberidaceae). Their structures were deduced on the basis of spectral data and chemical methods.

Keywords: *Polygonum perforliatum*; Polygonaceae; Guanyeliaoine I; Guanyeliaoine II

1. Introduction

Polygonum perforliatum L. is a traditional Chinese drug which is distributed in many places of China. In traditional Chinese folk medicine, it is used to cure yellow gallbladder, roundworm, hemorrhoids, etc. [1]. However, very little is known about its chemical constituents. We have carried out a detailed chemical investigation and have isolated two new apianen lactones along with seven known compounds. Their structures were deduced by spectral and chemical methods as follows: guanyeliaoine I (**1**), guanyeliaoine II (**2**), 3α-hydroxy-13β-furan-11-keto-apian-8-en-(20,6)-olide (**3**) [2], syringic acid [3], viviparum A [4], 3′,7-dihydroxy-2′,4′-dimethoxy isoflavone [5], 5,7-dimethoxy-4′-hydroxyflavone [6], 5-hydroxy-7,8-dimethoxyflavone [7], 5,2′-dimethoxy-6,7-methylene dioxyflavanone [8]. Among them **1** and **2** are new compounds. In this paper, we report on the isolation and structural determination of the two new compounds.

2. Results and discussion

Compound **1** was obtained as colourless powder mp 240–241°C (MeOH). Its HREIMS gave a molecular ion peak at *m/z* 410.1721 corresponding to the molecular formula of $C_{24}H_{26}O_6$, indicating 12 degrees of unsaturation. ^{1}H and ^{13}C NMR (tables 1 and 2) of **1** revealed signals due to three methyls, four methylenes, nine methines and eight quaternary carbons, which suggested

*Corresponding author. Tel.: +86-0931-7972293/13919251625. Email: zhengsz@nwnu.edu.cn
¶Email: jiazj@Lzu.edu.cn

Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/1028602042000324844

the presence of 24 carbons. The IR spectrum displayed absorption bands for a carbonyl group (1722 cm^{-1}) and a β-substituted furan ring (1524, 835 cm^{-1}). In the ^{13}C NMR, signals typical of a lactone group were observed at δ 175.76, which were supported by IR spectrum absorption (1763 cm^{-1}). The ^{13}C NMR resonance at δ 198.05 and IR band at 1750 cm^{-1} indicated the presence of a five-membered ring ketone. The signals at δ 142.10 and 161.35 were attributed to a tetrasubstituted double bond. The lack of a C-10 methyl signal suggested that C-10 is part of the lactone group. The downfield appearance of C-6 and H-6 (δ_C: 72.68; δ_H: 4.66, d, $J = 2.2$ Hz) fixed the position of the lactonic oxygen to C-6. Meanwhile, its ^1H NMR at δ 6.01 (brs H-3′a), 5.50 (t, H-3′b) and 1.91 (brs, CH_3-4′) and signals of ^{13}C NMR spectrum at δ_C 166.10 (CO), 135.08 (C), 126.21 (CH_2), 18.36 (CH_3) showed the presence of a methacrylate group. The peaks of cross C-1′(H-3, H-3′a, H-3′b, H-4′ and C-4′(H-3′a, H-3′b in the ^1H-^1H COSY and HMBC spectrum strongly confirmed the location of a methacrylate at C-3 (δ 72.41).

The structure of **1** was deduced on the basis of ^1H, ^1H COSY, HMBC data and compared with structurally related natural products [2]. The relative stereochemistry of compound **1** was determined on the basis of the NOESY information. The orientations of H-3β, H-4α, H-5α, H-6α, H-12α and H-13β were determined to be the same as those in typical limonoids [2]; the most important correlations in the NOESY spectrum showed cross-peaks of H-6/H-4, H-5/H-4 and H-7α/H-6, which established the axial orientation (α-H) of H-5 and a trans-junction between A and B ring. NOESY correlations for H-3/Me-19 and H-3/H-2 implied the α-orientation of C_3-methacrylate. Comparison of ^1H and ^{13}C NMR data of **1** with those of 3α-hydroxy-13β-furan-11-keto-apian-8-en-(20,6)-olide (**3**) showed that **1** and **3** were similar except for the presence of a methacrylate group (at C-3α). Thus, the structure of compound **1** was deduced as 3α-methacrylate-13α-furan-11-keto-apian-8-en-(20,6)-olide, named guanyeliaoine (**I**).

Table 1. ^1H NMR spectral data of compounds **1**–**3** (400 MHz, δ in ppm, $CDCl_3$, TMS).*

	δ_H coupling (Hz)		
Proton	**1**	**2**	**3**
1α	1.92 (m)	1.94 (m)	1.90 (m)
2β	2.80 (m)	2.83 (m)	2.80 (m)
2α	1.93 (m)	1.95 (m)	1.94 (m)
2β	2.83 (m)	2.81 (m)	2.82 (m)
3β	4.68 (d, 3.4)	4.54 (d, 3.4)	5.27 (d, 3.2)
4α	1.93 (m)	1.94 (m)	1.96 (m)
5	2.22 (d, 10.05)	2.20 (d, 10.5)	2.24 (d, 0.8)
6	4.66 (d, 2.3)	4.63 (d, 2.2)	4.60 (d, 2.4)
7α	1.99 (dd, 2.2,0.7)	1.97 (dd, 2.3,0.8)	1.98 (dd, 2.3,0.8)
7β	2.86 (d, 2.0)	2.88 (d, 2.0)	2.88 (d, 2.2)
12	1.80 (d, 4.2)	1.79 (d, 4.0)	1.82 (d, 4.1)
13	3.20 (d, 4.1)	3.20 (d, 4.2)	3.22 (d, 4.2)
15	7.33 (d, 1.5)	7.32 (d, 1.6)	7.36 (d, 1.5)
16	7.20 (dd, 1.5,0.5)	7.23 (dd, 1.5,0.5)	7.22 (dd, 1.5,0.5)
17	6.23 (d, 1.8)	6.24 (d, 1.8)	6.24 (d, 1.9)
Me-18	2.00 (s)	2.04 (s)	2.09 (s)
Me-19	1.22 (s)	1.20 (s)	1.22 (s)
OH			3.58 (s)
2′a		2.61 (dd, 8.9,15.0)	
2′b		2.75 (dd, 4.2,15.0)	
3′a	6.01 (brs)	4.36 (m)	
3′b	5.50 (t, 1.6)		
4′	1.91 (brs)	1.92 (d, 7.3)	

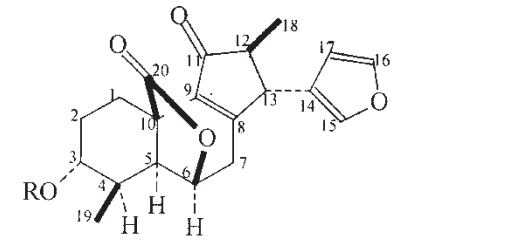
* Assignments from ^1H-^1H COSY, HMBC and HMQC.

Table 2. ^{13}C NMR spectral data of compounds **1**–**3** (100 MHz, δ in ppm, $CDCl_3$,TMS).*

	1			**2**			**3**		
Carbon	δ_C	DEPT	HMBC	δ_C	DEPT	HMBC	δ_C	DEPT	HMBC
1	22.23	CH_2	2, 10	22.20	CH_2	2, 10	22.90	CH_2	2, 10
2	17.68	CH_2	4	17.81	CH_2	4	17.71	CH_2	4
3	72.41	CH	1 5 1′, 2′	72.46	CH	1 5 1′, 2′	72.72	CH	1, 5′
4	31.10	CH	2 6 10	30.98	CH	2 6 10	30.08	CH	2 6 10
5	51.22	CH	3 7 19, 20	51.01	CH	3 7 19, 20	51.2	CH	3 7 19, 20
6	72.68	CH	4 8 10	72.66	CH	4 8 10	72.7	CH	4 8 10
7	18.20	CH_2	5, 13	18.19	CH_2	5, 13	18.2	CH_2	5, 13
8	161.35	C		161.40	C		161.40	C	
9	142.10	C		142.22	C		142.20	C	
10	44.80	C		44.85	C		44.8	C	
11	198.05	C		198.11	C		198.05	C	
12	31.18	CH	8 9 14	31.20	CH	8 9 14	31.1	CH	8 9 10
13	58.80	CH	7 11 14	58.80	CH	7 11 14	58.82	CH	7 11 14
14	121.16	C		121.22	C		121.2	C	
15	141.09	CH	13, 17	141.11	CH	13, 17	141.0	CH	13, 17
16	111.26	CH	14, 15	111.22	CH	14, 15	111.2	CH	14, 15
17	137.88	CH	13, 15	138.09	CH	13, 15	138.5	CH	13, 15
18	29.94	CH_3	11, 13	30.11	CH_3	11, 13	30.2	CH_3	11, 13
19	28.27	CH_3	3, 5	28.32	CH_3	3, 5	28.3	CH_3	3, 5
20	175.76	C		175.83	C		175.8	C	
1′	166.10	CO		170.10	CO				
2′	135.08	C		45.52	CH_2	3, 4′			
3′	126.21	CH_2	1′, 4′	63.79	CH	1′			1′, 4′
4′	18.36	CH_3	1′, 3′	22.10	CH_3	1′, 2′			1′, 3′

* Assignments from ^1H-^1H COSY, HMBC and HMQC.

Compound **2** was obtained as colourless amorphous powder. HREIMS gave a molecular formula of $C_{24}H_{28}O_7$, indicating 11 degrees of unsaturation. Its ^{13}C NMR and DEPT spectra (table 2) displayed 24 carbon signals (3 × CH_3, 4 × CH_2, 10 × CH, 7 × C); its spectral data (^1H, ^{13}C NMR, IR and NOESY) were very similar to those of **1**. This suggested that **1** and **2** have a similar skeleton; comparing the ^{13}C NMR and ^1H NMR spectra of **2** with those of **1** led to the conclusion that the main difference was the substitution of 3-hydroxybutyrate group (^{13}C NMR: δ_C 22.0 (q), 45.19 (t), 63.7 (d), 170.0 (s); ^1H NMR as shown in table 1) at C-3 in **2**. Furthermore, in the HMBC spectrum the correlation between H-3 and CO of the 3-hydroxybutyrate group was clearly observed. So this group must be attached to C-3. From the above information, guanyeliaoine II was determined to have the structure shown as **2**.



3. Experimental

3.1 General experimental procedures

Optical rotations were measured on a DIP-181 instrument. IR spectra were recorded on a Perkin-599B spectrophotometer. ^{1}H NMR, ^{13}C NMR and 2D NMR spectra were scanned on a Bruker AM-400 FT-NMR spectrometer with TMS as internal standard. HREIMS and EIMS data were obtained on a MAT-12 spectrometer at 70 eV. Silica gel (100–200, 200–300 mesh) was used for column chromatography and silica gel GF_{254} for TLC.

3.2 Plant material

The whole plants of *Polygonum perforliatum* were collected from the southwest of Sichuan province of China in 2001, and were identified by Prof. Lian Yong-shan of Northwest Normal University. A voucher specimen (No. 34691) is deposited in the herbarium of College of Life Science, Northwest Normal University, Lanzhou 730070, China.

3.3 Extraction and isolation

The dried and powdered whole plant (4.5 kg) was extracted with 95% EtOH three times at room temperature. The extract was concentrated under reduced pressure and about 420 g residue was obtained. The residue was extracted with $CHCl_3$ (42 g), EtOAc (125 g) and n-BuOH (65 g) successively. The $CHCl_3$ was chromatographed on silica gel using n-hexane-EtOAc (50:1–0:1) gradient, three fractions being obtained. From fraction 3 by rechromatography on silica gel and preparative TLC, compounds **7** (24 mg), **8** (31 mg) and **9** (19 mg) were obtained. The EtOAc extract was chromatographed on a silica gel column using a mixture of n-hexane-EtOAc (3:1) and EtOAc—HCOOH (10:1) of increasing gradient (40:1–0:1), four major fractions (A 31 g, B 39 g, C 18 g, D 23 g) being obtained. Fraction B was purified by preparative TLC [$CHCl_3$:EtOAc:CH_3OH (5:4:1)] to furnish **1** (46 mg), **2** (21 mg) and **3** (17 mg). Fraction A was purified by rechromatography on a silica gel column with $CHCl_3$—MeOH gradient elution (10:0–1:10, v/v) and by preparative TLC **5** (17 mg) and **6** (24 mg) were obtained. Fraction C was subjected to silica gel column chromatography and EtOAc—CH_3OH (10:1–1:10), yielding compound **4** (13 mg).

Compound 1 $C_{24}H_{26}O_6$, colourless powder, mp 240–241°C (CH_3OH); $[\alpha]_D^{20}$ -31.2 (c, 0.74, $CHCl_3$). HREIMS *m/z*: 410.1721 (calcd for $C_{24}H_{26}O_6$, 410.1729). IR (KBr): 3459, 2960, 2862, 1763, 1750, 1722, 1524, 1240, 835 cm^{-1}. UV λ nm: 306, 288, 274 nm. The ^{1}H NMR and ^{13}C NMR data are listed in tables 1 and 2, respectively.

Compound 2 $C_{24}H_{28}O_7$, colourless, amorphous powder, mp 246–247°C (CH_3OH). $[\alpha]_D^{20}$ -32.7 (c, 0.78, $CHCl_3$). HREIMS *m/z*: 428.1827 (calcd for $C_{24}H_{28}O_7$, 428.1834). IR (KBr): 3448, 2962, 2867, 1762, 1751, 1720, 1522, 1241, 836 cm^{-1}. UV λ nm: 305, 286, 272 nm. The ^{1}H NMR and ^{13}C NMR data are listed in tables 1 and 2, respectively.

Acknowledgements

This work was supported by the National Natural Science Foundation of China, No. 29972017.

References

[1] Jiangsu New Medicine College, *Dictionary of Chinese Crude Drugs*, p. 1749, Shanghai Science and Technology Press, Shanghai (1975) (in Chinese).
[2] S.Z. Zheng, Z. Guo, T. Shen, X. Shen. Indian. *J. Chem.*, **41**, 228 (2003).
[3] J.M. Yue, Z.W. Lin, D.Z. Wang. *Phytochemistry*, **36**, 717 (1994).
[4] S.Z. Zheng, K.L. Li, J.X. Wang, T. Shen, X. Shen. *Indian J. Chem.*, **40**, 167 (2001).
[5] X.W. Shen, L.P. Sun, Z.W. Song, L. Wang, S.Z. Zheng. *Acta Bot. Sin.*, **35**, 807 (1993).
[6] T.J. Mabry, K.R. Markham, M.B. Thomas. *The Systematic Identification of Flavonoids*, p. 156, Springer, Heidelberg (1970).
[7] S.Z. Zheng, R.H. Lu, X.W. Shen. *Acta. Bot. Sin.*, **32**, 215 (1996).
[8] J. Geigert, F.R. Stermitz, G. Johnson, D. Maag, D.K. Johnson. *Tetrahedron*, **29**, 2703 (1973).