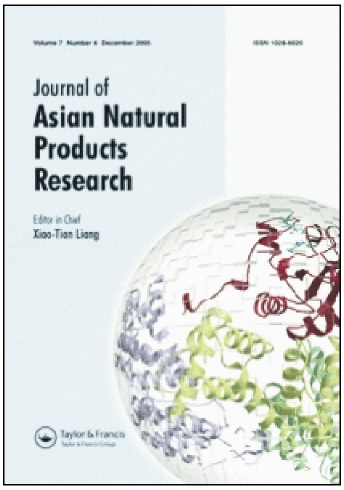
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Asian Natural Products Research

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

New hopane triterpene from *Dicranostigma leptopodum* (Maxim) Fedde

Fang Wang[ab]; Yu-Ming Li[a]
[a] School of Life Sciences, Lanzhou University, Lanzhou, China [b] Lanzhou General Hospital of PLA, Lanzhou, China

Online publication date: 01 February 2010

To cite this Article Wang, Fang and Li, Yu-Ming(2010) 'New hopane triterpene from *Dicranostigma leptopodum* (Maxim) Fedde', Journal of Asian Natural Products Research, 12: 1, 94 — 97

To link to this Article: DOI: 10.1080/10286020903443028

URL: http://dx.doi.org/10.1080/10286020903443028

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Asian Natural Products Research
Vol. 12, No. 1, January 2010, 94–97

Taylor & Francis
Taylor & Francis Group

NOTE

New hopane triterpene from *Dicranostigma leptopodum* (Maxim) Fedde

Fang Wang[ab] and Yu-Ming Li[a]*

[a]*School of Life Sciences, Lanzhou University, Lanzhou 730000, China;* [b]*Lanzhou General Hospital of PLA, Lanzhou 730050, China*

(*Received 21 August 2009; final version received 26 October 2009*)

Phytochemical investigation of the whole plant of *Dicranostigma leptopodum* (Maxim) Fedde led to the isolation of a new hopane triterpene, dicranostigmone (**1**), and a known compound, erythrodiol-3-*O*-palmitate (**2**). The structure of the new compound (**1**) was elucidated by various spectroscopic methods including 2D NMR techniques (gCOSY, HMQC, HMBC, NOESY), HR-ESI-MS, and X-ray.

Keywords: Papaveraceae; *Dicranostigma leptopodum*; dicranostigmone

1. Introduction

The genus *Dicranostigma* (Papaveraceae) has been used as a folk medicine for the treatment of tonsillitis, hepatitis, and inflammatory in China for a long time [1,2]. In the continuation of our phytochemical investigation to find medically active constituents from natural sources, we selected the whole plant of *Dicranostigma leptopodum* (Maxim) Fedde, which is mainly distributed in the northwest of China. Although the alkaloids of this plant have been reported previously [2,3], a new hopane triterpene named dicranostigmone (**1**), together with a known triterpene, erythrodiol-3-*O*-palmitate (**2**) [4], has been isolated (Figure 1). In the present paper, the isolation and structural elucidation of **1** are reported.

2. Results and discussion

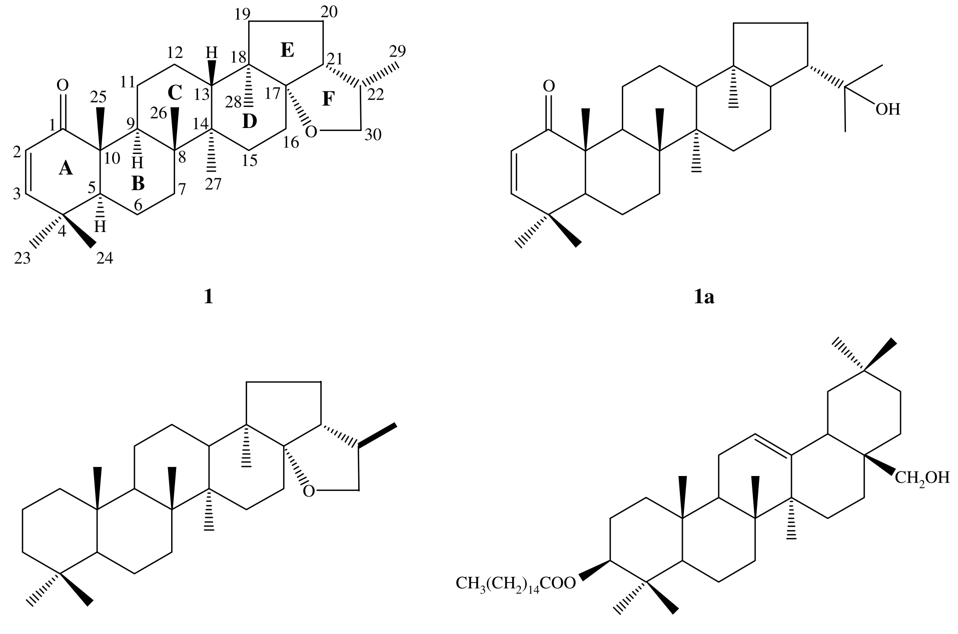
Compound **1** was obtained as a colorless needle crystal and was positive to the Liebermann–Burchard reaction. Its molecular formula was assigned as $C_{30}H_{46}O_2$ on the basis of the positive HR-ESI-MS at *m/z* 439.3567 $[M+H]^+$. The IR absorption bands at 1678 and 1642 cm^{-1} and the UV absorption maximum at 246 nm were supported by the presence of the α,β-unsaturated ketone group in the structure of **1**, which was in excellent agreement with compound **1a** [5]. The presence of six tertiary methyls at δ 1.03, 1.05, 1.17, 1.00, 1.02, 0.94 and one secondary methyl at δ 0.96 (d, $J = 6.4$ Hz, H-29) in the ^1H NMR spectrum (Table 1) suggested a hopane or lupane triterpene skeleton. The ^{13}C NMR spectrum was indicative of a triterpene of 21βH-hopan-17α,30-epoxide series by the comparison of the reported values of hopane and isohopane [5–7]. Specifically, the methyl signal at δ 11.8 (C-29) of **1** in the ^{13}C NMR spectrum is located at a very higher field than the methyl signal of **1b** at δ 19.2 (C-29), which was the characteristic

---

*Corresponding author. Email: liym@lzu.edu.cn

ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020903443028
http://www.informaworld.com



1 **1a** **1b** **2**

Figure 1. Chemical structures of **1**, **1a**, **1b**, and **2**.

of the 17α,30-epoxide series. In the $^1H-^1H$ COSY spectrum, the isopropyl side chain of the hopane triterpene and the methylene protons at δ 3.85 (1H, dd, $J = 1.0, 7.2$ Hz, H-30β) and δ 3.14 (1H, dd, $J = 2.8, 7.2$ Hz, H-30α) adjacent to the ether group in ring F could be assigned by the correlations of H-22 with H-30, H-29, and H-21. The oxo group located at C-1 in ring A was elucidated by the HMBC correlations (Figure 2) of H-25, H-2, H-3, and H-5 with C-1. The position of the attached epoxide was established by the HMBC correlations of H-30α and H-30β with

Table 1. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectral data of **1** in $CDCl_3$ (TMS, δ in ppm, J in Hz).

No.	δ_H	δ_C	No.	δ_H	δ_C
1		207.3	16	1.64 (m)	28.0
2	5.62 (d, 10.0)	124.3	17		96.7
3	6.25 (d, 10.0)	154.3	18		50.1
4		36.3	19	1.52 (m)	20.7
5	1.43 (m)	51.2	20	1.55 (m)	23.4
6	1.56 (m)	19.2	21	2.42 (m)	36.6
7	1.27–1.21 (m)	29.6	22	2.44 (m)	47.8
8		42.0	23	1.03 (s)	30.9
9	1.94 (dd, 12.0, 2.4)	41.1	24	1.05 (s)	21.8
10		47.9	25	1.17 (s)	15.9
11	2.11 (dd, 12.0, 2.4), 1.30 (m)	25.2	26	1.00 (s)	16.9
12	1.43 (m)	32.1	27	1.02 (s)	15.5
13	1.52 (m)	40.0	28	0.94 (s)	17.4
14		41.4	29	0.96 (d, 6.4)	11.8
15	1.75 (m)	39.8	30β	3.85 (dd, 1.0, 7.2),	73.3
			30α	3.14 (dd, 2.8, 7.2)	

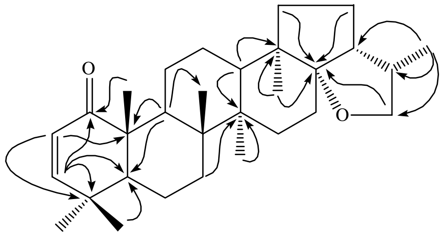


Figure 2. Key HMBC correlations of **1**.

C-17. In the NOESY experiment, cross-peaks were observed between H-24 and H-25, H-25 and H-26, H-27 and H-28, and protons of H-22 and H-30β. The above results showed that the methyl group at C-22 has an α-configuration (22*S*), which also could be deduced through comparing the chemical shift at C-29 in compound **1** with the literature value of **1b** [8]. Although there are no heavy atoms in the structure of **1**, the stereostructure for the carbon atom at C-17 could be easily determined through X-ray experiments and the relative stereochemistry of **1** could be assigned as shown in Figure 1. Consequently, the structure of **1** was concluded to be (22*S*)-hopan-1-oxo-2,3-ene-17α,30-epoxide, named as dicranostigmone. The structure of **1** was further confirmed by X-ray crystallography (Figure 3).

3. Experimental

3.1 General experimental procedures

Melting points were obtained on an X-4 digital display micro-melting point apparatus and are uncorrected. UV spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer in $CHCl_3$ solution. IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer using KBr pellets. NMR spectra were recorded on a Varian INOVA 400 MHz FTNMR spectrometer with TMS as the internal standard. HR-ESI-MS was recorded on a Bruker APEX II. X-ray crystallographic data were collected on a Bruker D8 SMART APEX II. Silica gel (200–300 mesh) was used for column chromatography (CC) and silica GF_{254} (10–40 μm) for TLC (silica gel; Qingdao Marine Chemical, Inc., Qingdao, China). Spots were detected on TLC under UV light or by heating after spraying with 98% H_2SO_4:EtOH (5:95, v/v).

3.2 Plant material

The whole plants of *D. leptopodum* (Maxim) Fedde were collected in Pinliang City of Gansu Province in May 2008, and identified by Prof. Zhi-Gang Ma in Lanzhou University, Lanzhou, China. A voucher specimen (No. ZY200802) has been deposited at Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China.

3.3 Extraction and isolation

The whole plants of *D. leptopodum* (5 kg) were powdered and extracted at room temperature with 95% ethanol (3× 20 liters,

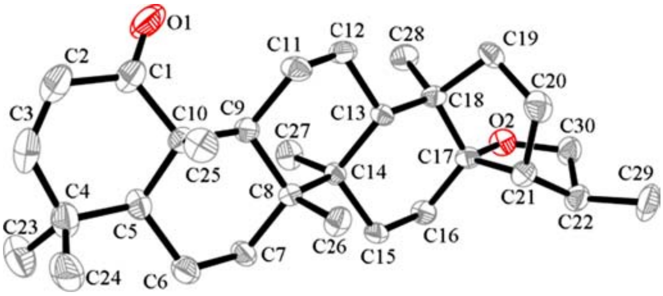


Figure 3. X-ray structure of **1**.

7 days each). The solvent was removed under reduced pressure to give the residue (200.0 g), which was suspended in water (2000 ml) and extracted with the same volumes of petroleum ether (60–90°C), EtOAc, and *n*-BuOH, successively. The petroleum ether extract (30 g) was subjected to CC on silica gel (200–300 mesh, 500 g, 8 × 180 cm) eluted with a gradient of petroleum ether–EtOAc (100:1 to 5:1, flow rate 10 ml/min) and five crude fractions A1 (5000 ml, 2 g, 100:1), A2 (4000 ml, 5 g, 50:1), A3 (5000 ml, 2.5 g, 25:1), A4 (8000 ml, 1.5 g, 10:1), and A5 (3000 ml, 1 g, 5:1) were obtained from differences in composition by TLC. A2 was further fractionated on CC over silica gel (3 × 40 cm, 200–300 mesh, 20 g) using petroleum ether–EtOAc (8:1, 500 ml) to give compounds **1** (20 mg) and **2** (15 mg).

3.3.1 Dicranostigmone (1)

Colorless needle crystal (EtOH), mp 226–228°C; $[\alpha]_D^{20}$ +10 ($c = 1.00$, $CHCl_3$); UV ($CHCl_3$) λ_{max} ($\log \varepsilon$): 246 (2.10) nm; IR (KBr) ν_{max}: 2924, 2876, 2841, 1678, 1642, 1456, 1377, 1047 cm^{-1}; HR-ESI-MS *m/z*: 439.3567 $[M+H]^+$ (calcd for $C_{30}H_{47}O_2$, 439.3571); ^1H and ^{13}C NMR spectral data, see Table 1.

3.4 X-ray crystal data and structure refinement

Crystal data for **1**: $C_{30}H_{46}O_2$, $M_r = 438.67$, $D_{cal} = 1.161\ g/cm^3$. X-ray diffraction data were collected by a Bruker APEX II area detector diffractometer with a graphite monochrome (φ- and ω-scans, $\theta_{max} = 26.4°$), Mo Kα radiation. The crystal (0.32 × 0.30 × 0.10 mm) belongs to the orthorhombic system, space group $P2_12_12_1$. Accurate cell parameters are $a = 7.5526$ (8) Å, $b = 11.8145$ (12) Å, $c = 56.275$ (6) Å, $V = 5021.4$ (9) $Å^3$, $Z = 8$. The total number of reflections measured was 28,521, of which 10,213 were independent reflections and 6742 were observed ($|F|^2 \geq 2\sigma|F|^2$). The crystal structure was solved by the direct method using SHELXS-97 and expanded using difference Fourier techniques, refined by the program and method SHELXL-97 [9] and the full-matrix least-squares calculation. The final R indices were $R_1 = 0.063$, $wR_2 = 0.190$, and the goodness of fit is 0.85. Crystallographic data for the structure of **1** have been deposited in the Cambridge Crystallographic Data Centre (Deposition No. CCDC-751737). Copies of the data of **1** can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK [fax +44(1223)336 033, or deposit@ccdc.cam.ac.uk].

Acknowledgement

This work was supported by the Science and Technology program of Gansu (090NKCA125).

References

[1] Delectis Florae Reipublicae Popularis Sinicae, Agendae Academiae Sinicae Edita, *Flora Republican Popularis Sinicae* (Science Press, Beijing, 1999), Vol. 32, p. 61.

[2] X.R. Chang, H.X. Wang, G.Z. Zhou, and G.G. Ma, *Chin. J. Pharm. Anal.* **2**, 273 (1982).

[3] Y. Dang, H.F. Gong, J.X. Liu, and S.J. Yu, *Chin. Chem. Lett.* **20**, 1218 (2009).

[4] T. Yoshitaka, K. Rie, K. Masafumi, Y. Yasunori, and K. Masao, *Chem. Pharm. Bull.* **51**, 89 (2003).

[5] S. Huneck, A. Preiss, J. Schmidt, and A. Mendez, *Phytochemistry* **22**, 2027 (1983).

[6] J.K. Lee, H. Miyashiro, N. Nakamura, and M. Hattori, *Chem. Pharm. Bull.* **56**, 711 (2008).

[7] H.F. Pi, Z.H. Zhong, H.L. Run, P. Zhang, Y.H. Zhang, and J.Z. Wu, *Chin. Chem. Lett.* **19**, 835 (2008).

[8] Y. Arai, N. Koide, F. Ohhki, H. Ageta, L.L. Yang, and K.Y. Yen, *Chem. Pharm. Bull.* **42**, 228 (1994).

[9] G.M. Sheldrick, SHELX-97 Program for crystal structure refinement (University of Gottingen, Gottingen, Germany, 1997).