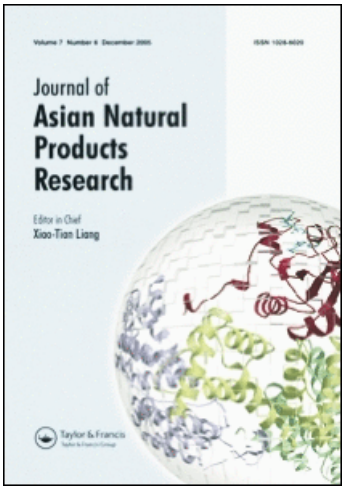


Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

A new cucurbitacin from *Bolbostemma paniculatum* Franguent

C. -H. Zheng[a]; H. -W. Fu[a]; Y. -H. Pei[a]
[a] School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang, China

To cite this Article Zheng, C. -H. , Fu, H. -W. and Pei, Y. -H.(2007) 'A new cucurbitacin from *Bolbostemma paniculatum* Franguent', Journal of Asian Natural Products Research, 9: 2, 187 — 190
To link to this Article: DOI: 10.1080/10286020500246725
URL: http://dx.doi.org/10.1080/10286020500246725

Journal of Asian Natural Products Research, Vol. 9, No. 2, March 2007, 187–190

Note

A new cucurbitacin from *Bolbostemma paniculatum* Franguent

C.-H. ZHENG, H.-W. FU and Y.-H. PEI*

School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang 110016, China

(Received 22 February 2005; revised 27 May 2005; in final form 23 June 2005)

A new cucurbitacin with an unusual ring A, isocucurbitacin D 25-*O*-acetate (1), was isolated from *Bolbostemma paniculatum* Franguent together with one known compound, cucurbitacin E (2). The structure of new compound was established by spectroscopic methods.

Keywords: *Bolbostemma paniculatum* (Maxim.) Franguent; Cucurbitacin; Isocucurbitacin

1. Introduction

Bolbostemma paniculatum (Maxim.) Franguent is one of the Chinese folk medicines often used for the treatment of tumours as well as for detoxification. It is distributed in most provinces of China. Many triterpenoids have been isolated from related species of the same family over the past decade. Cucurbitacins are a special group of triterpenoids having a cucurbitane skeleton characterised by a 19 ($10 \rightarrow 9\beta$) abeo-10α-lanost-5-ene. Most of the cucurbitacins are tetracyclic, but some representatives have an extra ring due to formal cyclisation between C-16 and C-24 (cucurbitacins S and T) [1,2]. Certain cucurbitacins have been discovered in the form of glycosides and some of them lack C-11 carbonyl function [3]. Biologically, they exhibit a wide range of activities including cytotoxicity and anti-tumour effects [4–6]. Chemically, cucurbitacins are classified according to the functionalities in rings A and C, side chain modifications, as well as stereochemical considerations. In this paper we report the isolation and structural elucidation of these two cucurbitacins.

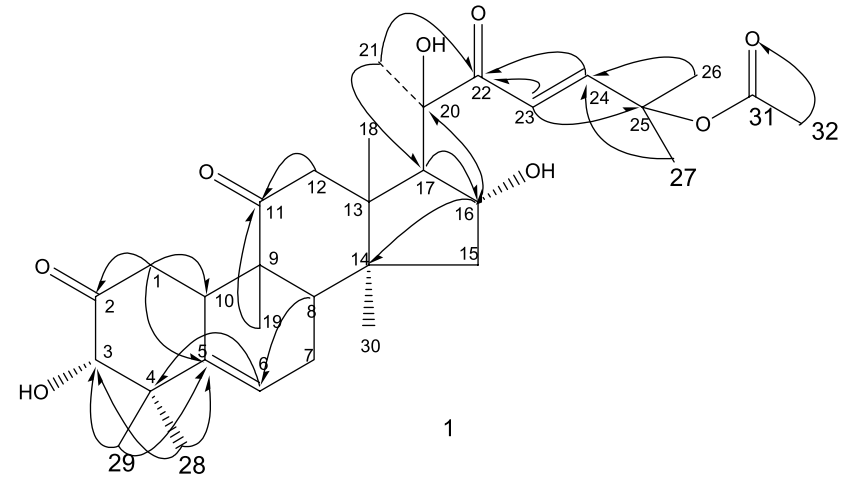
*Corresponding author. Email: peiyueh@vip.163.com

Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020500246725

2. Results and discussion

Chromatographic fractionation of the chloroform extract of *Bolbostemma paniculatum* Franguent on silica gel column followed by HPLC separation yielded two cucurbitacins, 1 and 2, which showed brown colour with H_2SO_4 spray reagent.

Compound **1** was obtained as a white powder, mp 228–230°C, $[\alpha]_D^{20} + 62.5$ (*c* 0.52, $CHCl_3$). Its molecular formula was determined as $C_{32}H_{46}O_8$ by HRESI-MS *m/z* 581.3090 $[M + Na]^+$. The IR spectrum indicated the presence of hydroxyls, carbonyls, and olefinic functionalities. The ^1H NMR (600 MHz, $CDCl_3$) spectrum showed a sharp singlet at δ 3.91 assigned to the α-hydroxylated methine group, indicating the presence of the isocucurbitacin skeleton with 2-keto-3-α hydroxy system in ring A [7]. Three olefinic signals at δ 5.94 (d, $J = 5.28$ Hz, H-6), 6.43 (d, $J = 15.60$ Hz, H-23) and 7.05 (d, $J = 15.60$ Hz, H-24) and an AB system at δ 2.64 (H-12β, d, $J = 14.64$ Hz) and 3.12 (H-12α, d, $J = 14.64$ Hz) were observed in the ^1H NMR spectrum. The signal at δ 4.34 was assigned to H-16β [8]. In addition, **1** showed nine methyl singlets at δ 0.81-2.00



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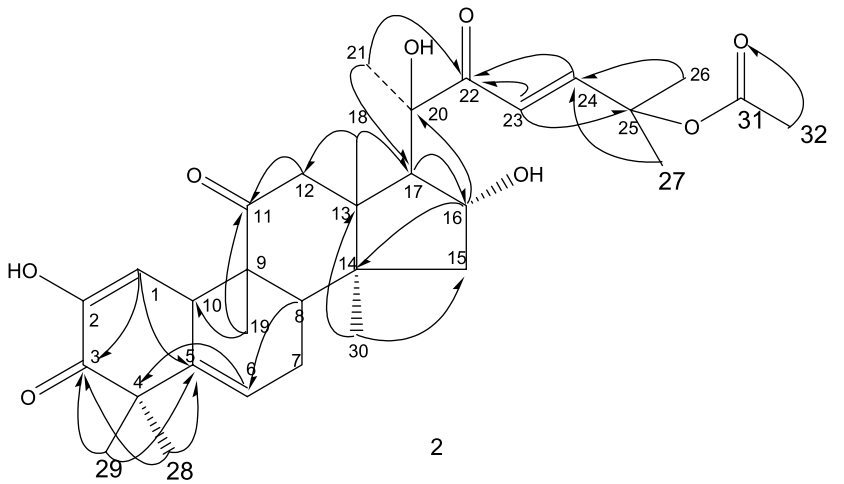

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Figure 1. Key HMBC correlations of compounds **1** and **2**.

among which one methyl singlet at δ 2.00 was assignable to the 25-*O*-acetate group (C-31) [8,9]. ^{13}C NMR experiments showed 32 carbon signals including four carbonyls, nine methyls and four olefinic carbons. Nine methyls were located by means of HMQC and HMBC experiments (figure 1). In the HMBC spectrum two protons at δ 2.41 (H-1β) and 2.23 (H-1α) showed long-range correlations with the carbonyl carbon at δ 210.6 (C-2). The complete structural elucidation of **1** was derived from the chemical shifts and coupling constant of the ^{1}H NMR and ^{13}C NMR spectra, and detailed spectral analysis of HMQC, HMBC experiments (table 1) and comparison with the data of the literature [10–12]. Therefore **1** was characterised as 19-norlanosta-5,23-diene-2,11,22-trione-25-(acetyloxy)-3α,16α,20β-trihydroxy-9-methyl.

Compound **2** was one known compound identified by spectroscopic methods and comparison with the data of the literature [13,14].

3. Experimental

3.1 General experimental procedures

The NMR data were recorded on a Bruker AV-600 spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C) in CD_3Cl with TMS as internal standard. The IR spectra were recorded on

Table 1. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) data of compound **1**.

H	δ_H	*C*	δ_C
H-1α	2.23 (m)	1	38.8
H-1β	2.41 (m)	2	210.6
H-3	3.91 (s)	3	80.2
H-6	5.94 (d, $J = 5.28$)	4	46.7
H-7α	1.99 (m)	5	138.1
H-7β	2.50 (m)	6	121.9
H-8	2.04 (d, $J = 7.68$)	7	23.8
H-10	2.74 (br d, $J = 12.06$)	8	42.7
H-12α	3.12 (d, $J = 14.64$)	9	48.3
H-12β	2.64 (d, $J = 14.64$)	10	36.3
H-15α	1.86 (dd, $J = 9.36, 13.14$)	11	211.8
H-15β	1.44 (m)	12	48.6
H-16	4.34 (m)	13	50.6
H-17	2.45 (d, $J = 7.14$)	14	47.9
H-23	6.43 (d, $J = 15.60$)	15	45.3
H-24	7.05 (d, $J = 15.60$)	16	71.3
Me-18	0.97	17	58.1
Me-19	1.18	18	19.9
Me-21	1.42	19	20.0
Me-26	1.56	20	78.1
Me-27	1.53	21	23.6
Me-28	0.81	22	202.4
Me-29	1.33	23	120.2
Me-30	1.26	24	152.1
Me-32	2.00	25	79.3
		26	25.9
		27	26.4
		28	20.9
		29	24.0
		30	18.8
		31	170.2
		32	21.9

a Bruker IFS-55 instrument (KBr). HRESI-MS spectra were measured on a Apex II FTICR mass spectrometer. Chromatography was performed with silica gel (200–300 mesh), Sephadex LH-20 and HPLC.

3.2 Plant material

The underground parts of *Bolbostemma paniculatum* (Maxim.) were offered by Changchun Huakang Pharmaceutical Company Ltd. and were identified by Professor Qi-shi Sun (Shenyang Pharmaceutical University). A sample has been deposited in the School of Chinese Medicine, Shenyang Pharmaceutical University.

3.3 Extraction and isolation

Dried and powdered underground parts of *B. paniculatum* (Maxim.) were extracted three times with EtOH. After evaporation of EtOH *in vacuo*, the concentrated extract was suspended in water and partitioned with $CHCl_3$, AcOEt, and n-BuOH, respectively. The $CHCl_3$ portion (103 g) was chromatographed on a silica gel (1030 g, Qingdao Haiyang Chemical Co. Ltd.) column and eluted with petroleum ether/acetone (100:20) to give fractions monitored by TLC. Fraction 1 (0.5 g) was rechromatgraphed by HPLC (MeOH/H_2O 60:40 v/v; flow rate 1 ml/min; UV detection 210 nm), to afford compounds **1** (20 mg) and **2** (16 mg).

3.3.1 Compound 1. White powder, mp 228–230°C, $[\alpha]_D^{20} + 62.5$ (*c* 0.52, $CHCl_3$), positive Libermann reaction; TLC: R_f 0.52, HPLC: t_R 34.5 min. HRESI-MS *m/z* 581.3090 $[M + Na]^+$ (calcd for $C_{32}H_{46}O_8$, 581.3097); IR (KBr) cm^{-1}: 3378, 1720, 1683, 1658, 1633, 1362, 1260, 1121, 1038, 990. ^1H NMR, ^{13}C NMR data: see table 1; HMBC data: see figure 1.

Acknowledgements

The authors give thanks to Wen Li and Yi Sha of the Analytical Centre of Shenyang Pharmaceutical University for recording the ^1H NMR, ^{13}C NMR and 2D NMR spectra. We are grateful to Bin Xin, Department of Instrumental Analysis of Institute, Chemistry of Chinese Academy of Sciences, for the HRESI-MS measurement.

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