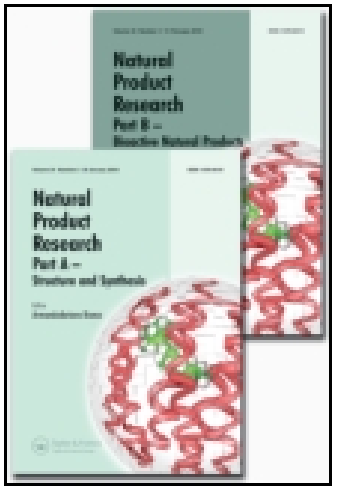

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A novel iridoid from *Torricellia angulata* var *intermedia*

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A new iridoid, named torricellate, was isolated from root bark of *Torricellia angulata* var *intermedia*, a Chinese folk medicinal plant used to treat bone fracture, tonsillitis and asthma. Its structure was elucidated by NMR, MS, IR and UV, and confirmed by X-ray diffraction studies.

Keywords: *Torricellia angulata* var *intermedia*; *Torricelliaceae*; iridoid; torricellate

1. Introduction

Torricellia angulata var *intermedia* (Harms.) Hu (*Torricelliaceae*) is a single family and single genus plant distributed in the Guizhou, Yunnan and Sichuan provinces in China, as well as in the Himalayas. It is used to treat bone fractures, tonsillitis and asthma in Chinese folk medicine (Bao & Ran, 1987). Several compounds of iridoid glycosides, phenylpropanoids and flavonoid glycosides have been previously isolated from this plant (Wu, Ma, Luo, Wu, & Liu, 2000). During our investigation of the chemical constituents of this plant, a new iridoid, named torricellate, has been isolated and identified as dimethyl-5-hydroxycyclopenta[c]pyran-4,7-dicaboxylate (ACD / mane software). Only 7 iridoid compounds with a degree of unsaturation of four in the cyclopenta[c]pyran ring, such as viburtinal, cerberic acid and cerberinic acid, were isolated from plants (Chemical Dictionary) (Brayer, Alazard, & Thal, 1983; Joshi, Singh, & Taneja, 1982; Koehn, Gunasekera, Niel, & Cross, 1991).

2. Results and discussion

Torricellate was obtained as a red column crystal. Its IR spectrum showed absorption bands at 3233, 1690, 1590, 1544 cm^{-1}, indicating hydroxyl group, conjugated carbonyl group and a highly unsaturated frame (cyclopenta[c]pyran ring), respectively. The UV spectrum consisted of a conjugation structure (λ max 250, 367 nm). ^{1}H-NMR showed a

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simple spectrum with δ8.57(1H, s), 7.98(1H, s) and 7.55(1H, s) for H-1, H-3 and H-7. The high field chemical shifts of ^{1}H-NMR and ^{13}C-NMR was exhibited by H-12 (δ 3.84, 3H, s), C-12 (δ 51.3) and H-13 (δ 3.96, 3H, s), C-13 (δ 53.2). gCOSY indicated H-7 was coupled with H-1 and OH. Noesy test showed no NOE effect on the protons. Assignment of all hydrogens and carbons is provided in Table 1, and were deduced with the aid of HMQC and HMBC experiments. HMBC showed long- range coupling between OH and C-6, indicating the OH location. It also showed the interaction between H-13 and C-4, as well as between H-7 and C-8 on the cyclopenta[c]pyran ring. Other interactions in the HMBC were shown in Figure 1. The EI-MS spectrum exhibited the M^+ at m/z 250 congruent with the molecular formula $C_{12}H_{10}O$, confirmed by HR-MS spectrum (found $[M+Na]^+$ m/z 273.0378, $C_{12}H_{10}O_6Na$ requires m/z 273.0375). It also exhibited two fragment ions at m/z 219 (M–OCH_3) and 190 (M–$HCOOCH_3$).

A single crystal of torricellate was obtained, and the proposed structure was confirmed by X-ray diffraction studies (Figure 2). The red column crystal is constituted by two ring and two carbonyl groups, which formed a big conjugation system. All of the atoms of the compound located on the same planar plate. There was a hydrogen innermolecular bond O17–O14: 2.692 Å, but no hydrogen intermolecular bond was found in the crystal.

Table 1. ^{13}C- and ^{1}H-NMR data for torricellate.

	^{13}C	^{1}H (Hz)		^{13}C	^{1}H (Hz)
1	146.2	8.57s, 1H	9	113.7	
3	144.9	7.98s, 1H	10	164.0	
4	113.6		11	168.4	
5	101.5		12	51.3	3.84s, 3H
6	143.6		13	53.2	3.96s, 3H
7	135.6	7.54s, 1H	OH		9.38s, 1H
8	122.7				

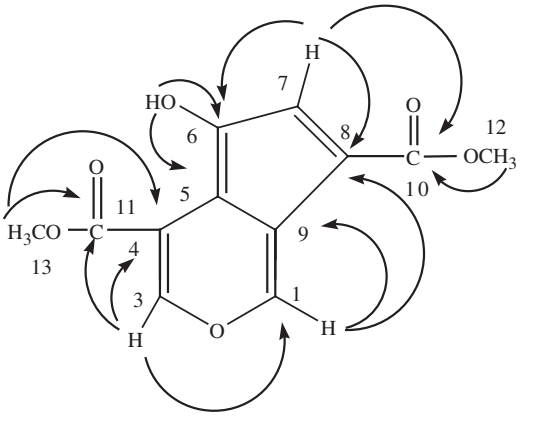

Figure 1. HMBC of torricellate.

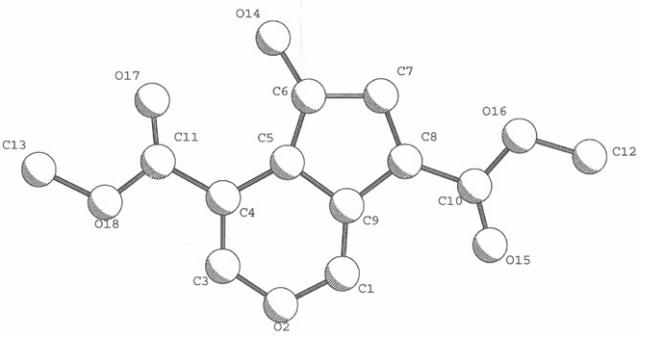

Figure 2. ORTEP projection of torricellate.

3. Experimental

3.1. *General*

All NMR data were collected on a Varian INOVA-400 spectrometer in $CDCl_3$. MS data were recorded on Hewlett Packard–1100 and STAR Pulsar I system spectrometers. IR spectrum was run on a VECTOR-22 FT-IR spectrophotometer; UV spectrum were measured on a HP8453E spectrophotometer. X-ray diffraction was measured on a Mac Dip2030k Diffractometer.

3.2. *Plant material*

Root bark of *Torricellia angulata* var *intermedia* was collected in Guiyang, Guizhou province, China in May, 2000. The specimen was authenticated by Prof. Deyuan Chen. The voucher specimen was deposited in the first author's laboratory.

3.3. *Extraction and isolation*

The fresh root bark (24 kg) was re-extracted exhaustively with 95% EtOH (3×24 h). The total EtOH extract was concentrated under reduced pressure till EtOH could not be smelt. The viscous concentrate was diluted with water (3 : 1), then partitioned with $CHCl_3$. The $CHCl_3$ extract (about 250 g) was subjected to silica gel column chromatography eluted with petrol, and then petrol containing increasing amounts of EtOAc. All fractions were analysed by TLC (Silica gel 254). Fraction eluted with petrol–EtOAc (90 : 10) gave torricellate (33 mg).

3.4. *Identification*

Torricellate was obtained as red column crystal (CH_3OH): m.p. 180–181°C, UV (CH_3OH) λ max 250, 367 nm; IR ν max 3233 (OH), 1690 (C = O), 1590, 1545 (cyclopenta[c]pyran ring); EI-MS m/z (%): 250 (99, M^+), 219 (25, M–OCH_3), 190 (100, M–$HCOOCH_3$), 163 (38), 147 (45); HR-MS found $[M + Na]^+$ m/z 273.0378, $C_{12}H_{10}O_6Na$ requires m/z 273.0375; ^{1}H–NMR ($CDCl_3$) and ^{13}C–NMR ($CDCl_3$) are shown in Table 1. Crystallographic data for the structure reported in this article has been deposited in the X-ray laboratory of the Institute of Materia Medica, Chinese Academy of

Medical Sciences. (Copies of the data can be obtained as supplementary publication, free of charge on application to one of the authors, Y. L.).

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