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PATRINIOSIDE, AN ESTERIFIED MONOCYCLIC IRIDOID GLUCOSIDE FROM *PATRINIA SCABRA*

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Key Word Index—*Patrinia scabra*; Valerianaceae; iridoid; patrinioside; ring-opened iridoid; isovaleric acid.

Abstract—A new esterified iridoid glucoside ring-opened between C-1 and C-2 has been isolated from the root of *Patrinia scabra* and characterized by intensive spectroscopic analysis.

INTRODUCTION

Patrinia scabra Bunge is indigenous to the northeastern part of China. Our previous phytochemical studies on the root of this plant led to the isolation of two kinds of enantiomeric iridomyrmecin-type iridolactones and five glycosides [1]. In a continuation of our investigation of this extract, we have now isolated a new iridoid glucoside, patrinioside (**1**), which has a ring-opened structure between the C-1 and C-2 bond.

RESULTS AND DISCUSSION

Compound **1** was obtained as an amorphous powder, $[\alpha]_D^{26}$ $-4.80°$ ($c = 0.5$, methanol). The IR spectrum showed a carbonyl absorption at 1710 cm^{-1}. The empirical formula, $C_{21}H_{36}O_{10}$, was established by the $[M + Na]^+$ peak at m/z 471 in the FAB mass spectrum. The ^1H and ^{13}C NMR spectra of **1** showed two doublet methyl signals at δ0.96 (*d*, 6H, $J = 6.4$ Hz), a methine and methylene carbon signals at δ26.9 and 45.3, respectively, and a carbonyl carbon signal at δ174.3, indicating an isovaleryloxyl ester moiety, the presence of which was confirmed by the 2D COSY of **1**. The presence of a glucose fragment was established by the ^{13}C NMR spectrum and the J value of the non-hydroxyl protons of a sugar moiety in the ^1H NMR spectrum. Five of the remaining 10 carbon signals were ascribable to a methyl (δ19.1), two exo-methylene (δ150.7 and 110.1) and two oxy-methylene (δ67.9 and 66.7) groups, respectively. The connectivities of the proton coupling sequence for the C-1–C-9–C-5–C-6–C-7 fragment in an iridoid skeleton were observed in the 2D COSY spectrum.

Further information about the iridoid skeleton was obtained by intensive analysis of the HMQC and HMBC spectra as shown in Fig. 1. The H-1 signal of glucose was correlated to the C-1 signal of the iridoid core in the HMBC spectrum, indicating that the glucose moiety was linked to C-1 of the iridoid. This was supported by the observation of a NOE enhancement of the H-1″ signal (glucose) on irradiation of the H-1a signal. The position

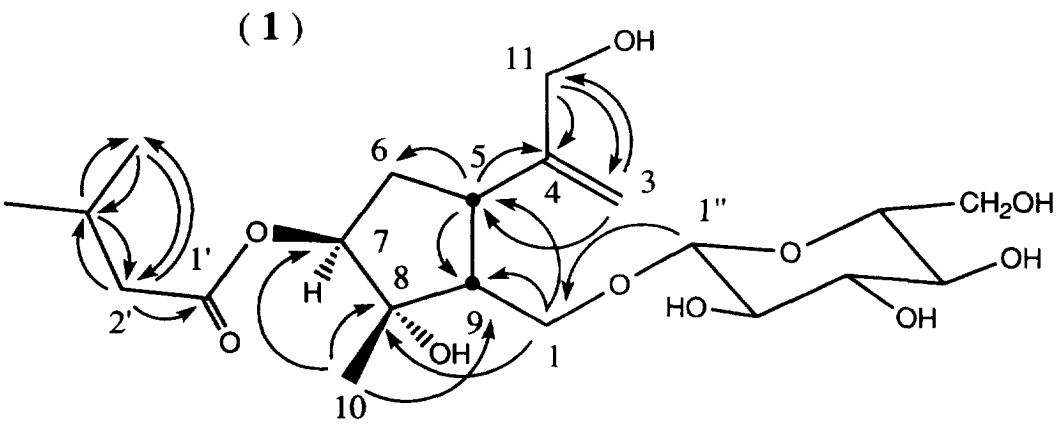
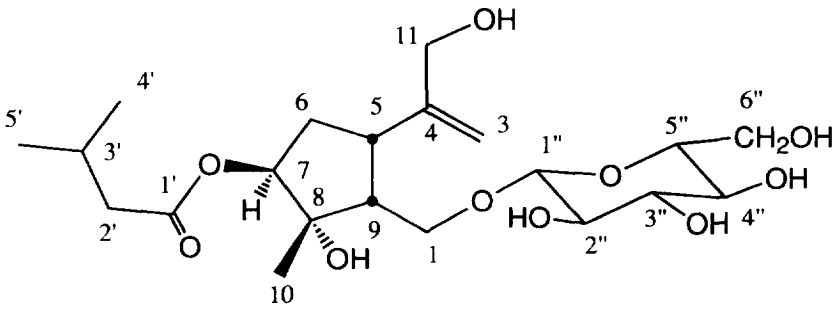


Fig. 1. HMBC correlations for patrinioside (1). Arrows point from carbon to proton resonances.



(1)

of the acyloxyl group was determined as C-7, on the basis of the lower field chemical shift of H-7 (δ4.49) in the ^{1}H NMR spectrum. The glucose was linked to the aglycone with a coupling constant of J = 7.5 Hz, indicating that it was connected through a β-glucosidic linkage. Thus, the plain structure of **1** was clarified.

The stereo-structure was examined by a NOE experiment. Irradiation of the signal of H-9 (δ2.57) caused the enhancement of the signals of H-5 (δ2.97) and Me-10 (δ1.60), indicating that H-5 and H-9 possess *cis*-configuration, together with the H-10 methyl group. On the other hand, when the signal of H-7 (δ4.49) was irradiated, no enhancement was observed for the Me-10 signal, indicating that the isovaleryloxyl group is linked to 7β-hydroxyl group of the iridoid. This assumption was supported by the enhancement of the H-6b signal (δ2.11) on irradiation of the H-7 signal (δ4.49). By contrast, NOE enhancement of H-5 (δ2.97) was observed on irradiation of H-6a (δ1.73). Consequently, the structure of **1** was established as shown in the diagram.

Compound **1** has a similar structure to those of lantanoside [2], a jureptoside [3], eucommioside [4], gelsemol 1-glucoside and gelsemol 3-glucoside [5] i.e. monocyclic iridoid glucosides ring-opened between C-1 and C-2.

EXPERIMENTAL

General experimental procedures and plant material were as reported in ref. [1]. ^{1}H NMR: 500 MHz; ^{13}C NMR: 125 MHz.

Extraction and isolation. The extraction procedures were described in ref. [1]. An Me_2CO-soluble portion was obtained from the *n*-BuOH-soluble part of the EtOH extract of air-dried roots. It gave two frs, F-1 and F-2, by silica gel CC. Fr. F-2 was subjected to CC on Sephadex LH-20 with MeOH as solvent, then purified by prep. HPLC (ODS column, RI detection, MeOH–H_2O, 1:1 to give **1** (10.1 mg).

Patrinioside (**1**). IR ν_{max}^{Nujol} cm^{-1}: 3275, 2930, 1710; ^{1}H and ^{13}C NMR: Table 1.

Table 1. ^{1}H and ^{13}C NMR spectral data for compound **1** (δ values in CD_3OD)

Position	C	H*
Iridoid moiety		
1a	69.7 *t*†	3.50 (*dd*, *J* = 10.0, 8.7)
b		4.02 (*dd*, *J* = 10.0, 4.1)
11a	110.1 *t*	4.98 (*br s*)
b		5.27 (*br*, *d*, *J* = 1.5)
4	150.7 *s*	
5	40.2 *d*	2.97 (*br q*, *J* = 9.0)
6a	37.1 *t*	1.73 (*ddd*, *J* = 12.4, 9.0, 6.4)
b		2.11 (*ddd*, *J* = 12.4, 8.7, 3.7)
7	77.8 *d*	4.49 (*dd*, *J* = 6.4, 3.7)
8	93.0 *s*	
9	51.3 *d*	2.57 (*dt*, *J* = 8.7, 4.1)
10	19.1 *q*	1.60 (*s*, 3H)
3a	66.7 *t*	3.99 (*br d*, *J* = 14.7)
b		4.10 (*br d*, *J* = 14.7)
Isovaleryloxyl moiety		
1′	174.3 *s*	
2′a	45.3 *t*	2.15 (*dd*, *J* = 14.5, 7.0)
b		2.18 (*q*, *J* = 14.5)
3′	26.9 *d*	2.07 (*br ddq*, *J* = 14.5, 7.0, 6.4)
4′, 5′	22.8 *q* × 2	0.96 (*d*, 6H, *J* = 6.4)
Glucose moiety		
1″	104.6 *d*	4.12 (*d*, *J* = 7.5)
2″	75.2 *d*	3.12 (*dd*, *J* = 8.5, 7.5)
3″	78.1 *d*	3.33 (*br t*, *J* = 8.5)
5″	76.6 *d*	3.28 (*m*)
6″ a	62.7 *t*	3.65 (*dd*, *J* = 11.9, 5.5)
b		3.85 (*dd*, *J* = 11.9, 2.3)

*Each proton signal is 1H except for the 4′, 5′ and 10 positions.

†Multiplicity in DEPT spectrum.

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