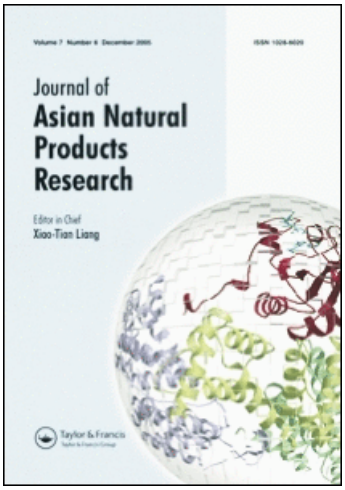

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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To cite this Article Yang, Gen-Jin , Gu, Zheng-Bing , Liu, Wen-Yong , Qiu, Yan , Li, Ting-Zhao and Zhang, Wei-Dong(2004) 'Two new iridoids from Patrinia scabra', Journal of Asian Natural Products Research, 6: 4, 277 — 280
To link to this Article: DOI: 10.1080/10286020310001595953
URL: http://dx.doi.org/10.1080/10286020310001595953

Journal of Asian Natural Products Research, December 2004, VOL. 6 (4), pp. 277–280

TWO NEW IRIDOIDS FROM *PATRINIA SCABRA*

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(Received 27 March 2003; Revised 18 April 2003; In final form 23 April 2003)

From the roots of *Patrinia scabra* two new iridoids, 3-methylbutyric acid 7-hydroxy-7-hydroxymethyl-4-(3-methyl-butyryloxymethyl)-6-oxo-1,6,7,7a-tetrahydrocyclopenta[*c*]pyran-1-yl ester (**1**) and 6-hydroxy-7-methylhexahydro-cyclopenta[*c*]pyran-3-one (**2**) have been isolated. Their structures were determined by means of NMR spectra and X-ray crystallographic analysis.

Keywords: *Patrinia scabra*; Iridoids

INTRODUCTION

Patrinia scabra Bunge is a wild plant growing mainly in the northeastern part of China. The plant is used as a traditional medicine to treat leukemia, cancer and for regulating host immune response in China. Some iridoids and iridoid glycosides have been found previously in this plant [1,2]. We report here the isolation and structural elucidation of two new iridoids, 3-methylbutyric acid 7-hydroxy-7-hydroxymethyl-4-(3-methyl-butyryloxymethyl)-6-oxo-1,6,7,7a-tetrahydrocyclopenta[*c*]pyran-1-yl ester (**1**) and 6-hydroxy-7-methylhexahydro-cyclopenta[*c*]pyran-3-one (**2**), from the roots of *Patrinia scabra*.

RESULTS AND DISCUSSION

By ethanolic extraction of the air-dried roots of *P. scabra*, an EtOAC-soluble fraction was obtained and further isolated by silica gel chromatography to afford two iridoids (Fig. 1).

Compound **1** was obtained as white needles, $[\alpha]_D^{25}$ −196.3 (*c* 1.0 in MeOH), mp 92–93°C. UV λ_{ma}^{MeOH} nm (log ε): 302 (4.14). The molecular formula, $C_{20}H_{28}O_8$, was established by the $[M + Na]^+$ peak at *m/z* 419 in the FAB-MS spectrum; EI-MS *m/z*: 396[M^+]. The IR spectrum indicated the presence of an hydroxy group (3276 cm^{-1}), two ester carbonyl groups (1750 and 1735 cm^{-1}) and a conjugated ketone carbonyl group (1683 cm^{-1}). The ^1H and ^{13}C NMR spectra of **1** (Table I) showed four secondary methyl proton signals at δ 0.92–1.01, two methine carbon signals at δ 25.6 and 25.7, two methylene

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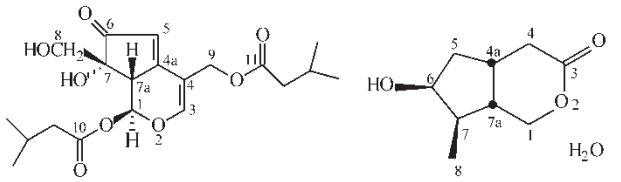
ISSN 1028-6020 print/ISSN 1477-2213 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/10286020310001595953



1 **2**

FIGURE 1 Structures of compounds **1** and **2**.

carbon signals at δ 42.1 and 43.0 as well as two carbonyl carbon signals at δ 170.4 and 172.9, indicating the presence of two isovaleryloxyl ester moieties, which were further confirmed by 2D COSY of **1**. The remaining 10 carbon signals gave rise to two oxy-methylenes (δ 65.1 and 59.8), two sp^3-hybridised methines (δ 92.4 and 42.1), two sp^2-hybridised methines (δ 154.2 and 118.5) as well as four quaternary carbons (δ 75.1, 102.3, 164.8 and 207.3), including a conjugated ketone, which yield a cyclopenta[*c*]pyran-type iridoid structure for **1**. The ^{1}H NMR spectrum of **1** also showed a singlet at δ 7.03 (H-3) and a doublet at δ 5.95 (H-5) from the two trisubstituted double bonds located at C-3-C-4 and C-4a-C-5. Consequently, the conjugated ketone carbonyl group was located at C-6. The presence of a CH_2OH group was confirmed by a signal at δ 3.82, 65.1. The signals at δ 6.39 (1H, d, $J = 11.0$ Hz, H-1) and 3.08 (1H, dd, $J = 2.3$, 11.0 Hz) indicated the α configuration of H-1 and β configuration of H-7a [3].

The relative stereochemistry for **1** was established by NOESY experiments which showed a correlation peak between H-7a and the CH_2OH group, indicating that the CH_2OH group is attached to C-7 with the β configuration. The absolute stereostructure has not been determined yet.

Compound **2** was also obtained as white needles, mp 98.5–100°C; EI-MS *m/z*: 170 [M^+], 152, 139, 126, 97, 81, 69 (base), 55. The IR spectrum showed a hydroxyl absorption at 3348 cm^{-1} and a lactone carbonyl at 1733 cm^{-1}. The ^{13}C NMR spectrum of **2** (Table I) exhibited 9 carbon signals which were resolved into one methyl, three methylenes, four methines and a lactone carbonyl with the help of DEPT experiments. The ^{1}H–^{1}H COSY spectrum showed the connectivities of the proton coupling sequence for the C-4-C-4a-C-5-C-6-C-7-C-7a-C-1 fragment. It also showed correlation peaks of H-4a with H-7a, and H-8

TABLE I NMR data of compounds **1** and **2** in $CDCl_3$

	1		***2***	
Position	δ_C	δ_H (J_{Hz})	δ_C	δ_H (J_{Hz})
1	92.4	6.39 (d, 11.0)	68.58	4.15 (dd, 11.7, 3.5) 4.33 (dd, 11.7, 4.0)
3	154.2	7.03 (s)	173.70	
4	102.3		34.41	2.37 (dd, 15.0, 4.0) 2.65 (dd, 15.0, 7.2)
4a	164.8		32.52	2.94 (m)
5	118.5	5.95 (d, 2.3)	41.48	1.40 (m), 2.04 (m)
6	207.3		75.28	4.11 (m)
7	75.1		41.55	1.91 (m)
7a	42.1	3.08 (dd, 2.3, 11.0)	41.38	2.17 (m)
8	65.1	3.82 (s)	12.57	1.08 (d, 6.8)
9	59.8	4.74 (d, 12.6) 4.81 (d, 12.6)		
10	170.4			
11	172.9			

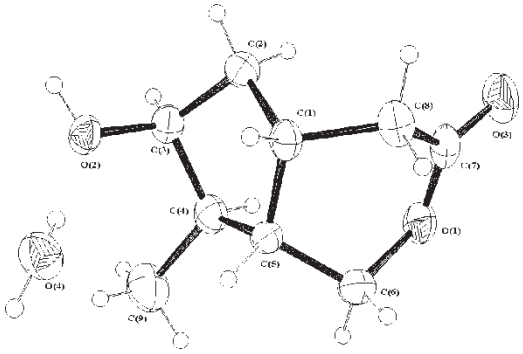


FIGURE 2 X-ray crystal structure for compound **2**.

(methyl group proton signal) with H-7. This yielded a 9C cyclopenta[*c*]pyran-type iridoid structure for **2**. The methine signal at δ 75.28 was clearly due to substitution at C-6 with a hydroxy group. The relative stereochemistry of **2** was elucidated by X-ray crystallographic analysis (Fig. 2); it was discovered that **2** is a monohydrate compound, which was further confirmed by the broad absorption from 3100 to 3467 cm^{-1} in the IR spectrum.

EXPERIMENTAL

General Experimental Procedures

The melting point was determined on a RY-2 (Tianjin Analysis Instrument Factory) and is uncorrected. The IR spectrum was recorded on a Bruker Vector-22. NMR spectra were acquired on a Varian INOVA-400 with TMS as internal standard. EI-MS data were obtained on a Varian Mat-212, by the direct inlet method, and UV data were obtained with a Shimadzu UV-265. Chromatographic column: silica gel H (10–40 μ, Qing Dao Oceanic Chemical Industry), Sephadex LH-20 (Pharmacia). All other solvents were analytically pure.

Plant Material

Roots of *P. scabra* Bunge were collected in 2000 from Henan province (China) and identified by Professor H.C. Zheng, Department of Pharmacognosy, School of Pharmacy, The Second Military Medical University. A voucher specimen has been deposited in the herbarium of this institute.

Extraction and Isolation

The air-dried roots of *P. scabra* (10 kg) were extracted with EtOH (3 × 20 L) at room temperature. After removal of the solvent under reduced pressure, the extract was suspended in water and then partitioned with light petroleum, EtOAc and *n*-BuOH successively. The EtOAc-soluble part (450 g) was separated and fractionated by silica gel chromatography, with petrol–EtOAc (10:1; 5:1; 2:1), into 25 fractions.

Fraction 9 (10 g) was chromatographed on a silica gel column (5 × 40 cm), eluted with light petroleum–acetone (10:1) to yield 10 further fractions, the sixth of which was chromatographed repeatedly on silica gel and finally yielded **1** (125 mg) as white needles from light petroleum–acetone (5:1).

Fraction 12 (25 g) was chromatographed on silica gel (8 × 65 cm), using $CHCl_3$–MeOH (20:1 and 10:1 successfully) to give five fractions, the third of which was subjected to a Sephadex LH-20 column (2 × 100 cm) with $CHCl_3$–MeOH (1:1) as eluent to afford crude crystals, which were recrystallized from light petroleum–acetone (5:1) to give **2** (38 mg).

Structure and Identification

Compound **1**, white needles, mp 92–93°C, $[\alpha]_D^{25}$ − 196.3 (*c* 1.0 in MeOH), HREI-MS *m/z*: 396.1781 (calcd for $C_{20}H_{28}O_8$ 396.1784). IR (KBr) ν_{max} (cm^{-1}): 3276 (OH), 1750, 1735, 1683 (C=O). EI-MS *m/z*: 396 [M^+], 295, 276, 192, 179, 151, 136, 85, 57 (base). ^1H and ^{13}C NMR data see Table I.

Compound **2**, white needles, mp 98.5–100°C. HREI-MS *m/z*: 170.0949 (calcd for $C_9H_{14}O_3$ 170.0943). EI-MS *m/z*: 170 [M^+], 152, 139, 126, 97, 81, 69 (base), 55. IR (KBr) ν_{max} (cm^{-1}): 3347 (OH), 2962, 2933, 2903, 2880, 1733 (C=O), 1434, 1389, 1347, 1281, 1187, 1167, 1078, 1054, 1017, 976. ^1H and ^{13}C NMR data see Table I.

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