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Phytochemistry 65 (2004) 3041–3047
PHYTOCHEMISTRY
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Flavonoid glycosides and isoquinolinone alkaloids from *Corydalis bungeana*

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Received 21 September 2004; accepted 21 September 2004

Abstract

Two flavonol *O*-glycosides identified as the 3-*O*-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranoside 7-*O*-β-glucopyranosides of kaempferol and quercetin were isolated from the whole plant of *Corydalis bungeana* Turcz. together with eight known flavonol *O*-glycosides. Two isoquinolinone alkaloids were also obtained from the same source, including the new derivative, 6,7-methylenedioxy-2-(6-acetyl-2,3-methylenedioxybenzyl)-1(2*H*)-isoquinolinone. The structures were determined by spectroscopic methods (NMR and high-resolution MS).

Keywords: *Corydalis bungeana*; Papaveraceae; Flavonol *O*-glycosides; Isoquinolinone alkaloids

1. Introduction

Corydalis bungeana Turcz. (Papaveraceae) is a perennial herb with violet to pink flowers distributed in northern and eastern parts of China, the south-east of Mongolia, the northern part of the Korean peninsula and the far east of Russia (Turczaninow, 1840; Wu et al., 1999). The dried whole plant is referred to in traditional Chinese medicine as Herba Corydalis Bungeanae (Pharmacopoeia of the People's Republic of China, 2000) and some local uses have been recorded for the treatment of influenza, upper respiratory tract infections, bronchitis, tonsillitis, acute nephritis and pyelonephritis (Qingdao TCM research group, 1972). It is also used as a constituent of the traditional Chinese medicine 'Zi Hua Di Ding', the formulation of which may involve a range of different species of plants (Qin et al., 1995). These include *Viola yedoensis* Makino, *V. prionantha* Bunge and some other species of *Viola*, *Gueldenstaedtia verna* (Georgi) Boriss., species of *Gentiana*, *Hypecoum leptocarpum* Hook.f. & Thoms., *Osbeckia chinensis* L., *Striga asiatica* (L.) Kuntze, *Vicia amoena* Fisch. & Ser. and *Zornia diphylla* (L.) Pers. (Qin et al., 1995; Song et al., 1995; Zeng et al., 1996; Xu, 1997). The selection of species can vary according to locality and availability. The present investigation of chemical constituents of *C. bungeana* was undertaken as part of a wider study to find chemical markers for authentication of the different plant species used in 'Zi Hua Di Ding' (Xie, 2002). Although the alkaloid chemistry of *C. bungeana* has been investigated previously (Pan et al., 1981, 1988; Zeng et al., 1987, 1988), little is known about other types of constituent. Here, we describe the flavonoid chemistry of *C. bungeana* and the characterisation of two new flavonol *O*-glycosides (Fig. 1). In addition, the identification of a new isoquinolinone alkaloid,

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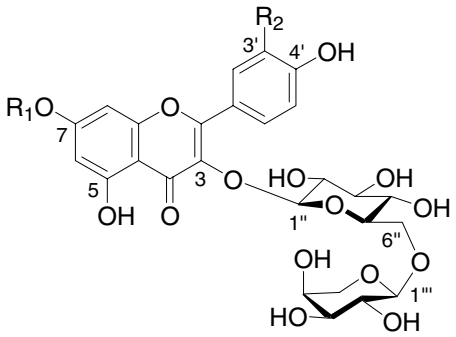
doi:10.1016/j.phytochem.2004.09.009



1 $R_1 = R_2 = H$
2 $R_1 = H$, $R_2 = OH$
3 $R_1 = \beta$-Glc, $R_2 = H$
4 $R_1 = \beta$-Glc, $R_2 = OH$

Fig. 1. Flavonol *O*-glycosides of *C. bungeana*.

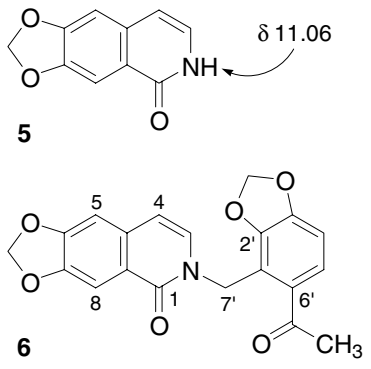


Fig. 2. Isoquinolinone alkaloids of *C. bungeana*.

6,7-methylenedioxy-2-(6-acetyl-2,3-methylenedioxybenzyl)-1(2*H*)-isoquinolinone, is reported (Fig. 2).

2. Results and discussion

Column chromatography and semi-preparative HPLC of MeOH and aqueous MeOH extracts of the whole plant of *C. bungeana* yielded **1**–**4** as yellow crystalline solids together with the known flavonol glycosides, kaempferol 3,7-di-*O*,*O*-glucoside, quercetin 3-*O*-glucoside, quercetin 7-*O*-glucoside, quercetin 3,7-di-*OO*-glucoside, quercetin 3-*O*-rutinoside and quercetin 3-*O*-rutinoside 7-*O*-glucoside. The UV spectra of **1** and **3** (λ_{max} 266, 347–349 nm) and **2** and **4** (λ_{max} 256–257, 355–356 nm) were characteristic of kaempferol and quercetin *O*-glycosides, respectively (Mabry et al., 1970). The presence of these common flavonoid aglycones was confirmed from the ^{1}H and ^{13}C NMR spectra of **1**–**4** (Tables 1 and 2). The ^{1}H NMR spectrum of **1** also contained two anomeric proton resonances at δ 5.33 (1H, *d*, J = 7.3 Hz) and 3.99 (1H, *d*, J = 6.4 Hz). These were used as the starting points for the assignment of the remaining sugar resonances in the spectrum by 2D NMR techniques. The characteristic ^{1}H and ^{13}C chemical shifts and coupling constant data for the two sugar residues (Tables 1 and 2) allowed them to be identified as β-glucopyranose and α-arabinopyranose, respectively. Long-range connectivities detected in an HMBC experiment from the 6-CH_2 protons of β-Glc to C-1 of α-Ara and from H-1 of α-Ara to C-6 of β-Glc indicated that the sugars were (1 → 6)-linked, as was also suggested by the downfield shift of the ^{13}C NMR resonance of β-Glc C-6 to 67.3 ppm. The site of attachment of this disaccharide to the aglycone was determined from a long-range connectivity between the anomeric proton of β-Glc and C-3. Thus, compound **1** was identified as kaempferol 3-*O*-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranoside (kaempferol 3-*O*-vicianoside), for which a molecular formula of $C_{26}H_{28}O_{15}$ was confirmed by high-resolution MS (see Section 3.6). This kaempferol glycoside is known from several sources (Harborne and Baxter, 1999), but a complete set of ^{1}H and ^{13}C NMR spectral assignments has not been published previously (Tables 1 and 2).

The ^{1}H and ^{13}C NMR spectra of **2** were similar to those of **1**, with the exception of those resonances corresponding to the B-ring of the flavonoid (Tables 1 and 2). These differences were consistent with the identification of the aglycone component of **2** as quercetin rather than kaempferol. The glycosidic resonances of the two compounds were essentially identical, and both were characterised by the same long-range connectivities describing the interglycosidic linkage and site of attachment to the aglycone. Thus, **2** was confirmed to be quercetin 3-*O*-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranoside (quercetin 3-*O*-vicianoside), a compound isolated previously from several sources (Harborne and Baxter, 1999). The NMR data for **2** were in good agreement with those published recently by Takemura et al. (2002).

Analysis of the ^{1}H and ^{13}C NMR spectra of the flavonoid glycosides **3** and **4** indicated that these compounds had the same glycosylation profiles but different aglycones, which were identified as kaempferol and quercetin, respectively. Both compounds possessed the 3-*O*-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranose moiety found in **1** and **2**. An additional anomeric proton resonance at δ 5.06 (1H, *d*, J = 7.3 Hz) in the ^{1}H NMR spectra of both **3** and **4** indicated the presence of a further sugar residue. This was characterised as β-glucopyranose on the basis of chemical shift and coupling constant data (Tables 1 and 2). The downfield shifts of the ^{1}H resonances of H-6 and H-8 compared to those of **1** and **2** and the NOE connectivities observed between these protons and the anomeric proton of the additional β-Glc residue in both **3** and **4** confirmed C-7 as the second site of glycosylation. Thus, **3** and **4** were identified as the 3-*O*-α-arabinopyranosyl(1‴ → 6″)-β-glucopyr-

Table 1
^{1}H NMR spectral assignments and coupling constant data for the flavonol glycosides **1**–**4** (δ in DMSO-d_6 at 37 °C)

	Atom	**1**	**2**	**3**	**4**
	6	6.14 *d* (1.9)	6.17 *d* (1.9)	6.44 *br s*	6.43 *d* (2.0)
	8	6.34 *d* (1.9)	6.37 *d* (1.9)	6.76 *br s*	6.73 *d* (2.0)
	2′	8.01 *d* (8.8)	7.57 *d* (2.0)	8.04 *d* (8.8)	7.60 *d* (2.0)
	3′	6.89 *d* (8.8)		6.88 *d* (8.8)	
	5′	6.89 *d* (8.8)	6.85 *d* (9.1)	6.88 *d* (8.8)	6.84 *d* (8.3)
	6′	8.01 *d* (8.8)	7.57 *dd* (9.0, 2.1)	8.04 *d* (8.8)	7.58 *dd* (8.3, 2.0)
	5-OH	12.53 *br s*	12.59 *br s*	12.56 *br s*	12.63 *br s*
3-*O*-β-Glc	1″	5.33 *d* (7.3)	5.36 *d* (7.2)	5.35 *d* (7.3)	5.38 *d* (7.3)
	2″	3.21 *m*	3.26 *m*	3.23 *m*	3.28 *m*
	3″	3.23 *m*	3.25 *m*	3.23 *m*	3.23 *m*
	4″	3.10 *m*	3.10 *m*	3.11 *m*	3.11 *m*
	5″	3.29 *m*	3.30 *m*	3.30 *m*	3.30 *m*
	6″	3.78 *dd* (11.8, 1.7)	3.78 *dd* (11.9, 1.6)	3.78 *dd* (11.8, 1.6)	3.79 *dd* (11.8, 1.5)
		3.44 *m*	3.45 *m*	3.43 *m*	3.45 *m*
6″-*O*-β-Ara	1‴	3.99 *d* (6.4)	3.98 *d* (6.6)	3.99 *d* (6.4)	3.98 *d* (6.6)
	2‴	3.21 *m*	3.18 *dd* (8.3, 6.5)	3.21 *m*	3.18 *m*
	3‴	3.05 *dd* (8.3, 3.5)	3.00 *dd* (8.3, 3.5)	3.05 *dd* (8.2, 3.3)	3.03 *dd* (8.3, 3.4)
	4‴	3.45 *m*	3.43 *m*	3.47 *m*	3.46 *m*
	5‴	3.51 *dd* (11.9, 3.6)	3.49 *dd* (12.0, 3.5)	3.51 *dd* (11.9, 3.7)	3.50 *m*
		2.99 *dd* (11.9, 1.8)	2.95 *dd* (11.9, 1.6)	2.99 *br d* (11.9)	2.96 *br d* (11.9)
7-*O*-β-Glc	1⁗			5.06 *d* (7.3)	5.06 *d* (7.3)
	2⁗			3.28 *m*	3.27 *m*
	3⁗			3.30 *m*	3.30 *m*
	4⁗			3.18 *m*	3.18 *m*
	5⁗			3.44 *m*	3.44 *m*
	6⁗			3.71 *m*	3.71 *br d* (11.6)
				3.48 *m*	3.48 *m*

anoside 7-*O*-β-glucopyranosides of kaempferol and quercetin, respectively. The molecular formulae of both compounds were confirmed by high-resolution MS (see Sections 3.8 and 3.9). Neither compound has been reported previously in the literature. It is not known at present whether flavonol *O*-vicianosides are typical constituents of *Corydalis* as the flavonoid chemistry of this genus is very poorly represented in the literature. A preliminary survey of flavonoids in 8 species of *Corydalis* (excluding *C. bungeana*) has been reported, but the compounds of interest were not fully characterised (Fahselt, 1972).

Fractionation of alkaloidal extracts of the whole plant of *C. bungeana* by column chromatography on Si gel and Sephadex LH-20 yielded the known compounds corycavine, corynoline and protopine together with two isoquinolinone derivatives, **5** and **6**. Compound **5** was identified as 6,7-methylenedioxy-1(2*H*)-isoquinolinone, an alkaloid found previously in *Thalictrum rugosum* Ait. (=*T. glaucum* Desf.) (Wu et al., 1980). The ^{1}H and ^{13}C NMR spectra of **6** included a subset of resonances corresponding to the 6,7-methylenedioxy-1(2*H*)-isoquinolinone moiety of **5**, with the exception of the broad singlet assigned to 2-NH. The remaining resonances were confirmed to be those of a 6-acetyl-2,3-methylenedioxybenzyl group from long-range correlations observed in the HMBC spectrum of **6** (Table 3). The correlations between the benzyl protons at δ 5.41 (2H, *s*) with C-1 and C-3 of the 6,7-methylenedioxy-1(2*H*)-isoquinolinone unit, and with C-1′, C-2′ and C-6′ of the 6-acetyl-2,3-methylenedioxybenzyl group confirmed that the two parts of the molecule were connected through the N-2 atom of the isoquinolinone ring. Thus, compound **6** was identified as 6,7-methylenedioxy-2-(6-acetyl-2,3-methylenedioxybenzyl)-1(2*H*)-isoquinolinone, an alkaloid that has not been reported previously in the literature. The molecular formula of **6** was confirmed to be $C_{20}H_{15}O_6N$ by high resolution MS (Section 3.11). The presence of the isoquinolinone derivatives **5** and **6** in *C. bungeana* is consistent with previous work showing that this species is rich in isoquinoline alkaloids (Pan et al., 1981, 1988; Zeng et al., 1987, 1988). However, the biogenetic origins of isoquinolinone alkaloids are still a matter of debate, although most commentators agree that they are likely to be oxidative products of structurally more complex isoquinoline alkaloids (Krane and Shamma, 1982; Guinaudeau and Bruneton, 1993). Krane and Shamma (1982) suggested two possible routes for their formation, either as naturally occurring oxidation products of benzylisoquinolines or as the result of in vivo oxidation of protoberberines, phthalideisoquinolines or spirobenzylisoquinolines. The mode of formation of isoquinolinone alkaloids in *C. bungeana* remains unknown at present.

Table 2
^{13}C NMR spectral assignments for the flavonol glycosides **1**–**4**

	Atom	**1**	**2**	**3**	**4**
Aglycone	2	156.0	156.1	157.0	156.9
	3	133.1	133.2	133.3	133.4
	4	177.0	177.2	177.4	177.3
	5	161.0	161.1	160.8	160.8
	6	98.9	98.7	99.2	99.2
	7	165.4	164.5	162.8	162.7
	8	93.7	93.4	94.5	94.4
	9	156.4	156.3	155.9	155.9
	10	103.5	103.8	105.6	105.6
	1′	120.8	121.0	120.0	120.4
	2′	130.7	116.1	130.8	116.0
	3′	115.0	144.7	115.3	144.9
	4′	159.8	148.5	160.8	149.3
	5′	115.0	115.2	115.3	115.1
	6′	130.7	121.5	130.8	121.7
3-*O*-β-Glc	1″	101.1	100.8	101.0	100.8
	2″	74.0	73.9	74.0	73.8
	3″	76.2	76.3	76.3	76.3
	4″	69.9	70.0	69.9	70.0
	5″	76.5	76.7	76.4	76.6
	6″	67.3	67.2	67.3	67.3
6″-*O*-β-Ara	1‴	102.6	102.6	102.7	102.7
	2‴	70.3	70.4	70.2	70.3
	3‴	72.3	72.3	72.3	72.3
	4‴	67.0	67.1	66.9	67.0
	5‴	64.5	64.6	64.4	64.5
7-*O*-β-Glc	1⁗			99.9	99.9
	2⁗			73.0	73.0
	3⁗			76.2	76.3
	4⁗			69.6	69.6
	5⁗			77.1	77.1
	6⁗			60.6	60.6

Table 3
^{1}H and ^{13}C NMR spectral assignments for the isoquinolinone alkaloid, **6** (δ in DMSO-d_6 at 37 °C)

Atom	δ ^{13}C	δ ^{1}H	HMBC
1	161.6		
2			
3	131.2	7.09 *d* (7.4)	C-1, C-4, C-4a, C-7′
4	105.2	6.28 *d* (7.4)	C-3, C-4a, C-5, C-8a
4a	134.4		
5	103.6	6.81 *s*	C-4, C-6, C-7, C-8a
6	151.7		
7	147.6		
8	105.9	7.76 *s*	C-1, C-4a, C-6, C-7, C-8a
8a	121.7		
OCH_2O-6,7	101.6	6.03 *s*	C-6, C-7
1′	118.0		
2′	148.2		
3′	150.4		
4′	107.0	6.78 *d* (8.2)	C-2′, C-3′, C-6′
5′	125.2	7.37 *d* (8.2)	C-1′, C-3′, 6′-*C*OCH_3
6′	132.9		
7′	45.0	5.41 *s*	C-1, C-3, C-1′, C-2′, C-6′
OCH_2O-2′,3′	102.0	5.96 *s*	C-2′, C-3′
6′-*C*OCH_3	199.9		
6′-CO*C*H_3	29.0	2.57 *s*	C-5′, C-6′, 6′-*C*OCH_3

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 at 37 °C on Bruker 400 MHz or Varian 500 MHz instruments. Standard pulse sequences and parameters were used for the experiments. Chemical shift references were obtained from the solvent resonances of DMSO-d_6 at δ_H 2.50 and δ_C 39.5, relative to TMS. High resolution ESI-MS (positive mode) were obtained on a Bruker Apex II instrument with an internal calibrant. Positive ion APCI-MS were obtained using a quadrupole ion-trap instrument (Finnigan LCQ) as described previously (Grayer et al., 2000). Analytical and semi-preparative HPLC were carried out using a Waters LC600 pump and a 996 photodiode array detector. All UV spectra were recorded online. A Merck LiChrospher 100RP-18 (250 × 4.0 mm i.d.; 5 μm particle size) column was used for analytical HPLC with a flow rate of 1 ml/min. The column temperature was maintained at 30 °C.

3.2. Plant material

Corydalis bungeana Turcz. was collected in May 2000 from the Botanical Garden of the Institute of Medicinal Plant Development (IMPLAD), Beijing, China. A voucher specimen has been deposited at the Herbarium, Royal Botanic Gardens, Kew (No. TCMK132).

3.3. General extraction procedures

Ground whole plant of *C. bungeana* (1400 g) was extracted with 14 l of petroleum ether twice at room temperature. The residue was moistened with 25% ammonia solution and then extracted three times with 10× $CHCl_3$ (v/w) at room temp. to obtain an alkaloid fraction (40 g). After ammonia and $CHCl_3$ were evaporated, the residue was extracted sequentially with 10× (v/w) MeOH and 50% aq. MeOH (MeOH:H_2O, 1:1) twice at room temp., respectively, to obtain a MeOH fraction (250 g) and a 50% MeOH fraction (150 g).

3.4. Isolation and quantitation of flavonol O-glycosides

The MeOH fraction (250 g) (Section 3.3) was adsorbed onto silica gel (250 g) and applied to a column (150 mm (i.d.) × 50 cm) prepared with 500 g of the same material. Following washing with $CHCl_3$, the column was eluted with $CHCl_3$:MeOH mixtures in which the $CHCl_3$ content was decreased successively from 95% to 90%, 80%, 70% and 60% to 0%. Only those fractions eluted with 60% $CHCl_3$:MeOH and 100% MeOH contained flavonoids (identified from their distinctive UV spectra recorded online by analytical HPLC coupled to diode-array detection). These were combined with the 50% MeOH fraction (150 g) from the original extraction (Section 3.3), dissolved in H_2O and subjected to column chromatography (150 mm (i.d.) × 45 cm) over Amberlite XAD-2, eluting with H_2O:MeOH mixtures in which the % MeOH was increased from 0 through 10, 30 and 50 to 90. Flavonoid-containing fractions (30% and 50% MeOH) were retained (36 g) and adsorbed onto 40 g Si gel which was applied to a column prepared with 600 g of the same material. An elution profile of $CHCl_3$:MeOH (12:88), $CHCl_3$:MeOH:H_2O (7:3:1) to (2:2:1) and MeOH:H_2O (1:1) in sequence yielded 22 fractions (F.1–F.22). Further purification of selected fractions using a combination of Sephadex LH-20 and semi-preparative HPLC yielded **1**–**4** together with the known compounds, quercetin 3-*O*-glucoside, quercetin 7-*O*-glucoside, quercetin 3,7-di-*O*,*O*-glucoside, quercetin 3-*O*-rutinoside, quercetin 3-*O*-rutinoside 7-*O*-glucoside, quercetin, kaempferol 3,7-di-*O*,*O*-glucoside and kaempferol. The structures of the known flavonol *O*-glycosides were confirmed from their ^{1}H and ^{13}C NMR spectra.

For quantitation purposes, ground plant material (100 mg) was extracted with 5 ml 50% aq. MeOH for 12 h at 25 °C then sonicated for 20 min. Analytical HPLC of the filtered extract was carried out using a gradient method (solvent A = MeOH:HOAc:H_2O (18:1:1), solvent B = 2% HOAc; A = 20%, B = 80% at $t = 0$ min; A = 20%, B = 80% at $t = 15$ min; A = 40%, B = 60% at $t = 16$ min; A = 40%, B = 60% at $t = 30$ min; A = 100% at $t = 31$ min; A = 100% at $t = 35$ min; A = 20%, B = 80% at $t = 36$ min) to separate the flavonol *O*-glycosides. The percentage amount of each compound in the whole plant of *C. bungeana* was evaluated using HPLC chromatograms at 335 nm and standard curves determined with the purified compounds. This gave the flavonoid glycoside content as <0.01% (**1**), 0.71% (**2**), <0.01% (**3**), 0.05% (**4**), 0.11% (quercetin 3-*O*-glucoside), <0.01% (quercetin 7-*O*-glucoside), 0.22% (quercetin 3,7-di-*O*,*O*-glucoside), 0.13% (quercetin 3-*O*-rutinoside), 0.04% (quercetin 3-*O*-rutinoside 7-*O*-glucoside) and <0.01% (kaempferol 3,7-di-*O*,*O*-glucoside).

3.5. Isolation of alkaloids

The alkaloid fraction (40 g) (Section 3.3) was dissolved in $CHCl_3$ and adsorbed onto silica gel (60 g) before application to a column of the same material (500 g). Elution with a gradient of $CHCl_3$:MeOH (100:0 to 0:100) afforded 20 fractions (A.1–A.20) after combination of similar fractions based on TLC profiles. Fraction A.10 (7.2 g) was further chromatographed over silica gel using a gradient of hexane:acetone (100:0–0:100) to give 10 fractions (A.10.1–A.10.10). Recrystallisation of the crystalline material formed in A.10.7 and A.10.8 using $CHCl_3$:MeOH (1:1) yielded corynoline (236 mg).

Fraction A.10.10 yielded **6** (2 mg) after purification over Sephadex LH-20. Fraction A.13 (2 g) was separated further by column chromatography with silica H (30 g) and hexane:$CHCl_3$:MeOH (40:50:1.5) to give 4 fractions (A.13.1–A.13.4) and similarly, A.13.1 yielded 6 fractions on column chromatography with silica H and hexane:acetone (4:1). Further purification of fraction A.13.1.2 over Sephadex LH-20 yielded corycavine (3 mg). Recrystallisation of the contents of fraction A.13.1.6 using $CHCl_3$:MeOH (1:1) gave **5** (3 mg) as brown crystals. Fraction A.15 (5 g) was separated into eight further fractions (A.15.1–A.15.8) by column chromatography on silica H (75 g) and elution with a hexane:acetone gradient (9:1–6:4). A white solid obtained from A.15.5 by acetone precipitation yielded protopine (300 mg) on recrystallisation with $CHCl_3$:MeOH (1:1).

*3.6. Kaempferol 3-O-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranoside (**1**)*

Yellow solid (MeOH); UV (MeOH) λ_{max} nm: 266, 349; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; HRESIMS *m/z*: 581.1511 $[M + H]^+$ (calc. for $C_{26}H_{29}O_{15}$, 581.1501).

*3.7. Quercetin 3-O-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranoside (**2**)*

Yellow solid (MeOH); UV (MeOH) λ_{max} nm: 257, 356; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; APCI-MS (positive mode) *m/z*: 597 $[M + H]^+$, 465 $[(M - 132) + H]^+$, 303 [aglycone + H]$^+$.

*3.8. Kaempferol 3-O-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranoside 7-O-β-glucopyranoside (**3**)*

Yellow solid (MeOH); UV (MeOH) λ_{max} nm: 266, 347; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; HRESIMS *m/z*: 743.2031 $[M + H]^+$ (calc. for $C_{32}H_{39}O_{20}$, 743.2029).

*3.9. Quercetin 3-O-α-arabinopyranosyl(1‴ → 6″)-β-glucopyranoside 7-O-β-glucopyranoside (**4**)*

Yellow solid (MeOH); UV (MeOH) λ_{max} nm: 256, 355; ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; HRESIMS *m/z*: 781.1801 $[M + Na]^+$ (calc. for $C_{32}H_{38}O_{21}Na$, 781.1798).

*3.10. 6,7-Methylenedioxy-1(2H)-isoquinolinone (**5**)*

Brown crystalline solid ($CHCl_3$:MeOH); ^{1}H NMR (DMSO-d_6) δ 11.06 (1H, *br s*, 2-NH), 7.49 (1H, *s*, H-8), 7.12 (1H, *s*, H-5), 7.04 (1H, *m* (collapsed to *d*, J = 7.1 Hz on addition of one drop of D_2O to the sample), H-3), 6.44 (1H, *d*, J = 7.2 Hz, H-4), 6.14 (2H, s, –OCH_2O–); ^{13}C NMR (DMSO-d_6) δ 160.9 (C-1), 151.3 (C-6), 147.0 (C-7), 135.0 (C-4a), 127.4 (C-3), 121.2 (C-8a), 104.6 (C-4), 103.9 (C-8), 103.8 (C-5), 101.6 (–OCH_2O–); APCI-MS (positive mode) *m/z*: 190 $[M + H]^+$.

*3.11. 6,7-Methylenedioxy-2-(6-acetyl-2,3-methylenedioxybenzyl)-1(2H)-isoquinolinone (**6**)*

White crystalline solid (MeOH); ^{1}H and ^{13}C NMR: see Table 3; HRESIMS *m/z*: 366.0974 $[M + H]^+$ (calc. for $C_{20}H_{16}O_6N$, 366.0972).

Acknowledgements

We thank Professor Yu-Lin Lin (Head of Herbarium, Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences, Beijing) for collection and identification of plant material, the Weston Foundation for financial support to C.X. as part of the Chinese Medicinal Plants Authentication Centre (CMPAC), Royal Botanic Gardens, Kew, and Christine Leon (Head, CMPAC) for advice and assistance. Access to higher-field NMR facilities (500 MHz) was kindly provided by the Medical Research Council Biomedical NMR Centre, National Institute for Medical Research, Mill Hill, London, UK. APCI-MS data were provided by Dr. Geoffrey Kite (Royal Botanic Gardens, Kew) and high-resolution MS data by chemiSPEC (North of England Business and Innovation Centre, Sunderland Enterprise Park East, Sunderland, UK).

References

Fahselt, D., 1972. The use of flavonoid components in the characterization of the genus *Corydalis* (Fumariaceae). Can. J. Bot. 50, 1605–1610.

Grayer, R.J., Kite, G.C., Abou-Zaid, M., Archer, L.J., 2000. The application of atmospheric pressure chemical ionization liquid chromatography-mass spectrometry in the chemotaxonomic study of flavonoids: characterization of flavonoids from *Ocimum gratissimum* var. *gratissimum*. Phytochem. Anal. 11, 257–267.

Guinaudeau, H., Bruneton, J., 1993. Isoquinoline alkaloids. In: Dey, P.M., Harborne, J.B. (Eds.), Methods in Plant Biochemistry, 8. Academic Press, London, pp. 373–419.

Harborne, J.B., Baxter, H. (Eds.), 1999. The Handbook of Natural Flavonoids, 1. John Wiley, Chichester.

Krane, B.D., Shamma, M., 1982. The isoquinolone alkaloids. J. Nat. Prod. 45, 377–384.

Mabry, T.J., Markham, K.R., Thomas, M.B., 1970. The Systematic Identification of Flavonoids. Springer-Verlag, Berlin.

Pan, X.-Q., Guan, M.-J., Fang, Q.-C., 1981. Initial study of alkaloids from *Corydalis bungeana*. Yao Xue Tong Bao 16, 249.

Pan, X.-Q., Guan, M.-J., Wang, J., Fang, Q.-C., 1988. The study of alkaloids in *Corydalis bungeana*. Zhong Cao Yao 19, 46–47.

Pharmacopoeia of the People's Republic of China (English Edition), 2000. Chemical Industry Press, Beijing, p. A-26.

Qin, P., Chen, Q.P., Wang, B.R., Shi, L.W., 1995. Studies of Zi Hua Di Ding. In: Lou, Z.Q., Qin, P. (Eds.), Species Systematization and

Quality Evaluation of Commonly used Chinese Traditional Drug, Publisher of Beijing Medical University and Beijing Union Medical University, Beijing, pp. 565–670.

Qingdao TCM Research Group, 1972. Zhong Cao Yao Tong Xun 5, 16.

Song, P.S., Zhao, J.B., Wei, Y.L., 1995. The investigation and authentication of species used in Di Ding produced in Gansu. Zhong Yao Cai 16, 75–76.

Takemura, M., Nishida, R., Mori, N., Kuwahara, Y., 2002. Acylated flavonol glycosides as probing stimulants of a bean aphid, *Megoura crassicauda*, from *Vicia angustifolia*. Phytochemistry 61, 135–140.

Turczaninow, N., 1840. Decades quatuor plantarum hucusque non descriptarum, Sibiriae, maxime orientalis et regionum confinum incolarum. 6. *Corydalis Bungeana*. Bull. Soc. Nat. Mosc., 62.

Wu, C., Chuang, H., Su, Z., Sun, B., 1999. Flora of China Editorial Committee, Chinese Academy of Sciences, *Corydalis bungeana* TurczFlora of China, 32. Science Press, Beijing, pp. 396–398.

Wu, W.-N., Beal, J.L., Doskotch, R.W., 1980. Alkaloids of Thalictrum XXX. Eleven minor alkaloids from *Thalictrum rugosum*. J. Nat. Prod. 43, 143–150.

Xie, C., 2002. A survey of the chemistry and biological activity of the traditional Chinese medicine Zi Hua Di Ding. PhD Thesis, University of London, UK, pp. 190.

Xu, G.B., 1997. The authentication of several *Viola* species used in herbal medicine. Zhong Yao Cai 20, 371–373.

Zeng, W.-G., Liang, W.-Z., Tu, G.-S., 1987. Chemical study of alkaloids from *Corydalis bungeana*. Planta Med. 53, 418–420.

Zeng, W.-G., Liang, W.-Z., He, C.-H., Zheng, Q.-T., Tu, G.-S., 1988. An alkaloid from *Corydalis bungeana*. Phytochemistry 27, 599–602.

Zeng, W.Z., Xu, G.B., Wan, D.G., 1996. The investigation and authentication of Zi Hua Di Ding traded in Sichuan. Zhong Yao Cai 19, 127–128.