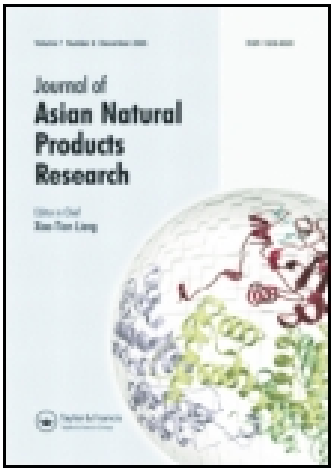

Journal of Asian Natural Products Research

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/ganp20

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Published online: 01 Feb 2010.

To cite this article: Ai-Xue Zuo, Yong Shen, Xue-Mei Zhang, Zhi-Yong Jiang, Jun Zhou, Jun Lü & Ji-Jun Chen (2010) Four new trace phenolic glycosides from Curculigo orchioides, Journal of Asian Natural Products Research, 12:1, 43-50, DOI: 10.1080/10286020903427344

To link to this article: http://dx.doi.org/10.1080/10286020903427344

Journal of Asian Natural Products Research
Vol. 12, No. 1, January 2010, 43–50

ORIGINAL ARTICLE

Four new trace phenolic glycosides from *Curculigo orchioides*

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(*Received 12 August 2009; final version received 13 October 2009*)

Four new trace phenolic glycosides named orcinosides D (**1**), E (**2**), F (**3**), and G (**4**) were isolated from the rhizomes of *Curculigo orchioides* Gaertn. Based on comprehensive spectroscopic analyses including IR, FAB-MS, HR-ESI-MS, 1D- and 2D NMR (HSQC, HMBC), their structures were elucidated as orcinol-1-*O*-β-D-xylopyranoside (**1**), orcinol-1-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranoside (**2**), orcinol-3-*O*-β-D-apiofuranosyl-1-*O*-β-D-glucopyranoside (**3**), and 1-*O*-β-D-glucopyranosyl-4-ethoxyl-3-hydroxymethylphenol (**4**).

Keywords: orcinosides D–G; phenolic glycosides; *Curculigo orchioides*

1. Introduction

Curculigo orchioides Gaertn., a traditional Chinese medicine known as 'Xian-Mao' in Chinese, is widely distributed in China, India, Malaya, Japan, and Australia. Its rhizomes were reported to possess the properties of warming kidney, invigorating yang, expelling cold, and eliminating dampness, and used to cure impotence, enuresis, cold sperm, cold pain of back and knee, and numbness of the limb [1]. Previous phytochemical studies on the rhizomes revealed the presence of cycloartane triterpenes [2], phenolic glycosides [3], and chlorophenolic glucosides [4]. Lakshmi *et al.* [5] reported that phenols and phenolic glycosides played an important biological role, being responsible for stimulating the immune response by acting on the macrophages and the lymphocytes. Additionally, Wu *et al.* [6] claimed that phenolic glycoside showed potent antioxidative activities. To find more biologically active substances from *C. orchioides*, we further undertook the investigation to furnish four new trace phenolic glycosides. This paper deals with the isolation and structural elucidation of four new trace orcinosides D (**1**), E (**2**), F (**3**), and G (**4**) from the rhizomes of *C. orchioides* (Figure 1).

2. Results and discussion

Compound **1** was isolated as a colorless powder, $[\alpha]_D^{27.7}$ −33.33 ($c = 0.15$, MeOH). Its molecular formula was determined to be $C_{12}H_{16}O_6$ based on *m/z* 291.0637 $[M+Cl]^-$ in the negative HR-

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ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020903427344
http://www.informaworld.com

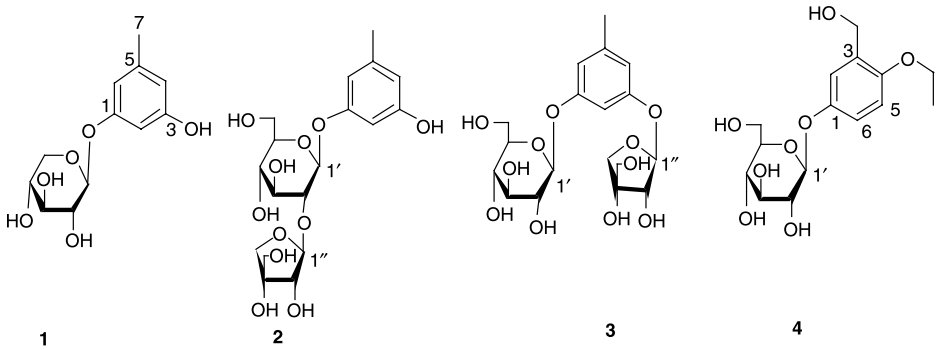

Figure 1. The structures of compounds **1**–**4**.

ESI-MS spectrum. The negative FAB-MS exhibited a quasi-molecular ion peak at *m/z* 255 $[M-H]^-$ and a fragment-ion peak at *m/z* 123 $[M-C_5H_9O_4]^-$, suggesting the presence of a pentose sugar moiety in compound **1**. The IR absorption bands at 3424 and 1619, 1500, 1468 cm^{-1} implied the existence of a hydroxyl and an aromatic ring. The ^1H NMR spectrum (Table 1) displayed one methyl at δ_H 2.22 (3H, s, H-7), three aromatic proton signals at δ_H 6.31 (1H, br s, H-2), 6.37 (1H, br s, H-4), 6.29 (1H, br s, H-6), and one anomeric proton resonance at δ_H 4.78 (1H, d, $J = 7.4$ Hz, H-1′). Analyses of the NMR spectral data of compound **1** suggested that the structure of compound **1** was very similar to that of orcinol glucopyranoside isolated from *C. orchioides* [7] except for a different sugar unit in compound **1**. The carbon signals due to the sugar moiety at δ_C 102.8, 74.7, 77.7, 71.0, 66.9 in the ^{13}C NMR spectrum (Table 2), which matched those of methyl-β-D-xylopyranoside [8], revealed that the sugar moiety was a β-D-xylopyranosyl unit. Hydrolysis of compound **1** gave orcinol and xylose by comparison with the authentic samples on TLC and PC. The β-linkage of the xylosyl unit was verified by the *J* value in the ^1H NMR spectrum at δ_H 4.78 (1H, d, $J = 7.4$ Hz, H-1′). The correlation of H-1′ with C-1 in the HMBC experiment (Figure 2) established that the xylopyranosyl unit was linked at C-1 of the aglycone. Consequently, compound **1** was deduced as orcinol-1-*O*-β-D-xylopyranoside, named orcinoside D.

Compound **2** was obtained as a colorless powder and assigned the molecular formula $C_{18}H_{26}O_{11}$ based on the negative HR-ESI-MS spectrum at *m/z* 417.1404 $[M-H]^-$. The IR spectrum showed absorption bands at 3431 cm^{-1} (hydroxyl) and 1627, 1506, 1464 cm^{-1} (aromatic ring). Compound **2** was hydrolyzed with 2 M H_2SO_4 in methanol to yield orcinol, glucose, and apiose identified by TLC and PC comparison with the authentic samples. In the ^1H NMR spectrum of compound **2**, a methyl at δ_H 2.21 (3H, s, H-7), three aromatic protons at δ_H 6.30 (1H, br s Hz, H-2), 6.37 (1H, br s, H-4), 6.27 (1H, br s, H-6), and two anomeric proton signals at δ_H 4.89 (1H, d, $J = 7.3$ Hz, H-1′), 5.44 (1H, d, $J = 1.2$ Hz, H-1″) were observed. Comparing the ^{13}C NMR spectral data of compound **2** with those of orcinol glucopyranoside [7] revealed that compound **2** had one more set of apiofuranosyl signals at δ_C 110.7, 78.0, 80.8, 75.5, 66.1 [4] than orcinol glucopyranoside. Moreover, C-2′ was downfield-shifted to δ_C 78.1 compared to δ_C 74.8 in orcinol glucopyranoside [7], which implied that the additional apiofuranosyl moiety was located at the C-2′ of compound **2**. The cross-peaks between

Table 1. ^{1}H NMR data of compounds **1**[a], **2**[b], **3**[b], and **4**[b] in CD_3OD, δ in ppm, J in Hz.

	δ_H			
No.	**1**	**2**	**3**	**4**
2	6.31 (1H, br s)	6.30 (1H, br s)	6.37 (1H, br s)	6.78 (1H, d, $J = 3.0$ Hz)
4	6.37 (1H, br s)	6.37 (1H, br s)	6.39 (1H, br s)	
5				7.06 (1H, d, $J = 8.8$ Hz)
6	6.29 (1H, br s)	6.27 (1H, br s)	6.29 (1H, br s)	6.66 (1H, dd, $J = 8.8$, 3.0 Hz)
7	2.22 (3H, s)	2.21 (3H, s)	2.22 (3H, s)	4.47 (1H, d, $J = 12.5$ Hz)
				4.65 (1H, d, $J = 12.5$ Hz)
OCH_2CH_3				3.55 (2H, q, $J = 7.0$ Hz)
				1.21 (3H, t, $J = 7.0$ Hz)
1′	4.78 (1H, d, $J = 7.4$ Hz)	4.89 (1H, d, $J = 7.3$ Hz)	4.78 (1H, d, $J = 7.3$ Hz)	4.69 (1H, d, $J = 7.6$ Hz)
2′	3.38–3.40 (m)	3.93–3.94 (m)	3.41–3.42 (m)	3.42–3.43 (m)
3′	3.38–3.40 (m)	3.56–3.58 (m)	3.91–3.92 (m)	3.35–3.36 (m)
4′	3.54–3.56 (m)	3.34–3.37 (m)	3.29–3.30 (m)	3.35–3.36 (m)
5′	3.90 (1H, dd, $J = 11.4$, 5.3 Hz)	3.36–3.58 (m)	3.91–3.92 (m)	3.42–3.43 (m)
	3.31–3.32 (m)			
6′		3.86 (1H, dd, $J = 12.0$, 1.5 Hz)	3.96–3.97 (m)	3.87 (1H, dd, $J = 12.5$, 1.5 Hz)
		3.68 (1H, dd, $J = 12.0$, 5.0 Hz)	3.74–3.76 (m)	3.68 (1H, dd, $J = 12.5$, 5.0 Hz)
1″		5.44 (1H, d, $J = 1.2$ Hz)	4.97 (1H, d, $J = 2.4$ Hz)	
2″		3.94 (1H, d, $J = 4.0$ Hz)	3.41–3.42 (overlapped)	
4″		4.04 (1H, d, $J = 9.5$ Hz)	3.95 (1H, d, $J = 9.7$ Hz)	
5″		3.34 (2H, s)	3.41–3.42 (overlapped)	

Notes: [a] Recorded at 400 MHz. [b] Recorded at 500 MHz.

Table 2. ^{13}C NMR data of compounds **1**[a], **2**[b], **3**[b], and **4**[b] in CD_3OD, δ in ppm.

	δ_C			
No.	**1**	**2**	**3**	**4**
1	159.9 (s)	159.3 (s)	159.9 (s)	153.9 (s)
2	102.2 (d)	102.0 (d)	102.2 (d)	116.7 (d)
3	159.3 (s)	159.3 (s)	158.9 (s)	130.7 (s)
4	109.7 (d)	109.4 (d)	109.9 (d)	150.3 (s)
5	141.2 (s)	141.3 (s)	141.1 (s)	119.2 (d)
6	111.2 (d)	111.2 (d)	111.2 (d)	116.0 (d)
7	21.7 (q)	21.7 (q)	21.7 (q)	68.7 (t)
OCH_2CH_3				66.8 (t)
OCH_2CH_3				15.4 (q)
1′	102.8 (d)	100.8 (d)	102.1 (d)	104.6 (d)
2′	74.7 (d)	78.1 (s)	74.6 (d)	75.1 (d)
3′	77.7 (d)	78.7 (d)	77.7 (d)	78.2 (d)
4′	71.0 (d)	71.4 (d)	71.3 (d)	71.5 (d)
5′	66.9 (t)	78.5 (d)	76.7 (d)	78.1 (d)
6′		62.5 (t)	61.5 (t)	62.7 (t)
1″		110.7 (d)	110.7 (d)	
2″		78.0 (d)	77.8 (d)	
3″		80.8 (s)	80.3 (s)	
4″		75.5 (t)	74.9 (t)	
5″		66.1 (t)	65.6 (t)	

Notes: [a] Recorded at 100 MHz. [b] Recorded at 125 MHz.

H-1′ and C-1, H-1″ and C-2′ in the HMBC (Figure 2) spectrum also implied that the inner glucopyranose was attached at C-1 of the aglycone and the apiofuranose was connected at C-2′ of the inner glucose. Thus, compound **2** was determined as orcinol-1-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranoside, named orcinoside E.

Compound **3**, colorless powder, had the molecular formula $C_{18}H_{26}O_{11}$ as determined by the negative HR-ESI-MS spectrum at *m/z* 417.1407 $[M-H]^-$. The IR spectrum showed absorption bands at 3422 cm^{-1} and 1615, 1462 cm^{-1}, implying the existence of hydroxyl and aromatic groups. Hydrolysis of compound **3** with 2 M H_2SO_4 in methanol liberated orcinol, glucose, and apiose identified by comparison with authentic samples on TLC and PC. The ^1H NMR spectrum (Table 1) showed three aromatic ring proton signals at δ_H 6.37 (1H, br s, H-2), 6.39 (1H, br s, H-4), 6.29 (1H, br s, H-4), one methyl signal at δ_H 2.22 (3H, s, H-7), together with two anomeric proton resonances at δ_H 4.78 (1H, d, $J = 7.3$ Hz, H-1′) and 4.97 (1H, d, $J = 2.4$ Hz, H-1″). The ^{13}C NMR spectrum (Table 2) contained 18 carbon signals, involving an orcinol unit signal (δ_C 159.9, 102.2, 158.9, 109.9, 141.1, 111.2, 21.7), a glucopyranosyl unit resonance (δ_C 102.1, 74.6, 77.7, 71.3, 76.7, 61.5), and an apiofuranosyl moiety (δ_C 110.7, 77.8, 80.3, 74.9, 65.6). Analysis of the NMR spectral data demonstrated that compound **3** had one more apiofuranosyl unit than orcinol glucopyranoside [7]. The HMBC correlations between the proton at δ_H 4.97 (1H, d, $J = 2.4$ Hz, H-1″) and the carbon at δ_C 158.9 (s, C-3) suggested that the additional apiofuranosyl moiety was located at C-3. Accordingly, compound **3** was deduced as orcinol-3-*O*-β-D-apiofuranosyl-1-*O*-β-D-glucopyranoside, named orcinoside F.

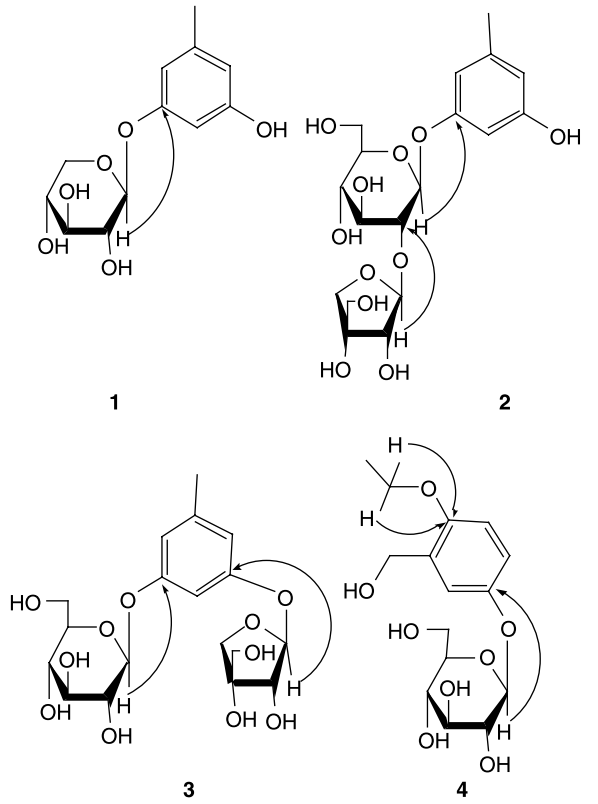

Figure 2. The key HMBC correlations of compounds **1**–**4**.

Compound **4** was obtained as a colorless powder. Its molecular formula was deduced as $C_{15}H_{22}O_8$ by the negative HR-ESI-MS spectrum at *m/z* 365.1010 $[M+Cl]^-$. The IR spectrum displayed absorption bands due to a hydroxyl group at 3415 cm^{-1} and an aromatic ring at 1628, 1500, 1453 cm^{-1}. Hydrolysis of compound **4** yielded glucose identified by comparing with the authentic sample on PC. The ^1H NMR spectrum of compound **4** presented proton signals ascribable to an $-OCH_2CH_3$ at δ_H 3.55 (2H, q, $J = 7.0$ Hz), 1.21 (3H, t, $J = 7.0$ Hz), a $-CH_2OH$ at δ_H 4.47 (1H, d, $J = 12.5$ Hz, H-7a), 4.65 (1H, d, $J = 12.5$ Hz, H-7b), and a trisubstituted aromatic ring at δ_H 6.78 (1H, d, $J = 3.0$ Hz, H-2), 7.06 (1H, d, $J = 8.8$ Hz, H-5), 6.66 (1H, d, $J = 8.8$, 3.0 Hz, H-6), together with an anomeric proton signal at δ_H 4.69 (1H, d, $J = 7.6$ Hz, H-1′), indicating a β-linkage of the sugar moiety. In the ^{13}C NMR spectrum for compound **4**, the carbon signals assignable to an aromatic ring at δ_C 153.9, 116.7, 130.7, 150.3, 119.2, 116.0, an $-OCH_2CH_3$ at δ_C 66.8, 15.4, and a $-CH_2OH$ at δ_C 68.7 were observed, in addition to a set of β-D-glucopyranosyl groups at δ_C 104.6, 75.1, 78.2, 71.5, 78.1, 62.7, which were in agreement with the ^{13}C NMR spectral data of methyl-β-D-glucopyranoside [8]. The NMR spectral data of compound **4** were similar to those of 4-ethoxy-3-hydroxymethylphenol [9], except that compound **4** had one more glucopyranose moiety. The long-range correlations between the anomeric proton at δ_H 4.69 (1H, d, $J = 7.6$ Hz, H-1′) and C-1 in the HMBC experiment ascertained that the glucopyranosyl unit was located at C-1. As a result, compound **4** was

corroborated as 1-*O*-β-D-glucopyranosyl-4-ethoxyl-3-hydroxymethylphenol, named orcinoside G.

3. Experimental

3.1 General experimental procedures

Optical rotations were performed on a Horiba SEPA-300 polarimeter (Tokyo, Japan). IR spectra were recorded on a Bio-Rad FTS-135 spectrometer (Richmond, CA, USA) with KBr pellets, ν in cm^{-1}. UV spectra were measured on a UV-210A spectrometer (Shimadzu, Japan). NMR spectra were conducted on Bruker AV-400 or DRX-500 spectrometers (Karlsruhe, Germany) with TMS as the internal standard. Chemical shifts (δ) were expressed in ppm and coupling constants (J) in Hz. FAB-MS was recorded on a VG-Auto-spec-3000 mass spectrometer (Manchester, UK). ESI-MS and HR-ESI-MS were taken on an API Qstar-Pulsar-1 mass spectrometer (Applied Biosystems/MDS Sciex, Ontario, Canada). Column chromatography (CC) separations were performed on silica gel (200–300 mesh; Qingdao Meigao Chemical Co., Ltd, Qingdao, China), Al_2O_3 (Shanghai Wusi Chemical Reagents Company, Shanghai, China), D_{101} macroporous resins (Tianjin Pesticide Chemical Company, Tianjin, China), Sephadex LH-20 (Pharmacia Fine Chemical Co. Ltd, Uppsala, Sweden), and Lichroprep RP-18 (40–63 μm; Merck, Darmstadt, Germany). Fractions were monitored by TLC and visualized by spraying with 10% H_2SO_4 in EtOH followed by heating.

3.2 Plant material

The rhizomes of *C. orchioides* Gaertn. were collected in Wenshan County, Yunnan Province, China, in November 2005, and authenticated by Prof. Dr Li-Gong Lei, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (No. 20051106) has been deposited in the Group of Anti-virus and Natural Medicinal Chemistry, Kunming Institute of Botany, Chinese Academy of Sciences.

3.3 Extraction and isolation

The air-dried and powdered rhizomes of *C. orchioides* (200 kg) were extracted with 70% EtOH (each 1000 liters, 2 h) three times under reflux to yield an extract which was combined and concentrated to a small volume (600 liters) and subjected to CC (macroporous resin D101, 200 kg), with gradient elution of H_2O, 10% EtOH–H_2O, 40% EtOH–H_2O, 70% EtOH–H_2O, 90% EtOH–H_2O to afford five fractions (I–V). Fraction II (10% EtOH–H_2O eluted, 800 g) was subjected to Al_2O_3 CC (8 kg, 14 × 50 cm), subsequently eluted with EtOAc–EtOH–H_2O (9:1:0.1), EtOAc–EtOH–H_2O (8:2:0.2), and EtOAc–EtOH–H_2O (7:3:0.2) to afford fractions A–C.

Fraction A (260 g) was successively subjected to RP-18 CC (1 kg, 6 × 60 cm) eluted with MeOH–H_2O (1:9) to afford fractions 1–3. Fraction 2 (2.0 g) was performed on silica gel CC (100 g, 3.4 × 27 cm) eluted with $CHCl_3$–MeOH–H_2O (9:1:0.1) to give a residue (1.2 g) which was subjected to Sephadex LH-20 CC (53 g, 2.2 × 62 cm) eluted with $CHCl_3$–MeOH (1:1), and further purified by silica gel CC (15 g, 1 × 15 cm) with EtOAc–EtOH–H_2O (9:1:0.1) as the solvent to yield compounds **4** (10 mg) and **1** (9 mg). Fraction 3 (3.0 g) was applied to a silica gel CC (100 g, 3.4 × 27 cm) eluted with $CHCl_3$–MeOH–H_2O (8.5:1.5:0.15) to give four portions. The second portion (2.0 g) was purified on RP-18 CC (120 g, 2.5 × 33 cm) eluted with MeOH–H_2O (3:97) to afford compounds **2** (12 mg) and **3** (1.2 g).

3.3.1 Orcinoside D (*1*)

Colorless powder. $[\alpha]_D^{27.7}$ −33.33 ($c = 0.15$, MeOH). UV (MeOH) λ_{max}^{MeOH}

(log ε): 279 (3.38) nm. IR (KBr) ν_{max}: 3424, 2921, 1619, 1500, 1468, 1325, 1073, 1043, 835, 670, 567 cm^{-1}. ^{1}H and ^{13}C NMR spectral (CD_3OD) data are listed in Tables 1 and 2. FAB-MS (negative): *m/z* 255 $[M-H]^-$, 239 $[M-OH]^-$, 123 $[M-H-xylose]^-$. HR-ESI-MS (negative): *m/z* 291.0637 $[M+Cl]^-$ (calcd for $C_{12}H_{16}O_6Cl$, 291.0653).

3.3.2 Orcinoside E (2)

Colorless powder. $[\alpha]_D^{20.8}$ −66.67 ($c = 0.3$, MeOH). UV (MeOH) λ_{max}^{MeOH} (log ε): 273 (3.21) nm. IR (KBr) ν_{max}: 3431, 2923, 1627, 1506, 1464, 1318, 1113, 1071, 1033, 577, 563 cm^{-1}. ^{1}H and ^{13}C NMR spectral (CD_3OD) data are listed in Tables 1 and 2. FAB-MS (negative): *m/z* 417 $[M-H]^-$. HR-ESI-MS (negative): *m/z* 417.1404 $[M-H]^-$ (calcd for $C_{18}H_{25}O_{11}$, 417.1396).

3.3.3 Orcinoside F (3)

Colorless powder. $[\alpha]_D^{20.9}$ −74.24 ($c = 0.3$, MeOH). UV (MeOH) λ_{max}^{MeOH} (log ε): 279 (3.30) nm. IR (KBr) ν_{max}: 3422, 2923, 1615, 1462, 1426, 1321, 1172, 1071, 994, 828, 677, 650, 571 cm^{-1}. ^{1}H and ^{13}C NMR spectral (CD_3OD) data are listed in Tables 1 and 2. FAB-MS (negative): *m/z* 417 $[M-H]^-$; HR-ESI-MS (negative): *m/z* 417.1407 $[M-H]^-$ (calcd for $C_{18}H_{25}O_{11}$, 417.1396).

3.3.4 Orcinoside G (4)

Colorless powder. $[\alpha]_D^{27.4}$ −35.16 ($c = 0.28$, MeOH). UV (MeOH) λ_{max}^{MeOH} (log ε): 286 (3.31) nm. IR (KBr) ν_{max}: 3415, 2974, 1628, 1500, 1453, 1383, 1293, 1074, 1044, 894, 803, 633, 582 cm^{-1}. ^{1}H and ^{13}C NMR spectral (CD_3OD) data are listed in Tables 1 and 2. FAB-MS (negative): *m/z* 329 $[M-H]^-$; HR-ESI-MS (negative): *m/z* 365.1010 $[M+Cl]^-$ (calcd for $C_{15}H_{22}O_8Cl$, 365.1003).

3.4 Acid hydrolysis

Each of compounds **1**–**4** (2 mg) was dissolved in MeOH (1.0 ml) and 4 M H_2SO_4 (1.0 ml) solution and hydrolyzed under reflux for 2 h. The hydrolysate was allowed to cool, diluted with 2 ml H_2O, and extracted with 2 ml EtOAc. The aqueous layer was neutralized with aqueous $Ba(OH)_2$ and concentrated *in vacuo* to give a residue, in which xylose (from **1**), glucose (from **2**–**4**) and apiose (from **2** and **3**) were identified by comparing with authentic samples on PC [BuOH–EtOAc–H_2O 4:1:5, upper layer, $R_f = 0.60$ (xylose); BuOH–EtOAc–H_2O 4:1:5, upper layer, $R_f = 0.45$ (glucose); PhOH–H_2O, 4:1, $R_f = 0.55$ (apiose) on PC, respectively]. Orcinol (from **1**–**3**) was detected from the EtOAc layer by TLC comparison with an authentic sample (silica gel, $CHCl_3$–MeOH 9:1).

Acknowledgements

This work was financially supported by the project of Yunnan Science and Technology Plan (No. 2008IF011), the major projects of new drugs development of China (No. 2009ZX09102-126), the 973 project of the Ministry of Sciences and Technology (No. 2009CB941300) and the Open Fund of the State Key Laboratory in KIB (No. 0807E31211). The authors are grateful to the members of the staff of analytical group of State Key Laboratory of Phytochemistry and Plant Resources, West China, Kunming Institute of Botany, Chinese Academy of Sciences, for the measurements of all spectra.

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