

A new hopane triterpene from *Dipentodon sinicus* (Celastraceae)

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1. Subject and source

Dipentodon sinicus Dunn is the only member of the genus *Dipentodon* (family Celastraceae), and a species which has been used as a medicinal plant in the treatment of inflammation and ache (Editorial Committee of the Administration Bureau of Traditional Chinese Medicine, 1998). *D. sinicus* was collected from Xishuang Banna, Yunnan Province, the People's Republic of China at 1500 m above sea level in August 2004, and identified by Prof. Hua Peng of Kunming Institute of Botany, Chinese Academy of Science. A voucher specimen (HCG-04008) has been deposited in the Herbarium of Shanghai Institute of Materia Medica.

2. Previous work

To the best of our knowledge, there is no previous phytochemical study on *D. sinicus*.

3. Present study

The air-dried powdered stem bark of *D. sinicus* (1.0 kg) was extracted with 95% EtOH (8 L × 3, 2 days each) at room temperature. After removal of solvent in vacuo, an extract of 100 g was afforded, which was partitioned between various organic solvents and water to afford EtOAc-soluble (12.3 g) and *n*-BuOH-soluble (30.2 g) parts. The EtOAc-soluble fraction was chromatographed on a silica gel column using eluents of increasing polarity, from CHCl₃ to CH₃OH. The fractions eluted with CHCl₃–CH₃OH (20:1) were further purified by Sephadex LH-20 column chromatography using MeOH as eluent to yield compound **1** (80 mg) (Fig. 1).

Compound **1** was obtained as white needle crystals (MeOH). Its HR-EIMS (*m/z* 456.3591) suggested a molecular formula of C₃₀H₄₈O₃ (calc. 456.3598). The ¹H NMR spectrum of **1** displayed seven tertiary methyl groups (δ 0.55, 0.74, 0.78, 0.82, 0.93, 0.93, 1.71), and one carbinolic methine proton at δ 3.16 (dd, *J* = 10.0, 6.0 Hz). The ¹³C and

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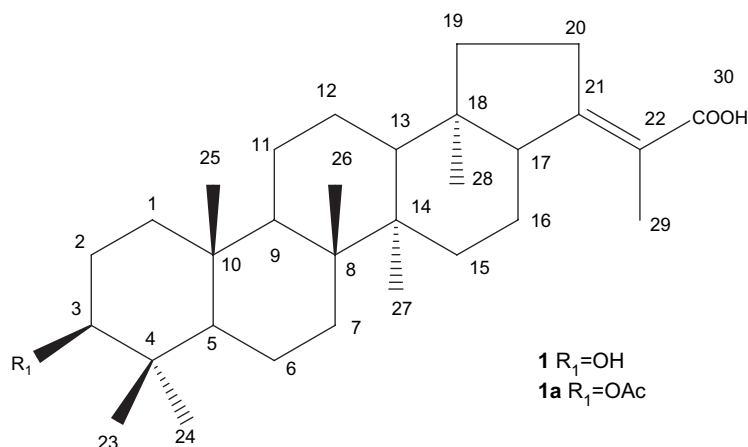


Fig. 1. Chemical structure of compounds **1** and **1a**.

DEPT NMR spectra of **1** showed 30 carbon signals, including one carboxyl carbon (δ 171.7), two olefinic carbons (δ 120.1, 144.3), seven tertiary methyls (δ 14.4, 15.5, 16.3, 16.5, 17.1, 22.1, 28.6), and 10 methylenes (δ 17.8, 19.2, 20.3, 23.2, 25.3, 28.1, 31.9, 32.8, 32.9, 37.8). In addition, the spectra also showed five other methines, including a hydroxy-bearing methine (δ 47.5, 48.1, 49.5, 55.1, 73.7) and five quaternary carbons (δ 36.7, 37.1, 41.3, 41.4, 44.7). However, the structure could not be elucidated from 1D NMR data alone, therefore, a series of 2D NMR measurements were carried out, including HMQC, HMBC, and NOESY spectra. Detailed analyses of these spectra led us to deduce that **1** is a pentacyclic triterpenoid and consists of rings A–E and a side chain (Fig. 1).

From the HMBC (Fig. 2) spectrum, the signal at δ 0.78 showed long-range correlations with the signals at δ 32.9 (C-1), δ 49.5 (C-9), δ 36.7 (C-10), and δ 48.1 (C-5), correlations between δ 0.82 (H-23) with δ 22.1 (C-24), δ 37.1 (C-4), δ 73.7 (C-3) and δ 48.1 (C-5); and δ 0.74 (H-24) with δ 28.6 (C-23), δ 37.1 (C-4), δ 73.7 (C-3) and δ 48.1 (C-5) gave ring A. The partial structures of rings B–E and the side chain were deduced in similar fashion. These partial structures suggested that **1** is a hopane triterpene. The relative stereochemistry of **1** was determined by analysis of the NOESY spectrum and a chemical method. Acetylation of **1** (Ac₂O–pyridine, 1:1) at room temperature for 24 h, gave the acetate **1a**, and on comparison of the ¹H NMR spectra of **1** and **1a**, the δ 3.16 in **1** was shifted downfield to δ 4.58 in **1a**, allowing assignment to H-3 α (Öksüz and Serin, 1997). From the NOESY spectrum, in which correlations were observed between H-3 α and H-24; H-25 and H-26; H-27 and H-28. Thus, the structure of **1** was assigned as 3 β -hydroxy-21 (22)-hopen-30-oic-acid.

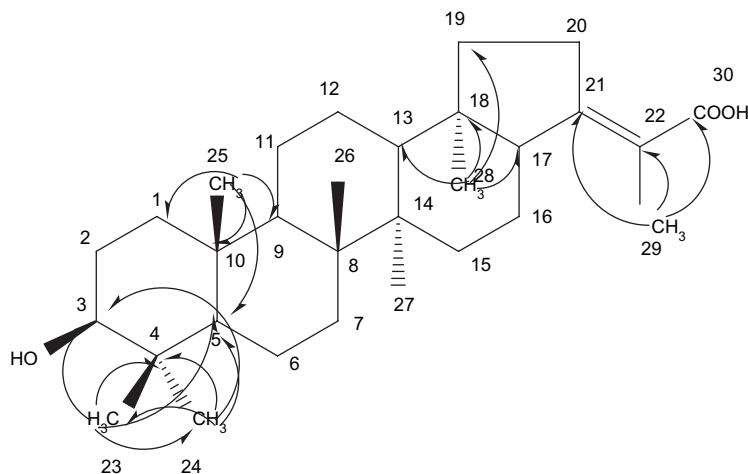


Fig. 2. Selected key HMBC correlations (H \rightarrow C) of compound **1**.

3 β -Hydroxy-21 (22)-hopen-30-oic-acid (**1**), mp. 229–231 °C; $[\alpha]_D^{20}$ 35.3° (c 0.16, MeOH). IR (KBr) ν_{\max} (cm⁻¹): 3350–2500, 1670, 1090, 1042, 1011; EIMS m/z : 456 (16), 438 (32), 423 (16), 279 (76), 229 (40), 207 (23), 189 (100), 161 (33), 135 (48); The ¹H NMR and ¹³C NMR spectral data of compounds **1** and **1a** are presented in Table 1.

4. Chemotaxonomic significance

The systematic position of *D. sinicus* has been controversial since it was established and placed in the family Celastraceae in 1911 by S.T. Dunn. For example, Sprague moved it into the family Samydaceae based on the same variation range of floral base numbers in *Dipentodon* and Samydaceae. Record considered that *Dipentodon* is close to Hamamelidaceae based on the wood anatomic characters. Merrill proposed an independent family Dipentodontaceae Merr. and placed the family in Rosales between Hamamelidaceae and Rosaceae. However, Cronquist put the Dipentodontaceae into the order Santalales based on similar characters of the gynoeical structure (Peng et al., 2003).

The family Celastraceae includes 98 genera with approximately 1264 species (Simmons et al., 2001). These are widespread in tropical and subtropical regions including North Africa, South America and East Asia, particularly in China (Spivey et al., 2002). There are 12 genera with 180 species of Celastraceae distributed in China (Qi and

Table 1
NMR spectral data of compounds **1** and **1a** (500 MHz for ¹H NMR and 125 MHz for ¹³C NMR in DMSO-*d*₆)

Position	1		1a	
	$\delta^{13}\text{C}^{\text{a}}$	$\delta_{\text{H}}^{\text{a}}$ (m ^b)	$\delta^{13}\text{C}^{\text{a}}$	$\delta_{\text{H}}^{\text{a}}$ (m ^b)
1	32.9	1.26 (m)	32.7	
2	25.3	1.40 (m); 1.79 (m)	21.7	
3	73.7	3.16 (dd, $J = 10.0, 6.0$ Hz)	75.7	4.58 (dd, $J = 10.2, 5.8$ Hz)
4	37.1		36.1	
5	48.1	1.18 (m)	48.2	
6	17.8	1.36 (m)	17.7	
7	31.9	1.12 (m); 1.33 (m)	31.8	
8	41.3		41.3	
9	49.5	1.29 (m)	49.5	
10	36.7		36.7	
11	20.3	1.34 (m); 1.51 (m)	20.2	
12	23.2	1.43 (m)	23.2	
13	47.5	1.47 (m)	47.6	
14	41.4		41.4	
15	32.8	1.17 (m); 1.43 (m)	32.6	
16	19.2	1.25 (m); 1.99 (m)	19.1	
17	55.1	1.73 (m)	55.2	
18	44.7		44.9	
19	37.8	1.03 (m); 1.56 (m)	37.7	
20	28.1	2.11 (m); 2.24 (m)	28.3	
21	144.3		144.1	
22	120.1		120.3	
23	28.6	0.82 (s)	28.5	0.82 (s)
24	22.1	0.74 (s)	23.1	0.73 (s)
25	15.5	0.78 (s)	15.4	0.78 (s)
26	16.5	0.93 (s)	16.6	0.93 (s)
27	16.3	0.93 (s)	16.3	0.93 (s)
28	14.4	0.55 (s)	14.3	0.57 (s)
29	17.1	1.71 (s)	17.2	1.72 (s)
30	171.7		171.5	
OCOCH ₃			169.9	
OCOCH ₃			21.3	2.01 (s)

^a δ (ppm).

^b Multiplicity.

Gao, 1994). Phytochemical studies have been carried out in the genera, *Celastrus*, *Maytenus*, *Tripterygium*, *Euonymus* and *Catha* (Guo and Li, 2003; Katakawa et al., 2000; Kuo et al., 2003; Lu et al., 2002; Xia et al., 2005; Zhang et al., 1998). According to these results, triterpenes are the most common constituents. However, the triterpene skeletons are of the oleanane, ursane, friedelane and lupane types. To our knowledge, **1** is the first hopane type triterpene isolated from the Celastraceae family. This information could be used as a chemical biomarker for chemotaxonomic identification of *D. sinicus*. On the other hand, in our continuing studies on *D. sinicus*, an abundance of ellagic derivatives have been isolated, and in this respect it is also different from other species of Celastraceae. It was in accord with the previous study that *D. sinicus* is a special species in the Celastraceae family (Liu and Cheng, 1991; Qi and Gao, 1994). A recent study on the phylogenetic position of *D. sinicus* also suggested that there is no close relationship between *Dipentodon* and various other groups, including Celastraceae (Peng et al., 2003). Thus, the systematic position of *D. sinicus* should be further considered.

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