Available online at www.sciencedirect.com
SCIENCE DIRECT
Phytochemistry 67 (2006) 511–515
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Acetylated flavonol diglucosides from *Meconopsis quintuplinervia*

Xiao-Ya Shang [a], Ying-Hong Wang [a], Chong Li [b], Cheng-Zhong Zhang [b], Yong-Chun Yang [a], Jian-Gong Shi [a,*]

[a] *Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China*
[b] *Lanzhou Medical College, Lanzhou University, Lanzhou 730000, China*

Received 11 March 2005; received in revised form 17 August 2005
Available online 18 January 2006

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.

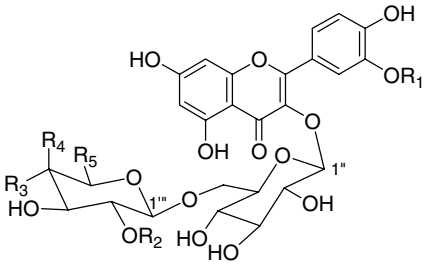
Keywords: *Meconopsis quintuplinervia* Regel; Papaveraceae; Acetylated flavonol glycosides

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**.

* Corresponding author. Tel.: +86 10 83154789; fax: +86 10 63017757.
E-mail address: shijg@imm.ac.cn (J.-G. Shi).

0031-9422/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2005.12.002



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 ^1H 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 ^1H–^1H 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 $1 \rightarrow 6$ 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
^1H 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*	

^1H 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,^1H–^1H COSY, HSQC and HMBC experiments.

Table 2
^{13}C NMR spectroscopic data for compounds **1**–**4**

No.	1	2	3	4
2	158.2	156.9	158.1	157.8
3	136.0	134.8	135.5	136.2
4	179.2	178.1	179.4	179.2
5	162.9	161.8	163.0	162.9
6	100.0	98.8	100.0	100.1
7	166.2	165.1	166.2	166.7
8	94.9	93.8	95.0	95.0
9	158.3	157.2	158.4	158.3
10	105.6	104.4	105.8	105.4
1′	122.6	121.4	122.8	122.6
2′	117.9	116.7	114.5	117.9
3′	145.9	144.8	148.5	146.0
4′	150.2	149.2	151.1	150.3
5′	116.5	115.4	116.2	116.3
6′	122.9	121.6	123.6	122.8
1″	105.7	104.4	104.5	106.0
2″	73.2	72.0	73.1	73.2
3″	74.8	73.5	74.7	74.8
4″	70.5	69.6	70.4	70.7
5″	77.3	76.6	77.3	77.8
6″	69.2	68.0	68.8	69.1
1‴	102.1	100.8	101.8	102.7
2‴	75.3	74.0	75.3	73.7
3‴	75.7	74.3	75.8	72.0
4‴	71.3	70.2	71.3	69.8
5‴	77.2	73.6	77.3	67.0
6‴	62.2	63.1	62.1	
Ac	20.3	19.3	20.6	20.6
	169.1	170.5	171.8	172.0
Ac		19.6		
		171.8		
OMe			57.0	

^{13}C NMR data were measured in methanol-d_4 at 75 MHz. The assignments were based on DEPT, ^{1}H–^{1}H COSY, HSQC and HMBC experiments.

4.40 (1H, *dd*, $J = 8.1$ and 9.0 Hz), demonstrating that the acetoxyl group was located at C-2‴ of the glucopyranosyl. Thus, **1** was quercetin 3-*O*-[2‴-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside].

Compound **2** was obtained as a yellow powder with a molecular formula $C_{31}H_{34}O_{19}$ as determined by the positive FABMS at *m/z* 711.1810 $[M + H]^+$ (calcd. for $C_{31}H_{35}O_{19}$, 711.1772). The UV, IR and NMR spectra of **2** were similar to those of **1**, except for the appearance of signals due to one more acetoxyl unit at δ_H 1.98 (3H, s) and δ_C 19.6 (q) and 171.8 (s) in the NMR spectra of **2**, indicating that it was an acetylated cognate of **1**. This was supported by acid hydrolysis and 2D NMR spectroscopic experiments of **2**. In the HMBC spectrum of **2** correlations from H-2‴ to one acetoxyl carbonyl and from H_2-6‴ to the other unequivocally established that the two acetyls were esterified at C-2‴ and C-6‴ of the outer glucosyl moiety, respectively. Therefore, **2** was quercetin 3-*O*-[2‴,6‴-*O*-diacetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside].

Compound **3** was obtained as a yellow powder. Its molecular formula was determined as $C_{30}H_{34}O_{18}$ by the positive FABMS at *m/z* 683.1854 $[M + H]^+$ (calcd. for $C_{30}H_{35}O_{18}$ 683.1823). The UV, IR and NMR spectra of **3** were similar to those of **1**, except for the appearance of signals attributed to an aromatic methoxyl group at δ_H 3.92 (3H, s) and δ_C 57.0 in the NMR spectra of **3**, indicating that it was a methylated derivative of **1**. A comparison of the NMR spectroscopic data of **3**, with those of the co-occurring isorhamnetin 3-*O*-[β-D-galactopyranosyl-(1 → 6)-β-D-glucopyranoside] (Degot et al., 1971), demonstrated that the aglycone of **3** was isorhamnetin. Therefore, **3** was isorhamnetin 3-*O*-[2‴-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside].

Compound **4** was obtained as a yellow powder with a molecular formula $C_{28}H_{30}O_{17}$ as established by the positive HRFABMS at *m/z* 639.1546 $[M + H]^+$. The UV and IR spectra of **4** were similar to those of **1**. A comparison of its NMR spectroscopic data with those of **1** (Tables 1 and 2) indicated that the only difference between **1** and **4** was replacement of the outer glucopyranosyl of **1** by an arabinopyranosyl (Simon et al., 1993) in **4**. This was supported by acid hydrolysis of **4** yielding glucose and arabinose as the sugars. The location of the acetyl linkage between the glycosyls in **4** was further confirmed by 2D NMR experiments (^{1}H–^{1}H COSY, HSQC and HMBC). Consequently, **4** was quercetin 3-*O*-[2‴-*O*-acetyl-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside].

Previous studies indicated that plants of the genus *Meconopsis* contained alkaloids (Hemingway et al., 1981; Allais et al., 1983; Liu and Wang, 1986; Wang and Chen, 1995), triterpenoids (Zhang et al., 1997) and flavonoids (Tanaka et al., 2001), although the emphasis of the chemical investigations thus far was focused on the alkaloids in species of this genus. However, our systematical chemical investigation of *M. quintuplinervia* has revealed that diverse flavonoids represent the main metabolites in this species while two morphinane alkaloids, *O*-methylflavinantine and meconoquintupline, and a benzophenanthrindine alkaloid norsanguinarine, were obtained (Shang et al., 2002, 2003a,b). The structures of the acetylated flavonol diglycosides and meconoquintupline from *M. quintuplinervia* were distinctive by the number and/or substitution position of acetyl in the acetylated flavonol diglycosides and the 8,14-dihydrogenation of the morphinane skeleton in meconoquintupline, i.e., even though flavonoids from *Meconopsis grandis* (Tanaka et al., 2001) and the morphinane/benzophenanthrindine alkaloids from several *Meconopsis* species (Hemingway et al., 1981) have been reported, respectively. Both alkaloids and flavonoids may, therefore, have chemotaxonomically important roles in the genus *Meconopsis* though flavonoids from this genus have received relatively little attention.

In the cytotoxic and antioxidant assays compounds **1**–**4** and the known flavonoids showed neither cytotoxicity against human colon cancer (HCT-8), hepatoma (Bel-7402), stomach cancer (BGC-823), and lung adenocarcinoma (A549) cell lines ($IC_{50} > 10$ μg/mL) nor significant antioxidant activity inhibiting rat liver microsomal lipid peroxidation ($IC_{50} > 5$ μg/mL).

3. Experimental

3.1. General

Melting points were determined on an XT-4 micro melting point apparatus and are uncorrected. IR spectra were recorded as KBr disks on a Nicolet Impact 400 FT-IR Spectrophotometer. 1D- and 2D NMR spectra were obtained at 300 and 75 MHz for ^{1}H and ^{13}C, respectively, on Inova 300 or 500 MHz spectrometers in methanol-d_4 or DMSO-d_6 with solvent peaks as references. FABMS and HRFABMS data were measured with a Micromass Autospec-Ultima ETOF spectrometer. Column chromatography was performed with silica gel (200–300 mesh), RP-18 reversed phase silica gel (43–60 μm) and Sephadex LH-20. HPLC separation was performed on an instrument consisting of a Waters 600 controller, a Waters 600 pump, and a Waters 2487 dual λ absorbance detector with an Alltima (250×22 mm) preparative column packed with C_{18} (10 μm). TLC was carried out with glass precoated silica gel GF_{254} plates. Spots were visualized under UV light or by spraying with 3% $FeCl_3$ in EtOH or 7% H_2SO_4 in 95% EtOH followed by heating.

3.2. Plant material

M. quintuplinervia Regel (4 kg) was collected at Daban mountain at an altitude of 3400–3600 m, Qinghai province, China, in August of 1999. The plant was identified by Prof. Guo-liang Zhang (Department of Biology, Lanzhou University, Lanzhou 730000, China). A voucher specimen (No. 200025) was deposited at the Herbarium of the Department of Medicinal Plants, Institute of Materia Medica, Beijing, China.

3.3. Extraction and isolation

Air dried aerial parts of *M. quintuplinervia* (4 kg) were extracted with 11.0 L of 90% EtOH at room temperature for 3×48 h. The ethanolic extract was evaporated to almost dryness in vacuo to yield a dark brown viscid residue (470 g). The residue was suspended in H_2O (1100 mL) and then partitioned successively with petroleum ether (4×800 mL), and EtOAc (4×650 mL). The aq. phase resulting from the partition was applied to a macroporous adsorbent resin (RA, Seventh Factory of Beijing Chemical Industry, China) (650 g, dried weight) column using H_2O and EtOH–H_2O (6:4) as eluents. After solvent removal, the fraction (7.8 g) eluted by EtOH–H_2O (6:4) was subjected to normal phase silica gel CC eluting with a gradient of increasing MeOH in $CHC1_3$. The $CHCl_3$–MeOH (4:1) eluent gave a mixture that was separated into three subfractions by gel chromatography over Sephadex LH-20 eluted with $CHCl_3$–MeOH (1:1). The third subtraction was purified by reversed-phase HPLC using MeOH–H_2O (45:55) as mobile phase to give quercetin 3-*O*-[β-D-galactopyranosyl-(1 → 6)-glucopyranoside] (35 mg) and quercetin 3-*O*-β-D-glucopyranoside (21 mg). The $CHCl_3$–MeOH (2:1) eluent was separated into four subfractions by gel chromatography over Sephadex LH-20 eluted with $CHCl_3$–MeOH (1:1). The third and fourth subfractions were further purified, respectively, by preparative reversed phase HPLC using MeOH–H_2O (40:60) as the mobile phase to afford **1** (18 mg), **2** (21 mg), **3** (17 mg), **4** (15 mg), kaempferol 3-*O*-β-D-glucopyranoside (27 mg), isorhamnetin 3-*O*-[β-D-galactopyranosyl-(1 → 6)-β-D-glucopyranoside] (31 mg) and kaempferol 3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] (13 mg).

3.4. Quercetin 3-O-[2‴-O-acetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] (1)

Amorphous yellow powder; $[\alpha]_D^{20}$ +20.6 (MeOH *c* 0.16); UV λ_{max}^{MeOH} nm (log ε): 207 (4.37), 257 (4.14), 270 (4.03), 296 (3.73), 362 (4.08); IR ν_{max}^{KBr} cm^{-1}: 3400, 2910, 1734, 1655, 1604, 1506, 1444, 1360, 1304, 1200, 1169, 1074, 1022. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; FABMS (*m/z*): 669 $[M + H]^+$. HRFABMS (*m/z*): 669.1615 $[M + H]^+$, $C_{29}H_{33}O_{18}$ requires 669.1666.

3.5. Quercetin 3-O-[2‴,6‴-O-diacetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] (2)

Amorphous yellow powder; $[\alpha]_D^{20}$ +30.8 (MeOH; *c* 0.25); UV λ_{max}^{MeOH} nm (log ε): 206 (4.45), 257 (4.18), 270 (4.07), 296 (3.77), 363 (4.13); IR ν_{max}^{KBr} cm^{-1}: 3419, 2908, 1732, 1653, 1604, 1506, 1444, 1361, 1244, 1078. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; FABMS (*m/z*): 711$[M + H]^+$, HRFABMS (*m/z*): 711.1810 $[M + H]^+$, $C_{31}H_{35}O_{19}$ requires 711.1773.

3.6. Isorhamnetin 3-O-[2‴-O-acetyl-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] (3)

Amorphous yellow powder; $[\alpha]_D^{20}$ +19.4 (MeOH; *c* 0.15); UV λ_{max}^{MeOH} nm (log ε): 206 (4.39), 255(4.08), 269(3.99), 298(3.75), 357(4.03); IR ν_{max}^{KBr} cm^{-1}: 3415, 2908, 1732, 1653, 1604, 1514, 1431, 1356, 1290, 1203, 1074, 1028. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; FAB MS *m/z*: 683 $[M + H]^+$; HRFABMS *m/z*: 683.1854 $[M + H]^+$, $C_{30}H_{35}O_{18}$ requires 683.1823.

3.7. Quercetin 3-O-[2‴-O-acetyl-α-L-arabinopyranosyl-(1 → 6)-β-D-glucopyranoside] (4)

Amorphous yellow powder; $[\alpha]_D^{20}$ +32.9 (MeOH; *c* 0.04); UV λ_{max}^{MeOH} nm (log ε): 207 (4.55), 257 (4.32), 269 (4.24), 298 (3.94), 363 (4.26); IR ν_{max}^{KBr} cm^{-1}: 3400, 2918, 1732, 1653, 1604, 1498, 1446, 1360, 1304, 1201, 1171, 1072, 1020. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2; FABMS *m/z*: 639 $[M + H]^+$; HRFABMS *m/z*: 639.1546 $[M + H]^+$, $C_{28}H_{31}O_{17}$ requires 639.1561.

3.8. Acid hydrolysis of **1–4**

A solution of each compound (5 mg) in 2 N HCl (2 mL) was individually refluxed for 16 h at 94 °C. The reaction mixture was partitioned with EtOAc, with the aqueous phase neutralized with 1 N NaOH and dried using a stream of N_2. The resulting residue was dissolved in EtOH (0.5 mL) and analyzed by TLC and PC together with authentic sugar samples, using as developing solvent systems $CHCl_3$–MeOH (2.5:1) for TLC and the upper layer of *n*-BuOH–AcOH–H_2O (4:1:5) for PC; products were visualized by spraying aniline hydrogen phthalate followed by heating at 105 °C.

Acknowledgements

The authors are grateful to A. Zeper for mass spectra measurements. Financial support is from the NSFC (Grant No. 20432030).

References

Allais, D.P., Guinaudeau, H., Freyer, A.J., Shamma, M., Ganguli, N.C., Talapatra, B., Talapatra, S.K., 1983. Limogine and himalayamine: a new class of alkaloids. Tetrahedron Lett. 24, 2445–2448.

Chaurasia, N., Wichtl, M., 1987. Flavonol glycosides from *Urtia dioica*. Planta Med. 53, 432–434.

Degot, A.V., Litvinenko, V.I., Kurinnaya, N.V., 1971. Flavonoids of *Orthantha lutea*. Khim. Prir. Soedin. 7, 117–119.

Hemingway, S.R., Phillipson, J.D., Verpoorte, R., 1981. *Meconopsis cambrica* alkaloids. J. Nat. Prod. 44, 67–74.

Liu, S.Y., Wang, X.K., 1986. Studies on chemical constituents of *Meconopsis punicea*. Zhong Yao Tong Bao 11, 360–362.

Luo, D.S., Sun, A.L., Xia, G.C., 1984. Tibetan drug in Qingzang plateau, a preliminary investigation of resources Meconopsis. Zhong Cao Yao 15, 359–360.

Shang, X.Y., Zhang, C.Z., Li, C., Yang, Y.C., Shi, J.G., 2002. Studies on chemical constituents of *Meconopsis quintuplinervia* Regel. Zhong Yao Cai 25, 250–252.

Shang, X.Y., Shi, J.G., Yang, Y.C., Liu, X., Li, C., Zhang, C.Z., 2003a. Alkaloids from a Tibetan medicine *Meconopsis quintuplinervia* Regel. Acta Pharmaceut. Sin. 38, 276–278.

Shang, X.Y., Jiao, H.S., Yang, Y.C., Shi, J.G., 2003b. A morphinane alkaloid from *Meconopsis quintuplinervia*. Chin. Chem. Lett. 14, 597–598.

Simon, A., Chulia, A.J., Kaouadji, M., Allais, D.P., Delage, C., 1993. Further flavonoid glycosides from *Calluna vulgaris*. Phytochemistry 32, 1045–1049.

Song, C.Q., 1990. Chemical constituents of saffron (*Crocus sativus*). II. The flavonol compounds of petals. Zhong Cao Yao 21, 439–440.

Tanaka, M., Fujimori, T., Uchida, I., Yamaguchi, S., Takeda, K., 2001. A malonylated anthocyanin and flavonols in blue *Meconopsis* flowers. Phytochemistry 56, 373–376.

Veit, M., Geiger, H., Czygan, F., Markham, K.R., 1990. Malonylated flavone 5-*O*-glucosides in the barren sprouts of *Equisetum arvense*. Phytochemistry 29, 2555–2560.

Waage, S.K., Hedin, P.A., 1985. Quercetin 3-*O*-galactopyranosyl-(1 → 6)-glucopyranoside, a compound from narrowleaf vetch with antibacterial activity. Phytochemistry 24, 243–245.

Wang, M.A., Chen, Y.Z., 1995. A new alkaloid from *Meconopsis quintuplinervia* Regel. Nat. Prod. Res. Develop. 7, 32–34.

Wang, M.A., Chen, S.N., Zhang, H.D., Chen, Y.Z., 1991. Studies on the chemical constituents of *Meconopsis quintuplinervia* Regel, a Tibetan medicinal herb. J. Lanzhou Univ. (Nat. Sci.) 27, 80–92.

Zhang, G.L., Li, B.G., Zhou, Z.Z., 1997. Non-alkaloidal constituents from *Meconopsis punicea* Maxim. Nat. Prod. Res. Develop. 9, 4–6.