

Bafoudiosbulbin H, a new clerodane diterpene from the flowers of *Dioscorea bulbifera* L. var *sativa*

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ABSTRACT

A new clerodane diterpenoid, bafoudiosbulbin H (**1**), was isolated from the flowers of *Dioscorea bulbifera* L. var *sativa*. Its acetylation using acetic anhydride-pyridine and catalytic amount of 4-DMAP at 60 °C yielded bafoudiosbulbin H acetate (**2**) together with a clerodane with an unprecedented acylation pattern (bafoudiosbulbin H1, **3**). The reaction of the known bafoudiosbulbin G (**4**) in the same conditions yielded demethylbafoudiosbulbin G (**5**). Structural elucidation of **5** led to the revision of the stereochemistry previously assigned to **4**. Structures were elucidated using spectroscopic techniques, including 1D and 2D NMR (¹H, ¹³C, HSQC, COSY, HMBC, ROESY, NOESY) and mass spectrometry (HRESIMS).

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1. Introduction

Clerodane diterpenoids represent a group of secondary metabolites that has attracted considerable interest because of a large variety of biological activities, such as antifeedant, cytotoxic, antifungal, antibiotic (Rodríguez-Hahn et al., 1994; Meritt and Ley, 1992; Ortega et al., 1982). In addition, unique features associated with the stereochemistry of these compounds stimulated a number of synthetic studies (Tokoroyama, 2000). Recently, some of us reported the isolation of seven new clerodane diterpenoids, namely bafoudiosbulbins A–G (Teponno et al., 2006, 2007, 2008), from the tubers and bulbils of *Dioscorea bulbifera* L. var *sativa* (Dioscoreaceae), a perennial vine used in African and Asian traditional medicines for the treatment of cuts (Tredgold, 1990), abscesses and wound infections (Neuwinger, 1996), leprosy and tumors (Murray et al., 1984). As an extension of our previous work we now report the isolation of a new clerodane diterpenoid, bafoudiosbulbin H (**1**), together with the known bafoudiosbulbins A, B, C, F, and G, from the flowers of *D. bulbifera* (Fig. 1). As far as we know, phytochemical investigations of the flowers of *D. bulbifera* have not been previously reported. Furthermore, compound **1** was subjected to acetylation with the

aim to confirm the presence of a tertiary hydroxyl group, and the unexpected results of this reaction are reported.

2. Results and discussion

A new clerodane diterpenoid, bafoudiosbulbin H (**1**), and the known bafoudiosbulbins A, B (Teponno et al., 2006), C (Teponno et al., 2007), F and G (Teponno et al., 2008), were isolated from the MeOH extract of the air-dried flowers of *D. bulbifera* L. var *sativa* by column chromatography. They were identified by using spectroscopic methods including HRESIMS, 1D and 2D NMR analysis and also by comparing experimental data with those described in the literature.

Compound **1** was obtained as a white amorphous powder from Hexane-EtOAc. Its molecular formula C₂₀H₂₀O₈ was established by the negative ion mode HRESIMS which showed the quasimolecular ion peak at *m/z* 423.0852 [M+Cl][−] (calcd for C₂₀H₂₀O₈Cl: 423.0847). This was confirmed by the ESIMS which exhibited the quasimolecular ion peaks at *m/z* 423 [M+Cl][−] and 387 [M−H][−]. Compound **1** should then be an isomer of bafoudiosbulbin B (C₂₀H₂₀O₈) (Fig. 1), previously isolated from the tubers and bulbils of *D. bulbifera* L. var *sativa* (Teponno et al., 2006, 2008). The IR spectrum indicated the presence of hydroxyl group (3500 cm^{−1}), carbonyl groups (1738, 1729 cm^{−1}), and furan moiety (870 cm^{−1}) (Murray et al., 1984). The ¹H NMR spectrum of compound **1** showed the characteristic signals of furoclerodanes at δ 7.72

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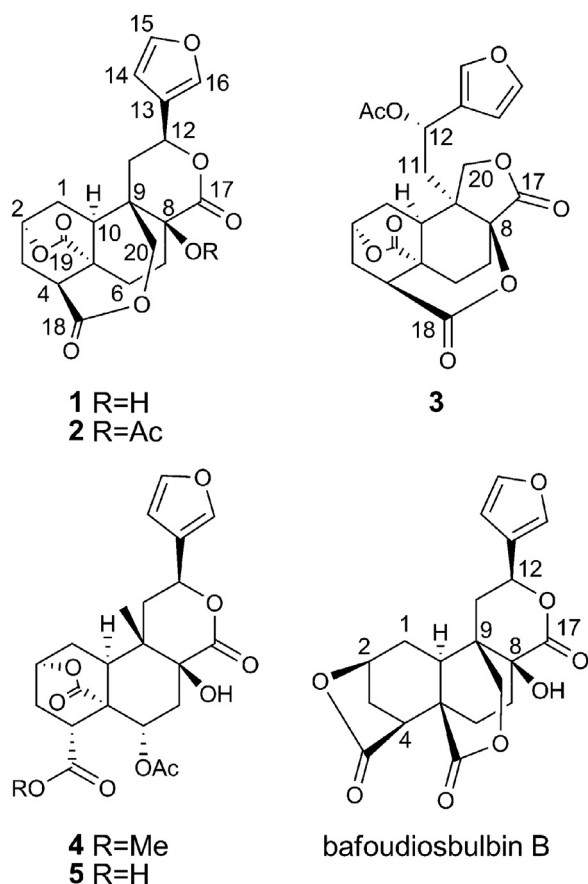


Fig. 1. Structures of compounds 1–5.

(brs, H-16), 7.68 (brs, H-15), and 6.53 (brs, H-14) (Kapingu et al., 2000). Other signals of interest were those of the oxymethine protons H-12 and H-2 at δ 5.49 (dd, J = 12.8, 3.4) and 4.89 (m), respectively, as well as those of the oxymethylene group at δ 4.60 (d, J = 14.1, H-20a) and 4.05 (d, J = 14.1, H-20b). The ^{13}C NMR spectrum of compound **1** revealed the presence of twenty carbon atoms, classified as seven methines, six methylenes and seven quaternary carbons based on the DEPT analysis. The three lactonic carbonyl groups were identified at δ 175.0 (C-19), 172.3 (C-18) and 171.5 (C-17). The signals observed at δ 144.6 (C-15), 140.9 (C-16), 125.0 (C-13) and 109.5 (C-14) were characteristic of the furan ring (Kapingu et al., 2000; Tane et al., 1997; Fayos et al., 1984) while those at δ 71.9 (C-2), 70.1 (C-12), 73.6 (C-8) and 67.0 (C-20) indicated the presence of two oxygenated methines, one oxygenated quaternary carbon and one oxymethylene group, respectively (Table 1). Comparison of ^1H and ^{13}C chemical shifts of compound **1** (Table 1) with those of bafoudiosbulbin B (Teponno et al., 2006, 2008) showed high similarities. The main difference was the presence of a lactone between C-2 and C-19 (C-2 and C-18 in bafoudiosbulbin B) supported by the HMBC correlations of protons at δ 4.89 (H-2) and 2.08 (H-6) with the carbon signal at δ 175.0 (C-19) (Fig. 2). The HMBC correlations observed between H-4 (δ 2.99) and C-18 (δ 172.3) as well as between H-20 (δ 4.05) and C-18 (δ 172.3) showed that carbons C-4 and C-20 were also implicated in a lactonic bridge (Fig. 2).

Further HMBC, HSQC, and COSY analysis enabled complete ^1H and ^{13}C assignment of **1** (Table 1). The relative stereochemistry was determined by comparison to that of related compounds (Murray et al., 1984) and on the basis of the NOESY spectrum. In particular, cross-peak correlations between H-12 (δ 5.49) and H-10 (δ 2.20), H-2 (δ 4.89) and H-1b (δ 1.70), H-4 (δ 2.99) and H-6b (δ 2.08) (Fig. 3) confirmed the relative stereochemistry to be the same as bafoudiosbulbin F (Teponno et al., 2008). Compound **1** was therefore elucidated as 15,16-epoxy-8 β -hydroxycyclocleroda-13(16),14-diene-17,12S;18,20;19,2 α -triolide, a new clerodane diterpenoid to which we gave the trivial name bafoudiosbulbin H.

Table 1

^1H and ^{13}C NMR data of compounds **1** (DMSO- d_6), **2** (CDCl₃), **3** (Acetone- d_6) and **5** (DMSO- d_6): δ in ppm, J in Hz.

Position	1		2		3		5	
	$\delta^{13}\text{C}$	$\delta^1\text{H}$ (mult, J)	$\delta^{13}\text{C}$	$\delta^1\text{H}$ (mult, J)	$\delta^{13}\text{C}$	$\delta^1\text{H}$ (mult, J)	$\delta^{13}\text{C}$	$\delta^1\text{H}$ (mult, J)
1	26.3	1.70 o; 1.88 m	27.7	1.90 o; 2.42 (brd, 11.1)	26.2	1.67 (brt, 13.4); 2.31 o	26.5	1.68 m; 2.25 (brd, 13.9)
2	71.9	4.89 m	72.4	4.89 brs	72.9	4.83 (brd, 6.2)	73.3	4.75 brs
3	29.6	1.55 m; 2.24 m	31.5	2.06 o; 2.58 o	37.3	2.59 (dd, 14.6, 12.1)	29.5	1.95 (brd, 14.1); 2.20 o
4	44.2	2.99 (dd, 12.4, 7.3)	44.4	3.09 (dd, 12.8, 7.3)	43.4	3.09 (dt, 12.1, 1.8)	40.0	3.32 (dd, 10.3, 4.3)
5	39.3	–	39.4	–	42.0	–	45.1	–
6	26.4	2.08 m; 2.44 m	25.2	2.02 o	21.4	2.38 o	68.2	5.30 (brd, 3.8)
7	27.9	1.70 o; 2.55 m	27.9	1.83 m 2.92 (dd, 14.9, 3.4)	23.4	2.28 o; 2.38 o	31.1	2.01 o; 2.57 o
8	73.6	–	79.3	–	87.1	–	72.2	–
9	43.4	–	44.2	–	47.6	–	45.1	–
10	35.6	2.20 (brd, 12.8)	35.7	2.21 o	37.3	2.77 (t, 10.6)	31.4	2.60 (brd, 11.5)
11	31.3	1.58 (dd, 14.5, 3.4) 2.22 (dd, 14.5, 12.8)	31.5	1.69 (dd, 14.5, 3.9) 2.16 (dd, 14.5, 12.8)	40.2	1.85 (dd, 14.9, 4.5) 2.11 (dd, 14.9, 8.9)	36.0	1.74 (dd, 14.5, 3.2) 2.10 o
12	70.1	5.49 (dd, 12.8, 3.4)	71.2	5.40 (dd, 12.8, 3.9)	65.1	5.97 (dd, 8.9, 4.5)	70.2	5.65 dd (12.6, 3.2)
13	125.0	–	123.6	–	123.7	–	125.7	–
14	109.5	6.53 brs	108.7	6.45 brs	108.3	6.36 brs	109.4	6.55 brs
15	144.6	7.68 brs	144.2	7.35 brs	144.1	7.41 brs	144.3	7.64 brs
16	140.9	7.72 brs	140.8	7.46 brs	140.6	7.44 brs	141.0	7.71 brs
17	171.5	–	167.0	–	169.1	–	172.4	–
18	172.3	–	171.0	–	171.1	–	174.0	–
19	175.0	–	173.6	–	174.0	–	171.0	–
20	67.0	4.60 (d, 14.1); 4.05 (d, 14.1)	67.2	4.61 (d, 14.1); 4.15 (d, 14.1)	69.9	4.34 (d, 9.3); 4.56 (d, 9.3)	19.3	1.16 s
MeCO	–	–	169.6	–	169.8	–	169.0	–
MeCO	–	–	21.4	2.07 s	21.2	2.05 s	21.6	1.80 s
OH	–	6.63 s	–	–	–	–	–	–

o: overlapped signals.

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