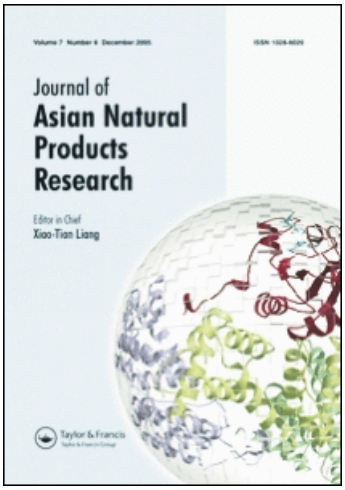


Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Two new flavone glycosides from the seeds of *Impatiens balsamina* L.

Jing Lei[ab]; Shi-Hui Qian[a]; Jian-Qin Jiang[b]
[a] Jiangsu Province Institute of Traditional Chinese Medicine, Nanjing, China [b] Department of Phytochemistry, China Pharmaceutical University, Nanjing, China

Online publication date: 01 December 2010

To cite this Article Lei, Jing , Qian, Shi-Hui and Jiang, Jian-Qin(2010) 'Two new flavone glycosides from the seeds of *Impatiens balsamina* L.', Journal of Asian Natural Products Research, 12: 12, 1033 — 1037
To link to this Article: DOI: 10.1080/10286020.2010.532315
URL: http://dx.doi.org/10.1080/10286020.2010.532315

Journal of Asian Natural Products Research
Vol. 12, No. 12, December 2010, 1033–1037

Taylor & Francis
Taylor & Francis Group

Two new flavone glycosides from the seeds of *Impatiens balsamina* L.

Jing Lei[ab], Shi-Hui Qian[a]* and Jian-Qin Jiang[b]*

[a]*Jiangsu Province Institute of Traditional Chinese Medicine, Nanjing 210028, China;*
[b]*Department of Phytochemistry, China Pharmaceutical University, Nanjing 210038, China*

(*Received 13 January 2010; final version received 13 October 2010*)

Two new flavone glycosides were isolated from the seeds of *Impatiens balsamina* L. and their structures were determined as quercetin-3-*O*-[α-L-rhamnose-(1 → 2)-β-D-glucopyranosyl]-5-*O*-β-D-glucopyranoside (**1**), and quercetin-3-*O*-[(6‴-*O*-caffeoyl)-α-L-rhamnose-(1 → 2)-β-D-glucopyranosyl]-5-*O*-β-D-glucopyranoside (**2**) on the basis of various spectral and chemical studies.

Keywords: *Impatiens balsamina* L.; flavone glycosides; 5-*O*-β-D-glycopyranosides

1. Introduction

Impatiens balsamina L., a well-known herbal medicine, is now widely cultivated as a medicinal and ornamental plant in most provinces of China. The seeds of *I. balsamina* L., commonly known as 'ji xing zi', have been used to treat lump in the abdomen and esophageal cancer, to act as an emmenagogue, to suppress puerperal pain, etc. The seeds have also been used as an expectorant, bactericide, and anticancer agent [1,2]. A number of flavones and flavone glycosides have been reported from *I. balsamina* L. [3–6], but the seeds of *I. balsamina* L. have not been investigated so widely. Our phytochemical investigation of the seeds of *I. balsamina* L. has resulted in the isolation of two new flavone glycosides (Figure 1).

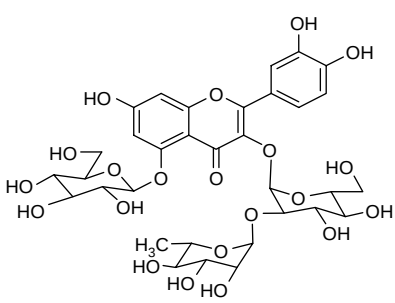
2. Results and discussion

Compound **1** was obtained as a yellow amorphous powder (MeOH) with $[\alpha]_D^{22}$ 137.1 ($c = 0.305$, MeOH). The ESI-MS afforded the quasi-molecular ion $[M - H]^-$ at *m/z* 771.2, consistent with a molecular formula of $C_{33}H_{40}O_{21}$, which was confirmed by the HR-TOF-MS, exhibiting a quasi-molecular ion $[M - H]^-$ at *m/z* 771.1995. In addition, a prominent fragment at *m/z* 609.1 $[M - H\text{-}162]^-$ indicated the loss of a hexose moiety. Another prominent fragment at *m/z* 487.1 $[M + Na\text{-}162\text{-}146]^+$ indicated the loss of a rhamnose unit. The IR spectrum showed the presence of hydroxyl (3422 cm^{-1}), phenyl ring groups (1609, 1515, 1448 cm^{-1}), carbonyl (1627 cm^{-1}), and glycosidic linkages (1066 cm^{-1}). The ^{13}C NMR spectrum of **1** showed 33 carbon signals, obviously 15 of which were for the flavone skeleton, and 18 from three hexose moieties. This indicated that **1** might be a flavone glycoside. In the ^1H NMR spectrum of **1** (Table 1), the presence of a trisubstituted ring B was confirmed by ABX pattern signals at δ_H 7.50 (d, $J = 2.0$ Hz, H-2′), 7.58 (dd, $J = 2.0, 8.5$ Hz, H-6′), and 6.82 (d, $J = 8.5$ Hz, H-5′). Furthermore, in the aromatic region, two meta-coupled doublets at δ_H 6.59 (d, $J = 2.0$ Hz, H-6) and 6.73 (d,

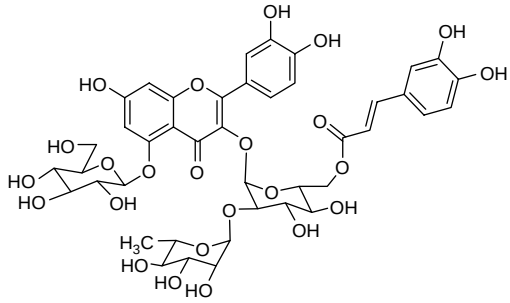
*Corresponding authors. Email: njqsh2005@126.com; njjjq@yahoo.com.cn

ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020.2010.532315
http://www.informaworld.com



1



2

Figure 1. The chemical structures of compounds **1** and **2**.

$J = 2.0$ Hz, H-8) were characteristic of the 5,7-hydroxylated A ring of flavonoid. Three anomeric proton resonances of the trisaccharide at δ_H 5.65 (d, $J = 7.5$ Hz), 5.09 (s), 4.78 (d, $J = 8.0$ Hz), two of which were identified as β-glucopyranose, another as α-rhamnose, can also be confirmed by HSQC and HMBC spectra. In the ^{13}C NMR spectrum of **1**, C-6 and C-8 were shifted downfield, indicating that the 5-OH group was glycosylated by comparing with echioidinin 5-glucoside [7]. The assignments of all protons and carbons were made by HSQC and HMBC experiments (Table 1). The HMBC correlation of C-5 at δ_C 159.2 and H-1″ of glucose at δ_H 4.78 (d, $J = 8.0$ Hz) confirmed the glucosylation of C_5—OH. Additionally, the long-range correlations between the anomeric proton of the terminal rhamnose (δ_H 5.09, H-1‴′) and C-2‴ of inner glucose (δ_C 77.7), H-2‴ (δ 3.50) and Rha C-1‴′ (δ 100.9), and the anomeric proton of the inner glucose (δ 5.65, H-1‴) and C-3 of compound **1** (δ_C 135.2) demonstrated the (1 → 2) interglycosidic linkage between rhamnose and glucose units and the site of glycosidation at C-3 (Figure 2). Based on these data, the structure of compound **1** was established as quercetin-3-*O*-[α-L-rhamnose-(1 → 2)-β-D-glucopyranosyl]-5-*O*-β-D-glucopyranoside (Figure 1).

Compound **2** was obtained as a yellow amorphous powder (MeOH) with $[\alpha]_D^{22}$ − 147.9 ($c = 0.69$, MeOH). The IR spectrum showed the presence of hydroxyl (3384 cm^{-1}), phenyl ring groups (1607, 1515, 1448 cm^{-1}), carbonyl (1633 cm^{-1}) and glycosidic linkages (1035 cm^{-1}). Its molecular formula, $C_{42}H_{46}O_{24}$, was established from HR-TOF-MS at *m/z* 933.2365 $[M - H]^-$. On comparison of the ^1H and ^{13}C NMR spectral data of compound **2** with those of **1**, we notice a striking resemblance between them. The only difference was the presence of *trans*-caffeoyl signals in the spectra of **2**. In the ^1H NMR spectrum of **2**, two characteristic doublets of olefinic protons at δ_H 6.07 and 7.25 (each d, $J = 15.8$ Hz), together with three aromatic protons of an ABX system at δ_H 6.72 (d, $J = 8.3$ Hz), 6.73 (dd, $J = 1.5$, 8.3 Hz), and 6.95 (d, $J = 1.5$ Hz), confirmed the presence of *trans*-caffeoyl moiety. To resolve the location of *O*-caffeoyl, the 2D NMR spectra of compound **2** were used. In the HMBC spectrum, the proton signals at δ_H 4.22 and 4.08 (m, H-6‴) showed long-range correlations with the carbon signal at δ_C 166.3 (C═O) (Figure 2), indicating that the *O*-caffeoyl group was located at C-6‴. Consequently, the structure of compound **2** was established as quercetin-3-*O*-[(6‴-*O*-caffeoyl)-α-L-rhamnose-(1 → 2)-β-D-glucopyranosyl]-5-*O*-β-D-glucopyranoside (Figure 1).

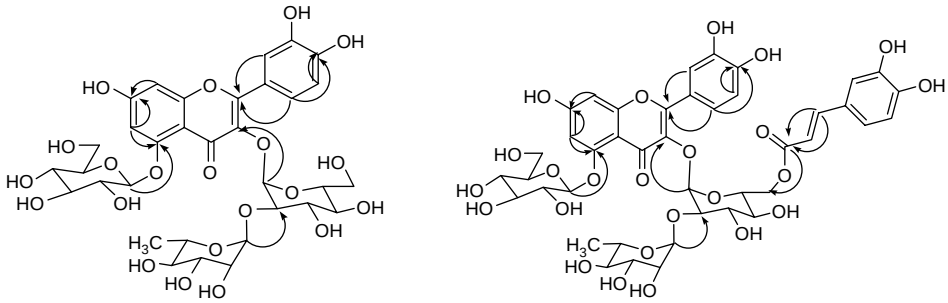
3. Experimental

3.1 General experimental procedures

IR spectra were run on a Bruker Fersor 27 spectrometer. Optical rotations were

Table 1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data of compounds **1** and **2** (DMSO-d_6, δ, ppm, J, Hz).

	1		**2**	
No.	δ_C	δ_H	δ_C	δ_H
Aglycone				
2	154.2		154.4	
3	135.2		134.6	
4	173.3		172.9	
5	159.2		158.9	
6	103.7	6.73 (1H, d, 2.0)	103.8	6.75 (1H, d, 2.1)
7	162.9		162.8	
8	97.8	6.59 (1H, d, 2.0)	97.6	6.56 (1H, d, 2.1)
9	157.8		157.4	
10	108.4		108.2	
1′	121.9		121.4	
2′	116.3	7.50 (1H, d, 2.0)	116.0	7.50 (1H, d, 2.0)
3′	145.3		145.1	
4′	148.4		148.1	
5′	115.5	6.82 (1H, d, 8.5)	115.1	6.80 (1H, d, 8.5)
6′	121.8	7.58 (1H, dd, 8.5, 2.0)	121.4	7.51 (1H, dd, 8.5, 2.0)
5-O-glucose				
1″	104.4	4.78 (1H, d, 8.0)	104.5	4.75 (1H, d, 7.5)
2″	74.0	3.37 (1H, m)	73.8	3.38 (1H, m)
3″	76.2	3.32 (1H, m)	75.8	3.30 (1H, m)
4″	70.1	3.23 (1H, m)	69.8	3.21 (1H, m)
5″	78.0	3.36 (1H, m)	77.8	3.34 (1H, m)
6″	61.3	3.75 (1H, m)	61.0	3.76 (1H, m)
		3.57 (1H, m)		3.57 (1H, m)
3-O-glucose				
1‴	98.0	5.65 (1H, d, 7.5)	97.7	5.68 (1H, d, 7.5)
2‴	77.7	3.43 (1H, m)	76.9	3.55 (1H, m)
3‴	77.8	3.50 (1H, m)	77.1	3.49 (1H, m)
4‴	71.1	3.44 (1H, m)	70.2	3.29 (1H, m)
5‴	77.8	3.10 (1H, m)	77.8	3.34 (1H, m)
6‴	63.4	3.32 (2H, m)	63.1	4.22 (1H, m)
				4.08 (1H, m)
Rhamnose				
1⁗	100.9	5.09 (1H, s)	100.5	5.09 (1H, s)
2⁗	70.8	3.12 (1H, m)	70.7	3.44 (1H, m)
3⁗	71.1	3.74 (1H, m)	70.7	3.74 (1H, m)
4⁗	72.4	3.11 (1H, m)	72.0	3.09 (1H, m)
5⁗	68.6	3.69 (1H, m)	68.3	3.69 (1H, m)
6⁗	17.5	0.72 (3H, d, 6.0)	17.1	0.70 (3H, d, 6.0)
Caffeoyl				
1			166.3	
2			113.7	6.07 (1H, d, 15.8)
3			145.1	7.25 (1H, d, 15.8)
4			125.5	
5			114.9	6.95 (1H, d, 1.5)
6			145.6	
7			148.4	
8			116.0	6.72 (1H, d, 8.3)
9			121.3	6.73 (1H, dd, 1.5, 8.3)



1 **2**

Figure 2. Key HMBC correlations of compounds **1** and **2**.

measured with a Perkin-Elmer 341 polarimeter. ^{1}H NMR spectra (DMSO-d_6) were taken on Bruker ACF-500 MHz spectrometer and ^{13}C NMR spectra (DMSO-d_6) were taken on Bruker ACF-125 MHz spectrometer, using TMS as internal standard. ESI-MS spectra were recorded on Agilent 1100 series LC/MS Trap, HR-TOF-MS spectra were recorded on Waters Synapt Q-TOF spectrometer. All solvents used were of analytical grade. Sephadex LH-20 (Pharmacia Biotech, Svensk, Sweden) and silica gel (200–300 mesh, Qingdao Marine Chemical Company, Qingdao, China) were used for column chromatography (CC), and precoated silica gel GF_{254} plates were used for TLC (Qingdao Marine Chemical Company, Qingdao, China).

3.2 Plant material

The seeds of *I. balsamina* L. were collected in Xuyi Prefecture, Jiangsu Province of China in March 2007 and identified by researcher Shi-Hui Qian. A voucher specimen (2007001) was deposited in the department of Resource of Traditional Chinese Medical Materials, Jiangsu Province Institute of Traditional Chinese Medicine.

3.3 Extraction and isolation

The 80 and 60% ethanol extracts of the seeds (16 kg) of *I. balsamina* were concentrated and suspended in H_2O, then partitioned by petroleum ether, EtOAc, and *n*-BuOH. The *n*-BuOH fraction (160 g) was sequentially subjected to CC on macroporous resin by gradient ethanol, to afford 30, 50, and 70% ethanol fractions. The 30% ethanol fraction (30.5 g) was subjected to repeated CC (silica gel, gradient mixtures, $CHCl_3$–MeOH, 1:0–0:1), to afford several fractions. The fraction eluted with $CHCl_3$–MeOH (7:3) (3.7 g) was successively purified over silica gel ($CHCl_3$–MeOH–H_2O, 25:6:1) and Sephadex LH-20 (MeOH) and ODS (MeOH–H_2O) column to afford compound **1** (20 mg). The fraction eluted with $CHCl_3$–MeOH (6:4) (1.3 g) was subjected to repeated column chromatographies on silica gel ($CHCl_3$–MeOH–H_2O, 25:6:1) and ODS (MeOH–H_2O), leading to the isolation of **2** (30 mg).

3.3.1 Compound *1*

Yellow amorphous powder. $[\alpha]_D^{22}$ 137.1 ($c = 0.305$, MeOH). IR (KBr) ν_{max}: 3422, 1627, 1609, 1515, 1448, 1066 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) spectral data see Table 1. ESI-MS: *m/z* 771.2 $[M - H]^-$. HR-TOF-MS: *m/z* 771.1995 $[M - H]^-$ (calcd for $C_{33}H_{39}O_{21}$, 771.1984).

3.3.2 Compound *2*

Yellow amorphous powder. $[\alpha]_D^{22}$ −147.9 ($c = 0.690$, MeOH). IR (KBr) ν_{max}: 3384,

1633, 1607, 1515, 1448, 1035 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) and ^{13}C NMR (125 MHz, DMSO-d_6) spectral data see Table 1. ESI-MS: *m/z* 933.2 $[M - H]^-$. HR-TOF-MS: *m/z* 933.2365 $[M - H]^-$ (calcd for $C_{42}H_{45}O_{24}$, 933.2301).

Acknowledgement

We are thankful to Prof. Dong-Jun Chen of China Pharmaceutical University for spectral measurements.

References

[1] Pharmacopoeia Commission of People's Republic of China, *Pharmacopoeia of the People's Republic of China* (Chemical Industry Press, Beijing, 2005), Vol. 1.

[2] X.L. Hu, H. Zhu, C.R. Liu, and P.F. Tu, *Chin. Tradit. Pat. Med.* **25**, 833 (2003).

[3] W. Charles and J. Hagen, *Am. J. Bot.* **53**, 46 (1966).

[4] F. Hisae, K. Ishiguro, T. Murashima, M. Yamaki, and K. Isoi, *Phytochemistry* **37**, 1486 (1995).

[5] H. Oku and K. Ishiguro, *Phytother. Res.* **15**, 506 (2001).

[6] S. Clevenger, *Arch. Biochem. Biophys.* **76**, 131 (1958).

[7] A.G. Damu, B. Jayaprakasam, K.V. Rao, and D. Gunasekar, *Phytochemistry* **49**, 1811 (1998).