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Glycosides of flavone methyl ethers from *Murraya paniculata*

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1. Subject and source

The leaves and shoots of *Murraya paniculata* (L.) Jack were collected in September 2008 from Guangxi, P.R. China. The plant material was identified by Prof. Pengfei Tu (School of Pharmaceutical Sciences, Peking University). A voucher specimen (NO. MP-GZ-0804) was deposited in the Herbarium of Peking University Modern Research Center for Traditional Chinese Medicine.

2. Previous work

In the Chinese Pharmacopeia, the leaves and shoots of *M. paniculata* and *Murraya exotica* are both named as "*Jiulixiang*", a traditional Chinese medicine which was commonly used as analgesic (Zhu et al., 2000), antibacterial (Yu et al., 2001; Luo et al., 2004), and anti-inflammatory agents (Liang, 2004). Previously phytochemical investigations on the species of this genus resulted in the isolation and structural elucidation of diverse components including coumarins (Barik et al., 1983a, 1983b, 1987; Ito and Furukawa, 1987, 1989; Imai et al., 1989; Kinoshita et al., 1996a, 1996b; Srivastava et al., 1996a, 1996b; Negi et al., 2005), alkaloids (Bhattacharyya et al., 1978; Ganguly and Sarkar, 1978; Roy and Bhattacharya, 1981; Kinoshita et al., 1989; Khan et al., 1994; Wu, 1991; Wu, et al., 1994, 1995a, 1995b, 1996a, 1996b), and flavonoids (Joshi and Kamat, 1969; Kinoshita and Firman, 1996, 1997; Ferracin et al., 1998; Zhang et al., 2010).

3. Present study

In the present study, we report the isolation and structural elucidation of two new glycosides of flavone methyl ethers from the leaves and shoots of *M. paniculata*.

Air-dried leaves and shoots (9.0 kg) of *M. paniculata* were extracted with 50% ethanol (v/v). The extract solution was filtered and concentrated under reduced pressure to yield 498.5 g residue which was suspended in H_2O and extracted with

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petroleum ether, EtOAc, and *n*-butanol, successively. A portion of *n*-butanol extract (95.0 g) was subjected to silica gel column chromatography eluting with a step-wise gradient of $CHCl_3$ and MeOH to obtain twelve fractions. The fraction eluted by $CHCl_3$–MeOH (1:3) (1.2 g) was further repeatedly separated by silica gel column chromatography (eluted with petroleum ether-$CHCl_3$-MeOH = 2:3:1) to obtain compounds **1** (56.0 mg) and **2** (78.9 mg).

Compound **1** was obtained as a yellow powder, with the molecular formula $C_{24}H_{26}O_{13}$, as deduced from the $[M + H]^+$ peak at *m*/*z* 523.1446 (calcd for $C_{24}H_{27}O_{13}$, 523.1446) by HRESI-MS and supported by ^{13}C NMR data. The UV spectrum of **1** showed typical absorptions of flavonoids at 281 and 347 nm. The ^1H NMR spectrum of **1** indicated the presence of four aromatic protons resonating at δ 6.81 (1H, s), 7.55 (1H, br.s), 7.06 (1H, br.d, J = 7.0 Hz), and δ 7.79 (1H, br.d, J = 7.0 Hz), respectively, three methoxy groups resonating at δ 3.82 (3H, s), 4.01 (3H, s), and δ 3.88 (3H, s), and two hydroxyl protons resonating at δ 9.31 (1H, s), and δ 12.87 (1H, s). The ^{13}C NMR spectrum of **1** showed the presence of 15 aromatic carbons containing one carboxyl carbon at δ 182.0, and three methoxyl carbons at δ 61.1, 59.9, and δ 55.3. Moreover, the ^{13}C NMR spectrum of **1** also indicated six carbons (δ 103.3, 73.5, 75.8, 69.6, 76.8, and 60.7) attributed to a glycosyl moiety, and the anomeric proton was presented at δ 4.81 (1H, d, J = 7.5 Hz) in the ^1H NMR spectrum. The NMR data mentioned above thus led us to propose that compound **1** was a trimethoxyl ether of a flavone *O*-glucoside. All the protons and carbons of **1** were unambiguously assigned by detailed analysis of its ^1H NMR, ^{13}C NMR, HMQC and HMBC spectra (Table 1). In the HMBC spectrum of **1**, the correlations between the proton resonating at δ 9.31 (1H, s) and C-3′ (δ 146.1) suggested that this hydroxyl group was linked at C-3′. The proton resonating at δ 12.87 (1H, s), the chemical shift of which was affected by the carboxyl group at C-4, and thus shifted downfield, was assigned as a chelating hydroxyl group at C-5 (δ 148.4); the long range correlations between 6-OCH_3 at δ 3.82 (3H, s) and C-6 (δ 135.5), between 7-OCH_3 at δ 4.01 (3H, s) and C-7 (δ 152.4), and between 4′-OCH_3 at δ 3.88 (3H, s) and C-4′ (δ 150.9) completely established the substituted positions of the methoxy groups (Fig. 1). Furthermore, the anomeric proton at δ 4.81 (1H, d, J = 7.5 Hz) showed a long range correlation with C-8 (δ 128.5), suggesting that the glycosyl moiety was linked to C-8, and the relatively large coupling constant (J = 7.5 Hz) of the anomeric proton suggested the glucopyranosyl moiety was β-configured. Finally, acid hydrolysis of **1** with 2 N CF_3COOH gave glucose. Accordingly, the structure of **1** was unambiguously established as 5, 8, 3′-trihydroxy-6, 7, 4′-trimethoxy flavone 8-*O*-β-glucopyranoside.

Compound **2** was obtained as a yellow powder. The HRESI-MS spectrum showed an accurate $[M + H]^+$ ion peak at *m*/*z* 537.1602 (calcd for $C_{25}H_{29}O_{13}$, 537.1603), in accordance with an empirical molecular formula of $C_{25}H_{28}O_{13}$. The UV spectrum of **2** showed typical absorptions of flavonoids at 280 and 346 nm. The comparison of the NMR data of **1** with that of **2** suggested that compounds **1** and **2** possessed almost the same skeleton, the only difference is that the hydroxy group at C-3′ in **1** was replaced by a methoxy group in **2**, which was demonstrated by the long range correlation between 3′-OCH_3

Table 1
NMR data of compounds **1** and **2** (in DMSO-d_6).

No.	Compound **1**[a]		Compound **2**[b]	
	^1H	^{13}C	^1H	^{13}C
2		163.7		164.1
3	6.81 (1H, s)	102.4	7.07 (1H, s)	103.3
4		182.0		182.7
5		148.4		148.9
6		135.5		136.1
7		152.4		152.3
8		128.5		128.9
9		145.0		145.5
10		105.7		106.2
1′		122.4		122.8
2′	7.55 (1H, br.s)	113.1	7.69 (1H, d, J = 1.5 Hz)	109.5
3′		146.1		149.0
4′		150.9		153.1
5′	7.06 (1H, br.d, J = 7.0 Hz)	111.3	7.11 (1H, d, J = 8.4 Hz)	111.6
6′	7.79 (1H, br.d, J = 7.0 Hz)	118.9	7. 93 (1H, dd, J = 8.4, 1.5 Hz)	120.9
5-OH	12.87 (1H, s)		12.89 (1H, s)	
6-OCH_3	3.82 (3H, s)	59.9	3.91 (3H, s)	60.4
7-OCH_3	4.01 (3H, s)	61.1	4.02 (3H, s)	61.6
4′-OCH_3	3.88 (3H, s)	55.3	3.84 (3H, s)	55.7
3′-OH/OCH_3	9.31 (1H, s)		3.87 (3H, s)	55.9
1″	4.81 (1H, d, J = 7.5 Hz)	103.3	4.84 (1H, d, J = 7.5 Hz)	103.7
2″	3.36–3.40 (overlapped)	73.5	3.34 (overlapped)	74.1
3″	3.24–3.28 (1H, m)	75.8	3.27 (1H, m)	76.3
4″	3.14–3.19 (1H, m)	69.6	3.15 (overlapped)	70.1
5″	3.09–3.12 (1H, m)	76.8	3.12 (overlapped)	77.3
6″a	3.36–3.39 (overlapped)	60.7	3.34 (overlapped)	61.0
6″b	3.62 (1H, dd, J = 4.0, 11.0 Hz)		3.60 (1H, dd, J = 5.4, 11.0 Hz)	

[a] ^1H NMR 500 MHz, ^{13}C NMR 125 MHz.
[b] ^1H NMR 300 MHz, ^{13}C NMR 75 MHz.