Three New Clerodane Diterpenoids from the Bulbils of *Dioscorea bulbifera* L. var. *sativa*

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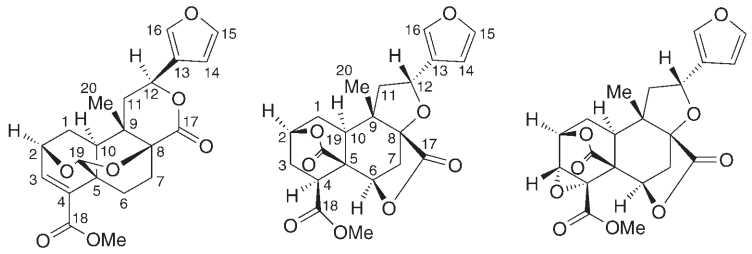
From the bulbils of *Dioscorea bulbifera* L. var. *sativa*, three new clerodane diterpenoids, bafoudiosbulbin C (= methyl (2*β*,8*α*,12*S*)-17-oxo-2,19:8,19:12,17:15,16-tetraepoxycleroda-3,13(16),14-triene-18-carboxylate; **1**), bafoudiosbulbin D (= methyl (2*β*,6*β*,12*R*)-17,19-dioxo-2,19:6,17:8,12:15,16-tetraepoxycleroda-13(16),14-diene-18-carboxylate; **2**), and bafoudiosbulbin E (= methyl (2*β*,3*α*,4*α*,6*β*,12*R*)-17,19-dioxo-2,19:3,4:6,17:8,12:15,16-pentaepoxycleroda-13(16),14-diene-18-carboxylate; **3**) were isolated, together with the known compounds bafoudiosbulbins A and B, 3-*O*-*β*-D-glucopyranosyl-*β*-sitosterol, and 6′-stearoyl-3-*O*-*β*-D-glucopyranosyl-*β*-sitosterol. Their structures were established by high-field NMR techniques (^{1}H,^{1}H-COSY, ^{13}C-DEPT, HSQC, HMBC, and NOESY), MS analyses, as well as by comparison of their spectral data with those of related compounds.

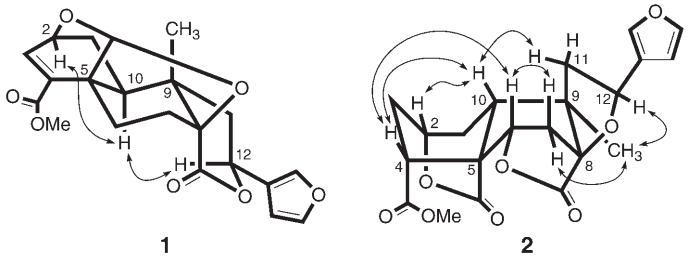
Introduction. – The *Dioscorea* genus (Dioscoreaceae) includes an important group of tropical food yams, the edible portion of which is the tuber, or occasionally the bulbil [1]. *Dioscorea bulbifera* L. var. *sativa* usually grows wild and is used in Bangladesh for treatment of leprosy and tumors [2]. The bubils are used by the native people of the western highlands of Cameroon for the treatment of pig cysticercosis, though the tubers after collection during the farming period are totally destroyed and burned because of their high bitterness. Steroidal saponins and clerodane diterpenoids are fairly widespread in this genus [3][4]. In our previous work, we reported the isolation and structural elucidation of two antityphoid clerodane diterpenoids as major components as well as a pennogenin glycoside from the tubers of this plant [5][6]. A large number of diterpenoids with the clerodane skeleton have been isolated from plants in the last few years. Interest in these compounds has been stimulated by their biological activities as insect antifeedants and antitumor, antimicrobial, and antifungal agents [5][7]. In continuation of a systematic investigation of the chemotaxonomic and bioactive components from Cameroonian medicinal plants [5][8], we herein report the isolation and characterization of three new clerodane diterpenoids, bafoudiosbulbin C–E (**1**–**3**), from the bulbils of *Dioscorea bulbifera* L. var. *sativa*, together with the known bafoudiosbulbins A and B, 3-*O*-*β*-D-glucopyranosyl-*β*-sitosterol, and 6′-stearoyl-3-*O*-*β*-D-glucopyranosyl-*β*-sitosterol.[1])

[1]) Trivial atom numbering; for systematic names, see *Exper. Part.*



1 [1] **2** [1] **3**

Results and Discussion. – Compound **1** was obtained as a white gum from CH_2Cl_2/MeOH. Its HR-FAB-MS (positive mode) displayed a pseudomolecular ion peak $[M+Na]^+$ at *m/z* 409.3879 corresponding to the molecular formula $C_{21}H_{22}NaO_7$. The EI-MS did not show the molecular-ion peak but significant peaks at *m/z* 358 ($[M-CO]^+$), 330 ($[M-2\,CO]^+$), and 312 ($[M-2\,CO-H_2O]^+$), establishing the molecular formula $C_{21}H_{22}O_7$ (*m/z* 386). The IR spectrum displayed bands indicating a furan ring (877 cm^{-1}), an ester function (1716 cm^{-1}), as well as an α,β-unsaturated ester (1654 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectral data of **1** (*Table*) were in part identical to those reported for bafoudiosbulbin B, a clerodane diterpenoid previously isolated from the tubers of the same plant [5], thus suggesting structural similarities between these two compounds. From further spectral data (*Fig. 1*), the structure of bafoudiosbulbin C (**1**) was determined as methyl (2β,8α,12*S*)-17-oxo-2,19:8,19:12,17:15,16-tetraepoxycleroda-3,13(16),14-triene-18-carboxylate[1]).



1 **2**

Fig. 1. *Key NOESY correlations of compounds* **1** *and* **2**

The ^{1}H-NMR spectrum of **1** showed the characteristic signals of a β-substituted furan ring [9] at δ(H) 7.59 (br. *s*, H–C(16)), 7.49 (*t*, *J* = 1.5 Hz, H–C(15)), and 6.54 (br. *s*, H–C(14)). A signal observed at δ(H) 7.44 (*d*, *J* = 5.5 Hz, H–C(3)) was ascribed to the olefinic proton H–C(3). Still in the downfield region of the ^{1}H-NMR spectrum, signals for three methine protons were observed at δ(H) 5.55 (*dd*, *J* = 12.5, 4.0 Hz, H–C(12)), 4.64 (overlapped, H–C(2)), and 4.62 (overlapped, H–C(19)). The spectrum also revealed the presence of a methyl ester group by the signal at δ(H) 3.80 (*s*, MeO). The analysis of the ^{13}C-NMR data of **1** through DEPT revealed 21 C-atoms among which those of a β-substituted furan at δ(C) 145.3 (C(15)), 141.8 (C(16)), 127.2 (C(13)), and 110.1 (C(14)). The presence of a lactone and an α,β-unsaturated methyl carboxylate was evidenced by signals at δ(C) 175.2, 167.2, 144.3, 135.6, and 52.6 ascribed to C(17), C(18), C(3), C(4), and MeO, respectively. The most striking feature of this spectrum

Table. *^{13}C- and ^{1}H-NMR Data* (125 and 500 MHz, resp.) *of* **1**–**3**[1]). δ in ppm, J in Hz.

	1[a])		**2**[b])		**3**[b])	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
CH_2(1)	29.4 (*t*)	2.21–2.26 (*m*), 1.34–1.36 (*m*)	26.6 (*t*)	2.32[c]), 1.74–1.78 (*m*)	23.4 (*t*)	2.43–2.47 (*m*), 1.69–1.74 (*m*)
H–C(2)	68.3 (*d*)	4.64[c])	74.0 (*d*)	4.94 (br. *t*, *J* = 4.5)	68.7 (*d*)	5.04 (*ddd*, *J* = 5.5, 3.5, 3.0)
H–C(3) or CH_2(3)	144.3 (*d*)	7.44 (*d*, *J* = 5.5)	30.1 (*t*)	2.32[c])	56.2 (*d*)	4.22 (*d*, *J* = 3.5)
C(4) or H–C(4)	135.6 (*s*)		41.8 (*d*)	3.16 (*dd*, *J* = 11.0, 8.0)	53.2 (*s*)	
C(5)	44.9 (*s*)		46.5 (*s*)		50.7 (*s*)	
CH_2(6) or H–C(6)	28.0 (*t*)	2.88 (br. *d*, *J* = 14.5), 1.34[c])	74.8 (*d*)	5.17 (*d*, *J* = 6.0)	73.2 (*d*)	5.60 (br. *d*, *J* = 6.0)
CH_2(7)	29.5 (*t*)	2.41–2.43 (*m*), 2.03–2.10 (*m*)	33.3 (*t*)	2.66 (*dd*, *J* = 12.5, 6.0), 1.96[c])	33.6 (*t*)	2.79 (*dd*, *J* = 12.5, 6.0), 2.17 (br. *d*, *J* = 12.5)
C(8)	77.0 (*s*)		87.8 (*s*)		87.4 (*s*)	
C(9)	41.5 (*s*)		45.5 (*s*)		45.4 (*s*)	
H–C(10)	38.9 (*d*)	1.65 (br. *d*, *J* = 5.5)	40.1 (*d*)	2.43 (br. *d*, *J* = 8.5)	40.3 (*d*)	2.34 (*dd*, *J* = 9.5, 8.5)
CH_2(11)	36.2 (*t*)	2.40 (*dd*, *J* = 13.5, 12.5), 1.62 (*dd*, *J* = 13.5, 4.0)	43.4 (*t*)	2.14 (*dd*, *J* = 11.5, 10.5), 1.99[c])	43.3 (*t*)	2.17 (*dd*, *J* = 11.5, 10.5), 2.00 (*dd*, *J* = 11.5, 5.5)
H–C(12)	73.3 (*d*)	5.55 (*dd*, *J* = 12.5, 4.0)	75.1 (*d*)	5.30 (*dd*, *J* = 10.5, 5.5)	74.9 (*d*)	5.28 (*dd*, *J* = 10.5, 5.5)
C(13)	127.2 (*s*)		124.6 (*s*)		124.5 (*s*)	
H–C(14)	110.1 (*d*)	6.54 (br. *s*)	110.1 (*d*)	6.91 (br. *s*)	109.9 (*d*)	6.90 (*d*, *J* = 1.0)
H–C(15)	145.3 (*d*)	7.49 (*t*, *J* = 1.5)	143.3 (*d*)	7.41 (*t*, *J* = 1.5)	143.5 (*d*)	7.42 (br. *d*, *J* = 1.5)
H–C(16)	141.8 (*d*)	7.59 (br. *s*)	141.5 (*d*)	7.58 (br. *s*)	141.4 (*d*)	7.59 (br. *s*)
C(17)	175.2 (*s*)		176.3 (*s*)		175.9 (*s*)	
C(18)	167.2 (*s*)		172.1 (*s*)		165.9 (*s*)	
H–C(19) or C(19)	101.3 (*d*)	4.62[c])	172.0 (*s*)		164.9 (*s*)	
Me(20)	18.0 (*q*)	0.75 (*s*)	17.6 (*q*)	1.30 (*s*)	17.9 (*q*)	1.23 (*s*)
MeO	52.6 (*q*)	3.80 (*s*)	53.0 (*q*)	3.82 (*s*)	53.8 (*q*)	3.89 (*s*)

[a]) In CH_3OD. [b]) In $CDCl_3$. [c]) Overlapping signals.

was the resonance typical of a dioxygenated C-atom at δ(C) 101.3 (C(19)) [10]. HSQC Analysis indicated that this C-atom was attached directly to the proton at δ(H) 4.62 (H–C(19)). Furthermore, other signals for oxygenated C-atoms were those observed at δ(C) 77.0, 73.3, and 68.3 ascribed to C(8), C(12), and C(2), respectively. The HMBC experiment clearly showed cross-peak correlations H–C(10) (δ(H) 1.65)/C(19) (δ(C) 101.3), H–C(3) (δ(H) 7.44)/C(18) (δ(C) 167.2), and MeO (δ(H) 3.80)/C(18) (δ(C) 167.2). Further HMBC, HSQC, and COSY analysis enabled the gross structural assignment of **1**. The C(12) configuration was deduced to be (*S*) from a careful comparison of the ^{1}H- and ^{13}C-NMR data with those of related compounds [2][5] and was corroborated by the axial orientation of H–C(12) which showed coupling constants of 12.5 and 4.0 Hz to the axial and equatorial protons CH_2(11). The relative configuration at other chiral centres was established by NOESY experiments. The lack of a NOESY correlation H–C(12) (δ(H) 5.55)/Me(20) (δ(H) 0.75) indicated their *trans* relationships. However, cross-peaks were observed for H–C(12) (δ(H) 5.55)/H–C(10) (δ(H) 1.65), and for H–C(10) (δ(H) 1.65)/H–C(2) (δ(H) 4.64) (*Fig. 1*). These correlations allowed us to deduce the configuration at C(9) and C(10), and to place the bicyclic ketal bridge on the β face of the molecule.

Compound **2** was isolated as a white gum from CH_2Cl_2/MeOH. The HR-FAB-MS displayed a pseudomolecular-ion peak $[M+Na]^+$ at *m/z* 425.3882 corresponding to the formula $C_{21}H_{22}NaO_8$. The FAB-MS (positive mode) gave a pseudomolecular-ion peak $[M+Na]^+$ at *m/z* 425 and an important ion peak at *m/z* 375 ($[M+H-CO]^+$). The IR spectrum showed absorption bands for two lactone carbonyl groups at 1786 and 1751 cm^{-1}, and for a furan ring at 869 cm^{-1}. Comparison of the ^{1}H- and ^{13}C-NMR chemical shifts of **2** (*Table*) with those of bafoudiosbulbin A, a clerodane diterpenoid previously isolated from the tubers of the same plant [5], showed high similarities (same number of H-, O- and C-atoms, same multiplicities in the DEPT spectrum). The only difference was the slight downfield shifts of some δ(C) and δ(H), probably due to the change of configuration at some stereogenic centers. Further spectral data (*Fig. 1*) elucidated the structure of bafoudiosbulbin D (**2**) as methyl (2β,6β,12*R*)-17,19-dioxo-2,19:6,17:8,12:15,16-tetraepoxycleroda-13(16),14-diene-18-carboxylate[1]), a stereoisomer of bafoudiosbulbin A.

The ^{13}C-NMR spectrum of **2** showed 21 signals, while the DEPT-135 and HSQC experiments confirmed that 14 out of the 21 C-atoms were attached to protons. These signals included those of a furan ring at δ(C) 143.3 (C(15)), 141.5 (C(16)), 124.6 (C(13)), and 110.1 (C(14)), and three carbonyl groups of the ester type at δ(C) 176.3 (C(17)), 172.1 (C(18)), and 172.0 (C(19)). The remaining peaks were due to two Me, four CH_2, and five CH groups and to three quaternary C-atoms. The ^{1}H-NMR spectrum showed characteristic signals of a β-substituted furan at δ(H) 7.58 (br. *s*, H–C(16)), 7.41(*t*, J = 1.5 Hz, H–C(15)), and 6.91 (br. *s*, H–C(14)) which were in accordance with the IR absorption and the ^{13}C-NMR data. Furthermore, two Me signals were observed at δ(H) 3.82 (*s*, MeO) and 1.30 (*s*, Me(20)) as well as three downfield signals at δ(H) 5.30 (*dd*, J = 10.5, 5.5 Hz, H–C(12)), 5.17 (*d*, J = 6.0 Hz, H–C(6)), and 4.94 (br. *t*, J = 4.5 Hz, H–C(2)), corresponding to three OCH groups. The gross structure of **2** was finally established from its 2D-NMR spectra (HSQC, HMBC, NOESY), as shown in *Fig. 1*. Important HMBC correlations were H–C(4) (δ(H) 3.16)/C(3) (δ(C) 30.1), MeO (δ(H) 3.82)/C(18) (δ(C) 172.1), H–C(6) (δ(H) 5.17)/C(17) (δ(C) 176.3), and H–C(12) (δ(H) 5.30)/C(16) (δ(C) 141.5). The C(12) configuration was deduced from comparison of the ^{1}H- and ^{13}C-NMR data with those of related compounds [3][5]. The careful analysis of the NOESY data allowed us to deduce that compound **2** is a stereoisomer of bafoudiosbulbin A. It showed a clear cross-peak H–C(12) (δ(H) 5.30)/Me(20) (δ(H) 1.30). Moreover, the lack of a NOESY correlation Me(20) (δ(H) 1.30)/H–C(10) (δ(H) 2.43) as well as H–C(12) (δ(H) 5.30)/H–C(10) (δ(H) 2.43) indicated their *trans* relationships (*Fig. 1*). Other correlations were H–C(10) (δ(H) 2.43)/H–C(2) (δ(H) 4.94), H–C(10) (δ(H) 2.43)/H–C(4) (δ(H) 3.16), and H–C(4) (δ(H) 3.16)/H–C(6) (δ(H) 5.17). From these data, rings *A* and *B* were assumed to have both boat conformations.

Compound **3** was also isolated as a white gum from CH_2Cl_2/MeOH. It exhibited the $[M+Na]^+$ pseudomolecular ion-peak at *m/z* 439.3699 in the positive HR-FAB-MS, corresponding to the molecular formula $C_{21}H_{20}NaO_9$. The EI-MS did not show the molecular-ion peak but significant peaks at *m/z* 356 ($[M-H-COOMe]^+$) and 312 ($[M-H-COOMe-CO-O]^+$). The peak at *m/z* 81 indicated the presence of a β-substituted furan ring [9]. The IR spectrum displayed absorption bands attributable to a γ-lactone (1774 cm^{-1}), a δ-lactone (1739 cm^{-1}), and a furan moiety (888 cm^{-1}). The ^{1}H- and ^{13}C-NMR data of **3** (*Table*) showed high similarities with those of compound **2**, except for the signals attributable to ring *A*. The type of *A*-ring substitution exhibited by **3** is present in bartemidiolide, a clerodane diterpene from *Baccharis artemisioides* [11]. Further data indicated that **3** and bartemidiolide have the same *A*-ring configuration, assumed to be a boat conformation (*Fig. 2*). Thus bafoudiosbulbin E (**3**) was elucidated as methyl (2β,3α,4α,6β,12*R*)-17,19-dioxo-2,19 : 3,4 : 6,17 : 8,12 : 15,16-pentaepoxycleroda-13(16),14-diene-18-carboxylate[1]).

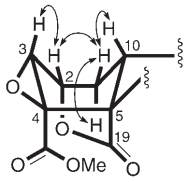


Fig. 2. *COSY Correlations of compound* **3** (Ring *A*)

The ^{13}C-NMR spectrum of **3** displayed the signals of 21 C-atoms, which were fully assigned by HSQC, HMBC, and DEPT-135 experiments. The resonances of three CH groups corresponding to C(15), C(16), and C(14) (δ(C) 143.5, 141.4, and 109.9 resp.) were characteristic of furoclerodanes [12]. Three deshielded quaternary C-atoms of the ester type at δ(C) 175.9, 165.9, and 164.9 were ascribed to C(17), C(18), and C(19), respectively. The remaining peaks were due to two Me groups including one MeO at δ(C) 53.8, three CH_2 groups, five CH sp^3 C-atoms, including four oxygenated ones at δ(C) 74.9, 73.2, 68.7, and 56.2 (corresponding to C(12), C(6), C(2), and C(3), resp.), and five quaternary C-atoms. The ^{1}H-NMR spectrum showed the characteristic signals of a furan ring at δ(H) 7.59 (br. *s*, H–C(16)), 7.42 (br. *d*, J = 1.5 Hz, H–C(15)), and 6.90 (*d*, J = 1.0 Hz, H–C(14)). The 1 H resonance at δ(H) 5.28 (*dd*, J = 10.5, 5.5 Hz, H–C(12)) together with the signals at δ(H) 2.17 (*dd*, J = 11.5, 10.5 Hz, H_α–C(11)) and 2.00 (*dd*, J = 11.5, 5.5 Hz, H_β–C(11)) were consistent with the *ABX* system formed by H–C(12) and CH_2(11). Signals at δ(H) 5.60 (br. *d*, J = 6.0 Hz, H–C(6)) and 5.04 (*ddd*, J = 5.5, 3.5, 3.0 Hz, H–C(2)) revealed that each lactone moiety was linked through a secondary OH group as in compound **2**. To satisfy the twelve degrees of insaturation deduced from the MS of **3**, an epoxy bridge was suggested between C(3) and C(4) in ring *A*, taking into account their chemical shifts (δ(C) 56.2 and 53.2, resp.). The MS further provided evidence of the structure with the characteristic loss of an O-atom for epoxy compounds [13]. The location of this epoxy group was also supported by the ^{1}H,^{1}H-COSY plot which showed a cross-peak H–C(2) (δ(H) 5.04)/H–C(3) (δ(H) 4.22). Many other correlations were also observed (*Fig. 2*). Comparison of ^{1}H- and ^{13}C-NMR data of **2** and **3** showed significant similarities in the chemical shifts of some C-atoms, namely of C(12) ($\Delta\delta$ = 0.2), C(9) ($\Delta\delta$ = 0.1), C(10) ($\Delta\delta$ = 0.2), and C(8) ($\Delta\delta$ = 0.4). The detected small ^{13}C-NMR chemical shift differences between these compounds, together with the ^{1}H,^{1}H-coupling constants observed for H–C(12) and H–C(6) (*Table*) allowed us to conclude that the configurations at the stereogenic centres C(6), C(8), C(9), and C(12) are identical in both compounds. Finally, the configuration of ring *A* was elucidated by using ^{1}H-NMR coupling constants. The epoxy H–C(3) at δ(H) 4.22 (*d*, J = 3.5 Hz) was coupled to the equatorial H–C(2) at δ(H) 5.04 (*ddd*, J = 5.5, 3.5, 3.0 Hz). The J values observed for these two protons are similar to those reported for the same protons in bartemidiolide bearing a similar ring *A* [13].

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Experimental Part

General. Column chromatography (CC): silica gel *60 Merck* (0.040–0.063 mm), gradient elution with the indicated solvent mixtures. TLC: silica gel *60 F_{254}* (*Merck*), visualization under UV light (254 and 365 nm) and by spraying with 50% H_2SO_4 soln. Optical rotation: *Perkin-Elmer 241* polarimeter. IR Spectra: *Shimadzu FT-IR-8400S* spectrometer; in cm^{-1}. ^1H-, ^{13}C-, and 2D-NMR Spectra: *Bruker AM-500* spectrometer; δ in ppm rel. to Me_4Si, J in Hz. EI-MS: *5975-Inert-XL* mass-selective detector; in m/z. FAB-MS and HR-FAB-MS: *Jeol JMS-700* mass spectrometer; in m/z.

Plant Material. The bulbils of *Dioscorea bulbifera* L. var. *sativa* were collected in Bafou village near Dschang (West province of Cameroon) in January 2006. The plant was identified by Dr. *G. Achoundong*, Cameroon National Herbarium, Yaoundé, where a voucher specimen (Ref: 22211/SRF/CAM) was deposited.

Extraction and Isolation. The dried and pulverized bulbils of *Dioscorea bulbifera* L. var. *sativa* (2 kg) were extracted three times (each time for 24 h followed by heating for 20 min) with 95% EtOH. The filtrate obtained was concentrated to yield a dark residue (92 g). Part of this extract (87 g) was suspended in H_2O (300 ml) and extracted with AcOEt. The AcOEt layer was concentrated: 60 g of residue. Part of this residue (55 g) was subjected to CC (SiO_2, hexane/AcOEt 100:0 → 30:70, then AcOEt/MeOH 100:0 → 50:50): *Fractions I–VII*. *Fr. III* (2.4 g) was subjected to CC (SiO_2, CH_2Cl_2/MeOH 98:2): **3** (7 mg). From *Fr. IV* (8.5 g), 6′-stearoyl-3-*O*-*β*-D-glucopyranosyl-*β*-sitosterol (80 mg) was obtained after further recrystallization in MeOH. The recrystallization of *Fr. V* (20 g) in MeOH yielded bafoudiosbulbin A (140 mg). The filtrates from *Fr. V* and *Fr. IV* were combined mainly on the basis of TLC patterns and were repeatedly subjected to CC (SiO_2, CH_2Cl_2/MeOH 98:2): bafoudiosbulbin B (125 mg), **2** (30 mg), and a mixture of three compounds. This mixture was further repeatedly subjected to CC (SiO_2, CH_2Cl_2/MeOH 95:5): **1** (35 mg). *Fr. VI* (2.8 g) mainly yielded 3-*O*-*β*-D-glucopyranosyl-*β*-sitosterol (52 mg) upon recrystallization in MeOH.

Bafoudiosbulbin C (= *Methyl (2β,8α,12*S*)-17-Oxo-2,19:8,19:12,17:15,16-Tetraepoxycleroda-3,13(16),14-triene-18-carboxylate* = *(2*S*,4a*R*,5*S*,5a*S*,7*S*,9a*S*,10a*R*)-7-(Furan-3-yl)-5,5a,6,7-tetrahydro-5a-methyl-9-oxo-9*H*,10a*H*-4a,9a-ethano-2,5-methano-2*H*-dipyrano[2,3-*b*:4′,3′-*e*]pyran-4-carboxylic Acid Methyl Ester*; **1**): White gum (CH_2Cl_2/MeOH). $[\alpha]_D^{21} = +56.2$ ($c = 0.8$, CH_2Cl_2). IR (KBr): 1716 (δ-lactone), 1654 (α,β-unsaturated ester), 1506, 1242, 1017, 951, 877 (β-substituted furan). ^1H- and ^{13}C-NMR: *Table*. EI-MS: 358 ($[M - CO]^+$), 330 ($[M - 2\ CO]^+$), 312 ($[M - 2\ CO - H_2O]^+$). HR-FAB-MS: 409.3879 ($[M + Na]^+$, $C_{21}H_{22}O_7Na^+$; calc. 409.3875).

Bafoudiosbulbin D (= *Methyl (2β,6β,12*R*)-17,19-Dioxo-2,19:6,17:8,12:15,16-Tetraepoxycleroda-13(16),14-diene-18-carboxylate* = *(2*R*,3a*R*,6*R*,6a*R*,9*S*,10a*S*,10b*S*,12*S*)-2-(Furan-3-yl)hexahydro-10b-methyl-4,7-dioxo-4*H*,7*H*-6a,9-ethano-3a,6-methano-6*H*-furo[2,3-*c*]pyrano[4,3-*e*]oxepin-12-carboxylic Acid Methyl Ester*; **2**): White gum (CH_2Cl_2/MeOH). $[\alpha]_D^{21} = -20.4$ ($c = 0.9$, MeOH). IR (KBr): 1786 (γ-lactone), 1751 (δ-lactone), 869 (furan ring). ^1H- and ^{13}C-NMR: *Table*. FAB-MS: 425 ($[M + Na]^+$), 375 ($[M + H - CO]^+$). HR-FAB-MS: 425.3882 ($[M + Na]^+$, $C_{21}H_{22}O_8Na^+$; calc. 425.3865).

Bafoudiosbulbin E (= *Methyl (2β,3α,4α,6β,12*R*)-17,19-Dioxo-2,19:3,4:6,17:8,12:15,16-pentaepoxycleroda-13(16),14-diene-18-carboxylate* = *(1a*S*,1b*S*,2*R*,4a*R*,6*R*,7a*S*,7b*S*,9*S*,9a*R*)-6-(Furan-3-yl)hexahydro-7a-methyl-4,11-dioxo-2*H*,4*H*-9,1b-(epoxymethano)-2,4a-methanofuro[2,3-*d*]oxireno[*i*][2]benzoxepin-1a(6*H*)-carboxylic Acid Methyl Ester*; **3**): White gum (CH_2Cl_2/MeOH). $[\alpha]_D^{21} = +35.0$ ($c = 0.7$, CH_2Cl_2). IR (KBr): 1774 (γ-lactone), 1739 (δ-lactone), 888 (furan ring). ^1H- and ^{13}C-NMR: *Table*. EI-MS: 356 ($[M - H - COOMe]^+$), 312 ($[M - H - COOMe - CO - O]^+$). HR-FAB-MS: 439.3699 ($[M + Na]^+$, $C_{21}H_{20}O_9Na^+$; calc. 439.3697).

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