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Acetylated flavonol diglucosides from *Meconopsis quintuplinervia*

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Abstract

Four acetylated flavonol diglucosides, quercetin 3-*O*-[2‴-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] (**1**), quercetin 3-*O*-[2‴,6‴-*O*-diacetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] (**2**), isorhamnetin 3-*O*-[2‴-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] (**3**), and quercetin 3-*O*-[2‴-*O*-acetyl-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside] (**4**), together with five known flavonol glycosides quercetin 3-*O*-β-D-glucopyranoside, kaempferol 3-*O*-β-D-glucopyranoside, quercetin 3-*O*-[β-D-galactopyranosyl-(1 → 6)-glucopyranoside], isorhamnetin 3-*O*-[β-D-galactopyranosyl-(1 → 6)-β-D-glucopyranoside], and kaempferol 3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] have been isolated from *Meconopsis quintuplinervia*. Their structures were determined using chemical and spectroscopic methods including HRFABMS, ^{1}H–^{1}H COSY, HSQC and HMBC experiments.

Keywords: *Meconopsis quintuplinervia* Regel; Papaveraceae; Acetylated flavonol glycosides

1. Introduction

Meconopsis quintuplinervia Regel, a plant belonging to the Papaveraceae family and widely distributed in the Qingzang plateau of the northwest of China (Luo et al., 1984), is used as a traditional Tibetan medicine for treatments of various diseases, such as inflammation, pain, hepatitis and tuberculosis (Luo et al., 1984). There are, however, very few reports (Wang et al., 1991; Wang and Chen, 1995) concerning secondary metabolites of *M. quintuplinervia*. As part of our program to assess systematically the chemical and biological diversity of medicinal plants distributed at higher altitude, we carried out a chemical investigation of this plant. In previous papers (Shang et al., 2002, 2003a,b), we described the isolation and structural identification of three alkaloids, norsanguinarine, *O*-methylflavinantine and meconoquintupline, and seven flavonoids, quercetin, dihydroquercetin, luteolin, chrysoeriol, apigenin, huazhongilexone and hydnocarpin from the less polar fraction of the ethanolic extract of the plant. In continuation of this work, four new acetylated flavonol diglucosides (**1**–**4**), together with five known flavonol glycosides, have been isolated from the polar fraction of the same material. By comparison of the spectroscopic data with those reported in the literature, the known compounds were characterized as quercetin 3-*O*-β-D-glucopyranoside (Veit et al., 1990), kaempferol 3-*O*-β-D-glucopyranoside (Chaurasia and Wichtl, 1987), quercetin 3-*O*-[β-D-galactopyranosyl-(1 → 6)-glucopyranoside] (Waage and Hedin, 1985), isorhamnetin 3-*O*-[β-D-galactopyranosyl-(1 → 6)-β-D-glucopyranoside] (Degot et al., 1971) and kaempferol 3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] (Song, 1990). The present paper deals with isolation and structural elucidation of compounds **1**–**4**.

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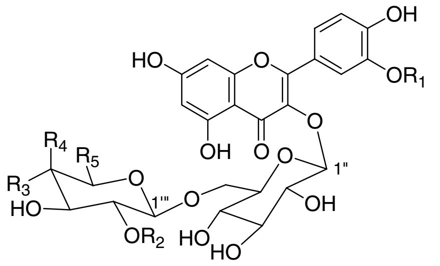

1 $R_1 = R_4 = H$, $R_2 = Ac$, $R_3 = OH$, $R_5 = CH_2OH$
2 $R_1 = R_4 = H$, $R_2 = Ac$, $R_3 = OH$, $R_5 = CH_2OAc$
3 $R_1 = Me$, $R_2 = Ac$, $R_3 = OH$, $R_4 = H$, $R_5 = CH_2OH$
4 $R_1 = R_3 = H$, $R_2 = Ac$, $R_4 = OH$, $R_5 = H$

2. Results and discussion

The water soluble portion of the ethanolic extract of *M. quintuplinervia* Regel was subjected successively to column chromatography on macroporous adsorbent resin, normal phase and reversed phase silica gels and Sephadex LH-20, to afford two mixtures which were further purified by preparative reversed phase HPLC to yield compounds **1**–**4** and the known compounds.

Compound **1** was isolated as a yellow amorphous powder. Its IR spectrum showed the presence of hydroxyl (3400 cm^{-1}), conjugated carbonyl (1734 and 1655 cm^{-1}) and aromatic ring (1506 and 1604 cm^{-1}) functional groups. Its UV spectrum exhibited absorption bands characteristic for flavonols at 207, 257, 270, 296, and 362 nm. The positive FABMS exhibited a quasi-molecular ion peak at *m*/*z* 669 $[M + H]^+$, with the molecular formula established as $C_{29}H_{32}O_{18}$ by the positive HRFABMS at *m*/*z* 669.1615$[M + H]^+$ (calcd. for $C_{29}H_{33}O_{18}$ 669.1666). The ^{1}H NMR spectrum of **1** showed two anomeric proton doublets at δ 5.06 (1H, *d*, $J = 7.8$ Hz, H-1″) and 4.15 (1H, *d*, $J = 8.1$ Hz, H-1‴) and an acetyl singlet at δ 1.61 (3H, s), in addition to resonances characteristic for a quercetin aglycone moiety (Table 1), as well as signals attributed to remaining protons of two glycosyl units between δ 2.84 and 4.40. These data indicated that compound **1** was an acetylated quercetin diglycoside, which was confirmed by analysis of the ^{13}C NMR spectroscopic data of **1** (Table 2). Acid hydrolysis of **1** produced glucose as the sole sugar as identified by TLC and PC comparison with authentic sugar samples. The ^{1}H–^{1}H COSY and HSQC experiments of **1** led to unambiguous assignments of signals of the protons and protonated carbons in the NMR spectra of **1**, while the resolvable axial-axial couplings between vicinal protons of the glycosyl units, excluding H-5″, H$_2$-6″, H-5‴ and H$_2$-6‴ (Table 1), confirmed that both glycosyl units were β-glucopyranosyls. The chemical shift of C-3 suggested that the quercetin aglycone was glycosylated at C-3, which was confirmed by a long range correlation from H-1″ to C-3 (δ 136.0) in the HMBC spectrum of **1**. Meanwhile, HMBC correlations from H-1‴ to C-6″(δ 69.2) and H$_2$-6″ to C-1‴ (δ 102.1) unequivocally revealed an 1 → 6 connectivity between the two β-glucopyranosyls. In addition, the carbonyl (δ 169.1) of the acetoxyl group correlated to H-2‴ of the outer β-glucopyranosyl unit at δ

Table 1
^{1}H NMR spectroscopic data for compounds **1**–**4**

No.	**1**	**2**	**3**	**4**
6	6.15 *d* (1.8)	6.16 *d* (2.1)	6.15 *d* (2.0)	6.15 *d* (2.1)
8	6.38 *d* (1.8)	6.39 *d* (2.1)	6.38 *d* (2.0)	6.38 *d* (2.1)
2′	8.01 *d* (2.4)	8.07 *d* (2.1)	8.16 *d* (1.8)	8.09 *d* (2.1)
5′	6.84 *d* (9.0)	6.85 *d* (8.5)	6.87 *d* (8.7)	6.84 *d* (9.0)
6′	7.65 *dd* (2.4, 9.0)	7.68 *dd* (2.1, 8.5)	7.63 *dd* (1.8, 8.7)	7.69 *dd* (2.1, 9.0)
1″	5.06 *d* (7.8)	5.08 *d* (7.8)	5.25 *d* (7.8)	5.01 *d* (7.8)
2″	3.80 *dd* (7.8, 8.4)	3.82 *dd* (7.8, 7.8)	3.80 *dd* (7.8, 8.1)	3.83 *dd* (7.8, 7.8)
3″	3.54 *dd* (8.4, 7.5)	3.55 *dd* (7.8, 7.5)	3.54 *dd* (8.1, 9.4)	3.55 *dd* (7.8, 7.5)
4″	3.72 *dd* (7.5, 7.2)	3.70 *dd* (7.5, 7.8)	3.70 *dd* (9.4, 7.2)	3.69 *dd* (7.5, 7.2)
5″	3.51 *m*	3.52 *m*	3.50 *m*	3.53 *m*
6″	3.68 *m*	3.64 *m*	3.68 *m*	3.64 *m*
1‴	4.15 *d* (8.1)	4.16 *d* (8.1)	4.22 *d* (7.8)	4.01 *d* (7.8)
2‴	4.40 *dd* (8.1, 9.0)	4.37 *dd* (8.1, 8.4)	4.40 *dd* (7.8, 9.3)	4.63 *dd* (7.8, 9.3)
3‴	3.04 *dd* (9.0, 9.3)	2.98 *dd* (8.4, 9.3)	3.06 *dd* (9.3, 9.3)	2.94 *dd* (9.3, 9.3)
4‴	3.20 *dd* (9.3, 9.6)	3.15 *dd* (9.3, 9.3)	3.19 *dd* (9.3, 9.6)	3.52 *m*
5‴	2.84 *m*	2.84 *m*	2.67 *m*	(a) 3.00 *brd* (12.3) (b) 3.70 *m*
6‴	(a) 3.69 *m* (b) 3.57 *m*	(a) 4.20 *dd* (2.1, 12.3) (b) 4.03 *dd* (5.5,12.3)	(a) 3.64 *dd* (2.4, 11.7) (b) 3.48 *m*	
Ac	1.61 *s*	1.59 *s*	1.64 *s*	1.56 *s*
Ac		1.98 *s*		
OMe			3.92 *s*	

^{1}H NMR data were measured in methanol-d_4 at 300 MHz. Proton coupling constants (*J*) in Hz are given in parentheses. The assignments were based on DEPT,^{1}H–^{1}H COSY, HSQC and HMBC experiments.