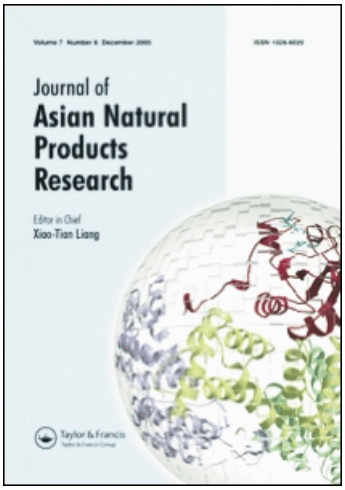

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

A new phenolic glycoside from the roots of *Paeonia veitchii*

R. Wang[a]; G. -X. Chou[b]; E. -Y. Zhu[b]; Z. -T. Wang[b]; K. -S. Bi[a]
[a] School of Pharmacy, Shenyang Pharmaceutical University, Shenyang, China [b] Institute of Chinese Materia Medica, Shanghai University of Traditional Chinese Medicine, Shanghai, China

To cite this Article Wang, R. , Chou, G. -X. , Zhu, E. -Y. , Wang, Z. -T. and Bi, K. -S.(2006) 'A new phenolic glycoside from the roots of *Paeonia veitchii*', Journal of Asian Natural Products Research, 8: 3, 277 — 280
To link to this Article: DOI: 10.1080/10286020500172608
URL: http://dx.doi.org/10.1080/10286020500172608

Journal of Asian Natural Products Research, Vol. 8, No. 3, April–May 2006, 277–280

A new phenolic glycoside from the roots of *Paeonia veitchii*

R. WANG†, G.-X. CHOU‡¶, E.-Y. ZHU‡¶, Z.-T. WANG‡¶* and K.-S. BI†

†School of Pharmacy, Shenyang Pharmaceutical University, Shenyang 110016, China
‡Shanghai R&D Center for Standardization of Traditional Chinese Medicines, Shanghai 201203, China
¶Institute of Chinese Materia Medica, Shanghai University of Traditional Chinese Medicine, Shanghai 201203, China

(Received 17 August 2004; revised 8 November 2004; in final form 25 November 2004)

From the roots of *Paeonia veitchii* Lynch., a new phenolic glycoside, 2-*O*-[α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside]-benzaldehyd (**1**) was isolated together with seven known phenolic compounds. Their structures were elucidated by spectroscopic method.

Keywords: *Paeonia veitchii*; Phenolic glycoside; 2-*O*-[α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside]-benzaldehyde

1. Introduction

Paeoniae Radix, including the dried roots of *Paeonia lactiflora* Pall. or *P. veitchii* Lynch., is a traditional Chinese herbal drug possessing the effects of relieving heat, cooling blood and promoting blood circulation, etc. [1]. Extensive chemical studies have been conducted for the roots of *P. albiflora* [2–6] and the constituents from the roots of *P. veitchii* have been studied and has led to the isolation of some compounds such as paeoniflorin, benzoylpaeoniflorin and catechin [7,8]. In the course of our chemical studies, a new phenolic glycoside, 2-*O*-[α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside]-benzaldehyde (**1**), along with seven known phenolic compounds (**2**–**8**) were isolated from the roots of *P. veitchii*. Compounds **2**–**4**, **6**–**8** were isolated from this plant for the first time.

2. Results and discussion

Compound **1** was obtained as a white amorphous powder, mp 228–230°C, $[\alpha]_D^{20}$ − 30.8 (*c* 0.5, MeOH). The UV spectrum showed absorptions at 209, 250 and 308 nm (log ε: 4.27, 3.97 and 3.51, respectively). Its IR spectrum indicated the presence of hydroxyl groups

*Corresponding author. E-mail: wangzht@hotmail.com

Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020500172608

(3402 cm^{-1}, br); aldehyde group (2920, 1681 cm^{-1}); aromatic rings (1600, 1483, 1460, 765 cm^{-1});—C—O—C— (1235 cm^{-1}) and the characteristic peaks for α-L- and β-D-pyranose (1072, 1006, 912, 846, 812 cm^{-1}). It exhibited the peaks at *m/z* 439$[M + Na]^+$ and 434$[M + NH_4]^+$ in the ESI-MS and its molecular formula of $C_{18}H_{24}O_{11}$ was determined by HRESI-MS, *m/z* 439.1226$[M + Na]^+$. The ^{13}C NMR spectrum of **1** showed 18 carbon signals, including an aromatic aldehyde at δ_C 190.0, six aromatic carbons (two quaternarys and four methines) and 11 carbons of sugar. The ^1H-NMR spectrum of **1** revealed an aldehyde proton signal at δ_H 10.49 (1H, s) and four aromatic protons signals at δ_H 7. 43 (1H, br. d, $J = 8.3$ Hz), 7.67 (1H, dd, $J = 8.3, 7.7$ Hz), 7.15 (1H, dd, J = 7.7, 7.7 Hz), 7.68 (1H, br. d, $J = 7.7$ Hz), suggesting a typical 1, 2-substituted benzene pattern. Based on the foregoing evidence, the structure of **1** was identified to be a 2-*O*-glycosyl substituted benzaldehyde derivative. In order to obtain further evidence for the structure of **1**, hydrolysis and acetylation of **1** were carried out. The sugars were confirmed as arabinose and glucose by GC analysis compared with those of acetylated authentic samples. The signal at δ_C 101.0 and the coupling constant of H-1′ (δ_H 4.92, d, $J = 7.6$ Hz) suggested that the glucose was in β-configuration. The signal at δ_C 103.4 and the coupling constant of H-1″ (δ_H 4.21, d, $J = 6.4$ Hz) indicated that the arabinose was in α-configuration. The downfield chemical shift of C-6′ (δ_C 68.0) suggested a 1 → 6 linkage of arabinose to glucose [9]. In the HMBC spectrum of **1** (figure 1), the signal of H-1′ at δ_H 4.92 showed correlation with resonance of C-2 at δ_C 159.7; the signal of H-1″ at δ_H 4.21 showed correlation with resonance of C-6′ at δ_C 68.0. Based on these evidences, the structure of **1** was deduced to be 2-*O*-[α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside]-benzaldehyde. The ^1H and ^{13}C NMR spectral data of **1** are shown in table 1.

In addition, by comparing their physical and spectral data with the references, compounds **2**–**8** were identified as isosalicin (**2**), salicin (**3**), salicyl alcohol (**4**) [10], gallic acid (**5**), methyl gallate (**6**) [11], pentagalloylglucose (**7**) [12] and paeonol (**8**) [13].

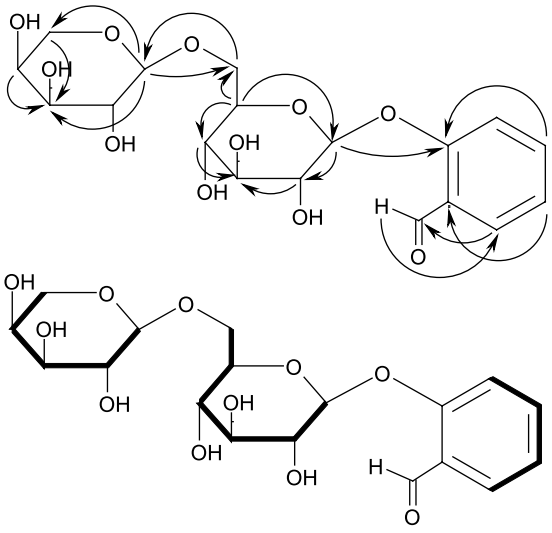

Figure 1. Key HMBC and ^1H-^1H COSY correlations for compound **1**.

Table 1. The ^{1}H and ^{13}C NMR data of compound **1**.

Position	δ_H *(J/Hz)*	δ_C *ppm*	*HMBC(H → C)*
1		124.7 (s)	
2		159.7 (s)	
3	7.43 (1H, br d, $J = 8.3$ Hz)	116.8 (d)	C-1,2,5
4	7.67 (1H, dd, $J = 8.3, 7.7$ Hz)	136.5 (d)	C-2,6
5	7.15 (1H, dd, J = 7.7, 7.7 Hz)	122.1 (d)	C-1,3
6	7.68 (1H, br d, $J = 7.7$ Hz)	126.7 (d)	C-CHO,4
CHO	10.49 (1H, s)	190.0 (d)	C-6
Glc 1′	4.92 (1H, d, $J = 7.6$ Hz)	101.0 (d)	C-2,2′
2′	3.42 (1H, m)	70.5 (d)	C-3′
3′	3.28 (1H, m)	76.1 (d)	
4′	3.15 (1H, m)	69.9 (d)	C-3′
5′	3.65 (1H, m)	75.9 (d)	C-1′,4′,6′
6′	3.98 (1H, d, $J = 11.1$ Hz)	68.0 (t)	C-5′,1″
	3.58 (1H, dd, $J = 11.1, 7.1$ Hz)		
Ara 1″	4.21 (1H, d, $J = 6.4$ Hz)	103.4 (d)	C-6′,3″,5″
2″	3.41 (1H, m)	73.1 (d)	
3″	3.28 (1H, m)	72.4 (d)	C-1″
4″	3.65 (1H, m)	67.3 (d)	C-3″
5″	3.70 (1H, dd, $J = 12.1, 3.3$ Hz)	64.8 (t)	C-1″,3″
	3.28 (1H, m)		

Note: NMR data were measured in DMSO (500 MHz for ^{1}H, 125 MHz for ^{13}C) and the signal assignments were aided by COSY, HMQC and HMBC spectra.

3. Experimental

3.1 General experimental procedures

Melting points were determined with a WRX-1 S Apparatus and are uncorrected. Optical rotations were measured in MeOH solution on a PERKIN-ELMER 341 automatic polarimeter at 20°C. UV spectra were performed on a Beckman DU 640 spectrometer in MeOH solution. IR spectra were recorded on a Bio-Rad FTS-185 spectrometer in KBr disks. HRESI/MS spectrum was performed on a Bruker-daltonics APES-III 7.0 JESLA FTMS spectrometer and ESI/MS was performed on a LCQ DECA XP mass spectrometer that was equipped with an ESI interface and an ion trap mass analyzer. NMR spectra were taken on 500 MHz, 125 MHz NMR on Bruker AM-500 spectrometer. GC were determined with a SHIMADZU GC-14D. Column chromatographic separations were performed with silica gel (200–300 mesh, Qingdao Haiyang Chemical Group Co. Ltd., China), Sephadex LH-20 (Pharmacia Sweden) and ODS (C^{18} Alltech 30–40 M).

3.2 Plant material

Dried plant material was collected at Chengdu (Sichuan Province, China), the plant was authenticated as *Paeonia veitchii* Lynch. by Dr. Zheng-Tao WANG and the voucher specimen is kept in the Herbarium of Shanghai R&D Center for Standardization of Traditional Chinese Medicines, Shanghai, China.

3.3 Extraction and isolation

Dried roots of *Paeonia veitchii* Lynch. (7.5 kg) were powdered and extracted with MeOH. The MeOH extract was then concentrated and partitioned with light petroleum, EtOAc and

MeOH successively. The EtOAc fraction was chromatographed over silica gel column in gradient eluting with $CHCl_3$-MeOH (100:1 → 0:100) to give fractions I-V. Fraction I was followed by silica gel column chromatography eluted with $CHCl_3$-MeOH (100:2) to yield compounds **4** (200 mg), **6** (500 mg) and **8** (30 mg); fraction III was subjected to silica gel column chromatography eluted with $CHCl_3$-MeOH (9:1) and rechromatographed on Sephadex LH-20 with $CHCl_3$-MeOH (1:1) to give compounds **2** (15 mg), **3** (10 mg) and **5** (30 mg); fraction IV was subjected to silica gel column chromatography eluted with $CHCl_3$-MeOH (85:25) to yield compound **1** (20 mg); fraction V was followed by ODS column chromatography with MeOH-H_2O (38:62) to give compound **7** (25 mg).

3.3.1 ***2O*-[α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside]-benzaldehyde (1)**. White amorphous powder, mp 228–230°C, $[\alpha]_D^{20}$ − 30.8 (*c* 0.5, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3402, 2920, 1681, 1600, 1483, 1460, 1235, 1072, 1006, 912, 846, 812, 765. UV λ_{max}^{MeOH} nm: 209 (log ε: 4.27), 250 (log ε: 3.97), 308 (log ε: 3.51). HRESI-MS *m/z*: 439.1226 $[M + Na]^+$ (calcd for $C_{18}H_{24}O_{11}$, 439.1211); ESI-MS *m/z*: 439$[M + Na]^+$, 434$[M + NH_4]^+$. The ^1H and ^{13}C NMR spectral data are shown in table 1.

3.3.2. Hydrolysis and acetylation of 1. Compound **1** (5 mg) was placed in a test tube and aqueous TFA (2 ml) was added. The tube was sealed and heated (120°, 1 h). The solvent was evaporated and MeOH was added and evaporated to remove residual traces of TFA. Aqueous $NaBH_4$ (2 ml) was added and the tube left at room temperature for 12 h. After removal of the solvent by evaporation, the residue was acetylated in acetic anhydride at 100° for 1 h and the solution evaporated to dryness. $CHCl_3$ (5 ml) was then added and the organic phase was extracted twice with H_2O (5 ml), discarding the top layer each time. The $CHCl_3$ layer, after being dried over $NaSO_4$, was evaporated to dryness. The residue was then dissolved in $CHCl_3$ and analyzed by GC. The sugars were identified as arabinose and glucose.

References

[1] The State Pharmacopoeia Commission of P.R. China. Chinese Pharmacopoeia [S] **1**, Chemical Industry Press, Beijing, 125 (2000).
[2] M. Kaneda, Y. Iitaka, S. Shibata. *Tetrahedron*, **28**, 4309 (1972).
[3] K. Yamasaki, M. Kaneda, O. Tanaka. *Tetrahedron Lett*, **44**, 3965 (1976).
[4] S. Shibata, M. Nakahara. *Chem. Pharm. Bull.*, **11**, 372 (1963).
[5] N. Aimi, M. Inada, M. Watanade, S. Shibata. *Tetrahedron*, **25**, 1825 (1969).
[6] M. Nishioka, M. Yamagishi, G. Nonaka, I. Nishioka. *Chem. Pharm. Bull.*, **28**, 2850 (1980).
[7] H.S. Chen, Y.X. Xu, S.X. Liao, Z.J. Hong. *Acad. J. Sec. Military Med. Univ.*, **15**, 72 (1994).
[8] H.S. Chen, S.X. Liao, Z.J. Hong. *Chin. Pharma. J.*, **28**, 137 (1993).
[9] H.Y. Lang, S.Z. Li, T. McCabe. *J. Clardy. Planta Med.*, **50**, 501 (1984).
[10] M. Mizuo, K. Masaya, M. Chiemi. *J. Nat. Prod.*, **54**, 1447 (1992).
[11] G.E. Ma, Y.W. Shen, X.Z. Lu. *J. Chin. Tradit. Herb. Drugs*, **30**, 84 (1998).
[12] C.B. Cui, Q.C. Zhao, B. Cai. *j. Asian Nat. Prod. Res.*, **4**, 243 (2002).
[13] R.A. Weeks, R.H. Dobberstein, N.R. Farnsworth. *J. Nat. Prod.*, **40**, 515 (1977).