http://dx.doi.org/10.5012/bkcs.2011.32.9.3251

Three New Iridoid Glucosides from the Roots of *Patrinia scabra*

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Received May 31, 2011, Accepted July 16, 2011

To probe the chemical constituents of *Patrinia scabra*, we undertook the phytochemical investigation on its roots, which led to the isolation and elucidation of three new iridoid glucosides, scabroside A-C (**1-3**), along with three known iridoids, jatamanin J (**4**), isopatriscabroside I (**5**) and loganic acid (**6**) from the aqueous fraction of the ethanolic extract of the roots. The structures and relative configurations of the three new compounds were elucidated by spectroscopic methods including IR, UV, MS, 1D and 2D NMR experiments. Compound **3** was an unusual iridoid with an oxygen bridge connecting C-3 and C-8.

Key Words : *Patrinia scabra*, Iridoid glucosides, Scabroside A, Scabroside B, Scabroside C

Introduction

Patrinia scabra Bunge is a perennial herb belongs to Valerianaceae family distributed in the northeastern part of China. The roots of *P. scabra* were used as a traditional medicine to treat malaria, dysentery, leukemia, gastric cancer and gynecological diseases.[1] Previous phytochemical investigation on this plant revealed that the roots of *P. scabra* contain iridoids,[2-4] flavonoids,[5] terpenoids,[5] and lignans.[6] In this paper, we report the isolation of three new iridoid glucosides, scabroside A-C (**1-3**), along with three known iridoids, jatamanin J (**4**),[7] isopatriscabroside I (**5**),[2] and loganic acid (**6**)[8] from the H_2O-soluble fraction of the roots of this plant as shown in Figure 1. Their structures were established by mass-spectrometric and spectroscopic analyses, especially 2D-NMR techniques (^{1}H-^{1}H COSY, HMQC, HMBC, and NOESY), and comparison of their data with literature values. Herein, the isolation and structural elucidation of compounds **1-3** are described.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Horiba SEAP-300 polarimeter. A Hitachi UV 210A spectrophotometer was used to obtain the UV spectra in methanol (MeOH). IR spectra were taken on a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. NMR spectra were measured on a Bruker AM-400 or a Bruker DRX-500 spectrometers with TMS as an internal standard. MS and HR-MS were performed on a API-QSTAR-Pulsar-1 spectrometer. Column chromatography was carried out on C8 MB (100-40/75 μm, Fuji Silysia Chemical Co. Ltd.), MCI gel CHP-20P (75-150 μm, Mitsubishi Chemical Co.), Chromatorex ODS (30-50 μm, Fuji Silysia Chemical Co. Ltd.), and silica gel (200-300 mesh, Qingdao Haiyang Chemical Co. Ltd., P. R. China). Thin layer chromatography (TLC) was carried out on silica gel G precoated plates (Qingdao Haiyang Chemical Co. Ltd.), and spots were detected by spraying with 5% H_2SO_4 in EtOH followed by heating.

Plant Material. The dry roots of *Patrinia scabra* Bunge were purchased from Bozhou herbal market in March 2010 and identified by Prof. Dr. Kai-Jin Wang from the School of Life Sciences, Anhui University, where a voucher specimen (No. 20100303) was deposited.

Extraction and Isolation. The dry roots of *P. scabra* (18.0 kg) were powdered and extracted exhaustively with 90% ethanol at room temperature. The extracts were combined and concentrated under vacuum to give a residue (1.35

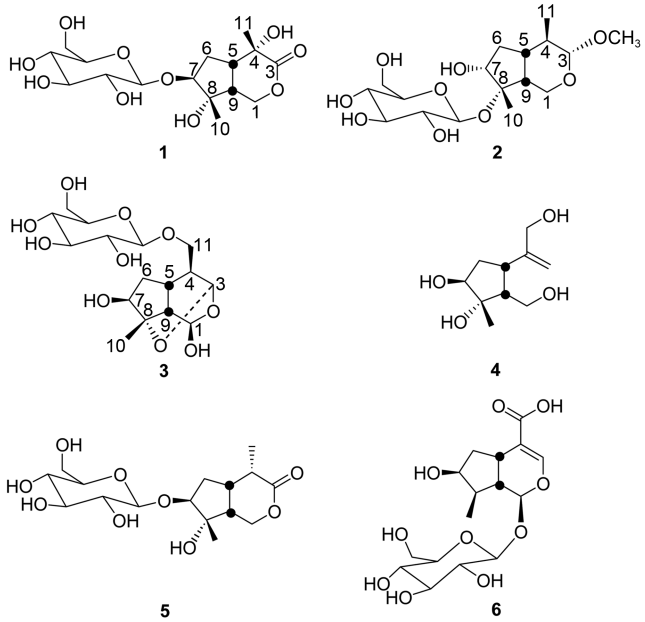

Figure 1. Structures of compounds **1-6**.

kg). The residue was suspended in H_2O and extracted with petroleum ether, ethyl acetate and *n*-butanol successively to give petroleum ether (487 g), ethyl acetate (243 g), *n*-butanol (252 g) and aqueous fraction (478 g). The aqueous fraction was suspended in H_2O and then passed though a D101 resin column eluted with MeOH-H_2O (0:1-1:0) to afford fraction D (132 g). The fraction D was chromatographed on silica gel column eluted with $CHCl_3$-MeOH (from 7:1 to 1:1) to give two fractions D_1 and D_2. The fraction D_1 was subjected to RP-8 (MeOH-H_2O, 0:1-1:1) to yield fractions $D_{1\text{-}1}$-$D_{1\text{-}4}$. The fraction $D_{1\text{-}1}$ was purified by ODS (MeOH-H_2O, 0:1-1:0) to afford **4** (110 mg). The fraction $D_{1\text{-}2}$ was performed by MCI (MeOH-H_2O, 0:1-1:0) to obtain compound **2** (30 mg). Compound **3** (35 mg) and **6** (22 mg) was obtained from fraction $D_{1\text{-}3}$ on silica gel column eluted with $CHCl_3$-MeOH (8:1). Fraction $D_{1\text{-}4}$ was chromatographed on silica gel column eluted with $CHCl_3$-MeOH (10:1) to afford **1** (12 mg). Fraction D_2 was further subjected to MCI (MeOH-H_2O, 0:1-1:0) and then RP-8 (MeOH-H_2O, 0:1-1:0) to yield **5** (165 mg).

Scabroside A (1). White powder; $[\alpha]_D^{18}$ = +45.2 (*c* 0.47, MeOH); UVλ_{max} MeOH (nm) (lgε_{max}): 200 (3.40); IR (KBr): ν_{max} cm^{-1} 3416 (OH), 2973, 2928, 1728 (C=O), 1461, 1401, 1381, 1270, 1200, 1150, 1101, 1044, 922, 633, 582; ^{1}H- and ^{13}C-NMR data: see Table 1; HR-ESI-MS (neg.): *m/z* 413.1215 $[M+Cl]^+$ (calcd. 413.1214 for $C_{16}H_{26}O_{10}Cl$).

Scabroside B (2). White powder; $[\alpha]_D^{16}$ = +78.2 (*c* 0.19, MeOH); UVλ_{max} MeOH (nm) (lgε_{max}): 202 (3.12); IR (KBr): ν_{max} cm^{-1} 3420 (OH), 2956, 2927, 1630, 1459, 1378, 1274, 1158, 1105, 1077, 1046, 636, 600; ^{1}H- and ^{13}C-NMR data: see Table 1; HR-ESI-MS (neg.): *m/z* 377.1809 $[M-H]^+$ (calcd. $C_{17}H_{29}O_9$ for 377.1811).

Scabroside C (3). White powder; $[\alpha]_D^{17}$ = –9.5 (*c* 0.30, H_2O); UVλ_{max} H_2O (nm) (lgε_{max}) 210 (2.72), 249 (2.20); IR (KBr): ν_{max} cm^{-1} 3424 (OH), 2935, 1638, 1449, 1381, 1324, 1294, 1165, 1130, 1077, 1037, 1013, 947, 634; ^{1}H- and ^{13}C-NMR data: see Table 1; HR-ESI-MS (neg.) *m/z*: 413.1214 $[M+Cl]^+$ (calcd. $C_{16}H_{26}O_{10}Cl$ for 413.1214).

Jatamanin J (4). White power. ^{1}H-NMR (400 MHz, CD_3OD): δ 3.62 (1H, dd, *J* = 11.1, 7.5 Hz, H-1a), 3.71 (1H, dd, *J* = 11.1, 6.3 Hz, H-1b), 4.01 (2H, s, H-3), 3.11 (1H, td, *J* = 10.4, 7.8 Hz, H-5), 1.77 (1H, ddd, *J* = 13.3, 7.8, 1.9 Hz, H-6a), 2.23 (1H, m, H-6b), 3.85 (1H, dd, *J* = 5.3, 1.9 Hz, H-7), 2.23 (1H, m, H-9), 1.39 (3H, s, H-10), 5.08 (1H, s, H-11a), 5.27 (1H, s, H-11b); ^{13}C-NMR (100 MHz, CD_3OD): δ 61.0 (t, C-1), 67.4 (t, C-3), 150.5 (s, C-4), 41.5 (d, C-5), 38.3 (t, C-6), 80.9 (d, C-7), 83.5 (s, C-8), 51.3 (d, C-9), 23.5 (q, C-10), 112.3 (t, C-11); FAB-MS (+) *m/z*: 225 $[M+Na]^+$.

Isopatriscabroside I (5). White power, ^{1}H-NMR (400 MHz, CD_3OD): δ 4.58 (1H, d, *J* = 12.1 Hz, H-1a), 4.28 (1H, dd, *J* = 12.1, 5.4 Hz, H-1b), 2.87 (1H, m, H-4), 2.81 (1H, m, H-5), 1.62 (1H, dt, *J* = 13.5, 6.6 Hz, H-6a), 1.88 (1H, m, H-6b), 3.80 (1H, m, H-7), 2.26 (1H, dd, *J* = 10.3, 5.3 Hz, H-9), 1.31 (3H, s, H-10), 1.09 (3H, d, *J* = 6.5 Hz, H-11), 4.35 (1H, d, *J* = 7.7 Hz, H-1'), 3.14 (1H, t, *J* = 8.2 Hz, H-2'), 3.19-3.34 (3H, m, H-3', 4', 5'), 3.80 (1H, d, *J* = 11.7 Hz, H-6'a), 3.65 (1H, dd, *J* = 11.8, 5.1 Hz, H-6'b); ^{13}C-NMR (100 MHz, CD_3OD): δ 67.3 (t, C-1), 180.2 (s, C-3), 38.8 (d, C-4), 39.3 (d, C-5), 34.2 (t, C-6), 88.2 (d, C-7), 82.2 (s, C-8), 47.9 (d, C-9), 23.9 (q, C-10), 14.3 (q, C-11), 105.7 (d, C-1'), 76.2 (d, C-2'), 78.8 (d, C-3'), 72.4 (d, C-4'), 78.4 (d, C-5'), 63.2 (t, C-

Table 1. ^{1}H-NMR and ^{13}C-NMR data for **1-3** (400 and 100 MHz, **1** in CD_3OD, **2** in DMSO, **3** in D_2O, *J* in Hz and δ in ppm)

Position	1		2		3	
	δ(C)	δ(H)[b]	δ(C)	δ(H)	δ(C)	δ(H)
1	67.2 (t)	4.52 (dd, 11.2, 2.1) 4.90 (dd, 11.2, 6.2)	60.3 (t)	3.65 (d, 12.4) 3.71 (dd, 12.4, 6.0)	90.3 (d)	5.48 (d, 2.8)
3	176.1 (s)		103.4 (d)	4.13 (d, 8.3)	92.7 (d)	5.05 (d, 3.1)
4	74.4 (s)		34.8 (d)	1.56 (m)	48.0 (d)	1.91 (t, 8.3)
5	46.0 (d)	2.78 (m)	35.7 (d)	2.22 (m)	30.6 (d)	2.19 (m)
6	34.4 (t)	1.64 (m) 2.00 (ddd, 12.6, 9.0, 3.4)	29.8 (t)	1.29 (ddd, 13.6, 11.3, 6.2) 1.91 (m)	41.9 (t)	1.55 (m) 2.18 (m)
7	88.1 (d)	3.81 (dd, 5.0, 4.1)	75.3 (d)	4.22 (m)	79.8 (d)	3.91 (m)
8	82.1 (s)		86.1 (s)		84.1 (s)	
9	44.9 (d)	2.29 (ddd, 10.7, 5.9, 1.2)	48.1 (d)	1.94 (m)	43.1 (d)	2.05 (dd, 4.8, 2.8)
10	22.6 (q)	1.35 (s)	19.1 (q)	1.16 (s)	18.8 (q)	1.28 (s)
11	23.5 (q)	1.34 (s)	14.6 (q)	0.84 (d, 6.8)	71.6 (t)	3.90 (m)
OCH_3			55.1 (q)	3.27 (s)		
Glucose						
1	105.0 (d)	4.36 (d, 7.8)	97.7 (d)	4.41 (d, 7.7)	103.5 (d)	4.36 (d, 7.9)
2	75.4 (d)	3.16 (d, 8.3)	73.8 (d)	2.93 (td, 8.4, 3.1)	74.1 (d)	3.18 (t, 8.5)
3	78.1 (d)[a]	3.22 (m)	76.66 (d)[a]	3.12 (m)	76.8 (d)[a]	3.40 (m)
4	71.5 (d)	3.10 (m)	70.3 (d)	3.00 (m)	70.6 (d)	3.33 (m)
5	77.8 (d)[a]	3.13 (m)	76.73 (d)[a]	3.03 (m)	76.7 (d)[a]	3.40 (m)
6	62.6 (t)	3.66 (dd, 11.9, 5.3) 3.83 (dd, 12.0, 2.3)	61.3 (t)	3.37 (dd, 11.5, 5.7) 3.64 (dd, 11.5, 2.3)	61.7 (t)	3.65 (dd, 12.3, 5.5) 3.83 (dd, 12.4, 2.4)

[a]Values may be interchangeable in the same column. [b]in 500 MHz.

6'); FAB-MS (+) *m/z*: 385 $[M+Na]^+$.

Loganic Acid (6). White power, ^{1}H-NMR (400 MHz, CD_3OD): δ 5.22 (1H, d, J = 4.1 Hz, H-1), 7.29 (1H, s, H-3), 3.05 (1H, q, J = 8.0 Hz, H-5), 1.62 (1H, dd, J = 13.7, 5.9 Hz, H-6a), 2.18 (1H, dd, J = 13.7, 7.8 Hz, H-6b), 3.99 (1H, t, J = 5.1 Hz, H-7), 1.82 (1H, m, H-8), 1.97 (1H, td, J = 9.0, 4.2 Hz, H-9), 1.04 (3H, d, J = 6.8 Hz, H-10), 4.60 (1H, d, J = 7.9 Hz, H-1'), 3.15 (1H, d, J = 8.5 Hz, H-2'), 3.32 (1H, m, H-3'), 3.21 (1H, m, H-4'), 3.33 (1H, m, H-5'), 3.61 (1H, dd, J = 11.9, 5.4 Hz, H-6'a), 3.84 (1H, d, J = 11.9 Hz, H-6'b); ^{13}C-NMR (100 Hz, CD_3OD): δ 97.5 (d, C-1), 151.3 (d, C-3), 115,0 (s, C-4), 32.2 (d, C-5), 42.7 (t, C-6), 74.7 (d, C-7), 42.1 (d, C-8), 46.6 (d, C-9), 13.4 (q, C-10), 171.8 (s, C-11), 100.0 (d, C-1'), 75.1 (d, C-2'), 78.0 (d, C-3'), 71.6 (d, C-4'), 78.3 (d, C-5'), 62.7 (t, C-6'); ESI-MS (−) *m/z*: 375 $[M-H]^-$.

Results and Discussion

Scabroside A (1). Compound **1** obtained as white powder, has a molecular formula of $C_{16}H_{26}O_{10}$ based on HR-ESI-MS (neg.), showing a quasi-molecular ion peak at *m/z* 413.1215 $[M+Cl]^+$ ($C_{16}H_{26}O_{10}Cl$, calcd. 413.1214). The IR spectrum indicated the presence of the hydroxy groups (3416 cm^{-1}) and a lactone carbonyl group (1728 cm^{-1}). The ^{1}H-NMR spectrum (Table 1) exhibited signals for two tertiary methyl groups at δ_H 1.35 (s) and 1.34 (s), two methylene groups at δ_H 4.52 (dd, J = 11.2, 2.1 Hz, H-1a), 4.90 (dd, J = 11.2, 6.2 Hz, H-1b), 1.64 (m, H-6a), and 2.00 (ddd, J = 12.6, 9.0, 3.4 Hz, H-6b), as well as three methine groups at δ_H 2.29 (ddd, J = 10.7, 5.9, 1.2 Hz), 2.78 (m), and 3.81 (dd, J = 5.0, 4.1 Hz). The ^{13}C-NMR (DEPT) spectrum (Table 1) showed 16 carbon signals including two methyl carbons at δ_C 22.6 (C-10) and 23.5 (C-11), two methylene carbons at δ_C 34.4 (C-6) and 67.2 (C-1), three methine carbons at δ_C 44.9 (C-9), 46.0 (C-5), and 88.1 (C-7), two quaternary carbons at δ_C 74.4 (C-4) and 82.1 (C-8), and a lactone carbonyl carbon signal at δ_C 176.1 (C-3), as well as six carbon signals of one glucosyl moiety. The ^{1}H-^{1}H COSY spectrum showed the connectivities of the proton coupling sequence for the C(1)-C(9)-C(5)-C(6)-C(7) fragment. The HMBC correlations (Figure 2) of H-1,-5 with C-3, H-5 with C-4, -11, H-1, -6 -7 with C-8, and H-7, -9 with C-10 were observed. Detailed analysis of the ^{1}H-^{1}H and ^{1}H-^{13}C correlations, exhibited in the ^{1}H-^{1}H COSY, HMQC and HMBC spectra, allowed the establishment of an iridomyrmecin-type iridolactone structure[2] for **1**. The long range ^{1}H-^{13}C correlations between the proton of GlcH-1 and C-7 confirmed that the glucosyl moiety was located at C-7 of the iridolactone. The anomeric proton of the glucosyl moiety signal appearing as a doublet at δ 4.36 (d, J = 7.8 Hz) suggested a β-configured glucose unit. All the carbons of the glucosyl moiety were assigned through direct ^{1}H-^{13}C correlations in the HMQC spectrum and were situated between δ 62.6 and 78.1 except for that at the anomeric position, which was assigned to the signal at δ 105.0.

The relative configuration of **1** was determined by the 2D-NOESY spectrum and NMR spectra. Comparison of the coupling constant of **1** ($J_{(1b,9)}$ = 6.2 Hz) with that of the structurally similar compound, patriscabroside I,[2] indicated that H-1b [δ 4.90 (dd, J = 11.2, 6.2 Hz)] and H-9 were *trans*-diaxial configured, so H-9 was β-oriented. According to the increment for calculation of chemical shifts of C-9 in the literature,[9,10] the chemical shift of C-9 are 56.6 and 44.4 ppm for the OH group at C-8 in β- and α-orientation, respectively. Therefore, the OH group at C-8 in **1** was α-oriented, since the C-9 signal was detected at 44.9 ppm in the ^{13}C-NMR spectrum. These were further supported by NOESY experiments (Figure 2). The NOESY correlations between H-9 and H-1b, H-1b and H-10 or H-11, H-9 and H-5, H-5 and H-6b [δ 2.00 (ddd, J = 12.6, 9.0, 3.4 Hz)], and H-7 and H-6a [δ 1.64 (m)], but no NOESY correlations between H-9 and H-7, H-5 and H-7, and H-7 and H-10 or H-11, indicated that H-5, the two methyl groups and the glucosyl moiety were in β-orientation. Therefore, the structure of **1** was determined as an iridolactone glucoside, named scabroside A.

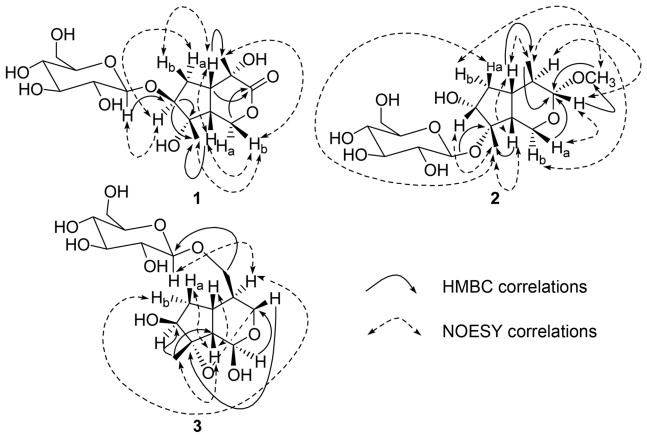

Figure 2. The key HMBC and NOESY correlations of compounds **1-3**.

Scabroside B (2). Compound **2** obtained as white powder, has a molecular formula of $C_{17}H_{30}O_9$ based on HR-ESI-MS (neg.), showing a quasi-molecular ion peak at *m/z* 377.1809 $[M-H]^+$ ($C_{17}H_{29}O_9$, calcd. 377.1811). The IR spectrum showed the hydroxyl absorption at 3420 cm^{-1}. The ^{1}H-NMR spectrum (Table 1) exhibited signals for one methoxyl group at δ_H 3.27 (s), one secondary methyl group at δ_H 0.84 (d, J = 6.8 Hz), one tertiary methyl group at δ_H 1.16 (s), two methylene groups at δ_H 3.65 (d, J = 12.4 Hz, H-1a), 3.71 (dd, J = 12.4, 6.0 Hz, H-1b), 1.29 (ddd, J = 13.6, 11.3, 6.2 Hz, H-6a), and 1.91 (m, H-6b), as well as five methine groups at δ_H 1.56 (m), 1.94 (m), 2.22 (m), 4.13 (d, J = 8.3 Hz), and 4.22 (m). The ^{13}C-NMR (DEPT) spectrum (Table 1) showed showed 17 carbon signals including one methoxyl at δ_C 55.1, two methyl carbons at δ_C 14.6 (C-11) and 19.1 (C-10), two methylene carbons at δ_C 29.8 (C-6) and 60.3 (C-1), five methine carbons at δ_C 34.8 (C-4), 35.7 (C-5), 48.1 (C-9), 75.3(C-7) and 103.4 (C-3), one quaternary carbon at δ_C 86.1 (C-8), as well as six carbon signals of one glucosyl moiety. The ^{1}H-^{1}H COSY spectrum showed the connectivities of the proton coupling sequences for the C(3)-C(4)-C(5)-C(6)-C(7), C(1)-C(9)-C(5) and C(4)-C(11) fragments. Further

study of the correlations of H-7, H-9 with C-8 in HMBC (Figure 2) led to the establishment of a cyclopenta [*c*] pyran-type iridoid structure for **2**. The methoxyl proton signal was correlated to the C-3 signal in the HMBC spectrum, indicating that the methoxyl group was linked to C-3 of the iridoid. the HMBC correlations of Me-10 with C-8, and GlcH-1 with C-8, suggested that the 10-methyl and the glucosyl moiety were located at C-8 of the iridoid. The anomeric proton of the glucosyl moiety signal appearing as a doublet at δ 4.41 (d, J = 7.7 Hz) suggested a β-configured glucose unit. All the carbons of the glucosyl moiety were assigned through direct ^{1}H-^{13}C correlations in the HMQC spectrum and were situated between δ 61.3 and 76.7 except for that at the anomeric position, which was assigned to the signal at δ 97.7.

The relative configuration of **2** was determined by the 2D-NOESY spectrum, and based upon comparison of NMR data of **2** with those reported in the literature.[9] According to the data in the literature, the chemical shift of C-9 at a relatively high field (δ 48.1) indicated that the glucosyl moiety at C-8 was α-oriented and the methyl group at C-8 was β-oriented.[9-11] The NOESY correlations (Figure 2) between H-10 and H-9, H-10 and H-7, H-9 and H-5, H-5 and H-11, H-10 with H-6a [δ 1.29 (ddd, J = 13.6, 11.3, 6.2 Hz)], H-OCH_3 with H-6b [δ 1.91 (m)], but no NOESY correlations between H-9 and H-4, H-9 and H-OCH_3, indicated that H-3, H-5, H-7, H-9 and two methyl groups were in β-orientation, the methoxyl group and the glucosyl moiety were α-oriented. Therefore, the structure of **2** was deduced as an iridoid glucoside derivative, named scabroside B (Figure 1).

Scabroside C (3). Compound **3** obtained as white powder, has a molecular formula of $C_{16}H_{26}O_{10}$ based on HR-ESI-MS (neg.), showing a quasi-molecular ion peak at *m/z* 413.1214 $[M+Cl]^+$ ($C_{16}H_{26}O_{10}Cl$, calcd. 413.1214). The IR spectrum showed the hydroxyl absorption at 3424 cm^{-1}. The ^{1}H-NMR spectrum (Table 1) exhibited signals for one tertiary methyl signal at δ_H 1.28 (s), two methylene signals at δ_H 1.55 (m, H-6a), 2.18 (m, H-6b), and 3.90 (m, H-11) as well as six methine signals at δ_H 1.91 (t, J = 8.3 Hz), 2.05 (dd, J = 4.8, 2.8 Hz), 2.19 (m), 3.91 (m), 5.05 (d, J = 3.1 Hz), and 5.48 (d, J = 2.8 Hz), respectively. The ^{13}C-NMR (DEPT) spectrum (Table 1) showed 16 carbon signals, including one methyl signal at δ_C 18.8 (C-10), two methylene signals at δ_C 41.9 (C-6) and 71.6 (C-11), six methine signals at δ_C 30.6 (C-5), 43.1 (C-9), 48.0 (C-4), 79.8 (C-7), 90.3 (C-1), and 92.7 (C-3), and one quaternary signal at δ_C 84.1 (C-8), as well as six carbon signals of one glucosyl moiety. The ^{1}H-^{1}H COSY spectrum showed the connectivities of the proton coupling sequences for the C(1)-C(9)-C(5)-C(6)-C(7), C(5)-C(4)-C(3) and C(4)-C(11) fragments. In HMBC spectrum, correlations were observed between H-1 and C-3, H-5 and C-4, -11, H-6, -7, -10 and C-8, H-7, -10 and C-9. Further analysis of NMR data and the ^{1}H-^{1}H COSY and ^{13}C-^{1}H HMBC connectivities (Figure 2) revealed the presence of a cyclopenta [*c*] pyran-type iridoid skeleton. The long range ^{1}H-^{13}C correlation of GlcH-1 with C-11 suggested that the glucosyl moiety was located at C-11. The C(3)-atom was linked to C-8 forming an oxo bridge, based on the downfield-shift value of C-3, and the existence of HMBC between the 3-proton and the 8-carbon. The anomeric proton of the glucosyl moiety signal appearing as a doublet at δ 4.36 (d, J = 7.9 Hz) suggested a β-configured glucose unit. All the carbons of the glucosyl moiety in **3** were assigned through direct ^{1}H-^{13}C correlations in the HMQC spectrum and were situated between δ 61.7 and 76.8 except for that at the anomeric position, which was assigned to the signal at δ 103.5.

The relative configuration of **3** was determined by the 2D-NOESY spectrum, and by comparison of NMR data with those reported in the literature.[9] The H-10 at C-8 was determined to be β-oriented on the basis of the C-9 chemical shift (δ 43.1), which is at relatively high field.[9-11] Hence, the formation of intramolecular acetal of C-3 with C-8 confirmed the H-3 to be in β-orientation. The NOESY spectrum (Figure 2) exhibited correlations of H-10 with H-9, H-5 with H-9, H-9 with H-6a, and H-4 with H-6b, but there was no correlations of H-5 with H-1 and H-7, indicating the α-, α-, β-, α-, and β-orientations of H-1, H-4, H-5, H-7 and H-9, respectively. Therefore, the structure of compound **3** was determined as shown in Figure 1, and named scabroside C.

Three known iridoids, jatamanin J (**4**),[7] isopatriscabroside I (**5**),[2] and loganic acid (**6**),[8] were also isolated from the H_2O-soluble fraction of the roots of this plant. Their structures were determined by spectral data and their comparison with literature values.

Acknowledgments. This work was financially supported by the Postgraduate Academic Innovation Foundation of Anhui University. The authors are grateful to the staffs of the analytical group at the Modern Experiment Technology Center, Anhui University and the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences for their measuring spectral data.

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