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JAMAICOLIDES A–D, FOUR SESQUITERPENE LACTONES FROM *CALEA JAMAICENSIS*

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Key Word Index—*Calea jamaicensis*; Asteraceae; Heliantheae; sesquiterpene lactones; guaianolides; heliangolide; germacranolide; flavonoids; chromene.

Abstract—Chemical analysis of *Calea jamaicensis*, the type species for the genus *Calea*, yielded in addition to a chromene and two flavonoids, four new sesquiterpene lactones, jamaicolides A–D, which include two guaianolides, a heliangolide, and a 12,8α-germacranolide. The structures of the new compounds were established by spectroscopic methods.

INTRODUCTION

In continuation of our chemical studies of the genus *Calea*, we have analysed *Calea jamaicencis* from Jamaica, which represents the type species for the genus *Calea*. Besides prunichromene B (**1**), a chromene previously isolated from *C. prunifolia* [1], we also isolated the known flavones *O*-methylacacetin (**2**) and acacetin (**3**) [2], and four new sesquiterpene lactones. The new lactones correspond to two guaianolides, jamaicolide A (**4a**) and B (**5**), the heliangolide jamaicolide C (**7a**), and a 12,8α-lactonic germacranolide, jamaicolide D (**8**). The known compounds were identified by spectral comparison with authentic samples, and the structures of the new compounds were established by spectroscopic methods, mainly ^{1}H NMR and mass spectrometry.

RESULTS AND DISCUSSION

Jamaicolide A (**4a**), $C_{22}H_{26}O_8$, is a gum with an ^{1}H NMR spectrum showing typical signals for an α-methylene-γ-lactone moiety [two one-proton doublets at δ6.31 (H-13a) and 5.65 (H-13b) coupled with a one-proton multiplet at δ3.63 (H-7)]. A strong IR absorption at 1755 cm^{-1} corroborated the presence of a γ-lactone. Other IR bands showed the presence of hydroxyl(s) (3360 cm^{-1}), a saturated ester (1730 cm^{-1}), an unsaturated ester (1710 cm^{-1}), and double bonds (1645 cm^{-1}). The ester side chain was shown to be a 4-acetoxyangelate group [3] based on characteristic ^{1}H NMR signals together with strong mass spectral peaks at *m/z* 99 [A – A^3], 82 [A^1 – A^3] and 43 [A^4]. These assignments were confirmed by spin decoupling experiments of the side chain signals (Table 1). Furthermore, the assignment of all skeletal ^{1}H NMR signals of compound **4a** were deduced from detailed double irradiation experiments in $CDCl_3$ and benzene-d_6 (Table 1). Comparison of the ^{1}H NMR spectrum of **4a** with that of subcordatolide A (**4b**) from *Calea subcordata* [4] showed, with the exception of the side chain signals, absorptions which were nearly superimposable. Based on this close similarity of the spectra, we conclude that jamaicolide A (**4a**) represents a guaianolide with configurations at C-1, C-4, C-5, C-6, C-7 and C-8 as in subcordatolide A (**4b**). Therefore, we propose a stereostructure for jamaicolide A as shown in **4a**.

Jamaicolide B (**5**), $C_{22}H_{26}O_9$, exhibited in the ^{1}H NMR spectrum two one-proton doublets at δ6.26 (H-13a) and 5.46 (H-13b), and a one-proton multiplet at δ3.77 (H-7). These signals and a strong IR absorption at 1760 cm^{-1}, indicated an α-methylene-γ-lactone in compound **5**. Further IR absorptions at 1740, 1705, 1650 and 3490 cm^{-1} suggested the presence of saturated and unsaturated ester side chains, double bond(s) and hydroxyl(s), respectively. As outlined for compound **4a**, the ester side chain was identified as a 4-acetyloxyangelate group on the basis of the diagnostic ^{1}H NMR signals, and characteristic mass spectral peaks. A distinct feature in the mass spectrum of **5** was the presence of only very weak high mass peaks and a base peak at *m/z* 111, which corresponds to $C_6H_7O_2^+$ (**C**). The formation of this ion can be accounted for by fragmentation of a diepoxycyclopentane moiety in **5**, suggesting a structure similar to either canin [5] and artecanin [6].

Exhaustive spin decoupling experiments allowed the assignment of all signals (Table 1). The chemical shift and splitting patterns of H-5 and H-6, together with the absence of an angular methyl signal indicated a guaianolide-type skeleton for **5**. The coupling constants $J_{5,6} = J_{6,7} = 11.2$ Hz suggested an antiperiplanar arrangement of H-5, H-6 and H-7, and therefore an α-orientation for H-5 and a β-orientation for H-6. On the basis of chemical shifts arguments, the 4-acetoxyangelate side chain had to be attached to C-8, and the small coupling constant ($J_{7,8} = 3.0$ Hz) indicated a β-orientation of the ester group at C-8. The chemical shifts of the three-proton methyl signals at δ1.12 (H-14) and 1.58 (H-15) were in agreement with the presence of a hydroxyl group at C-10 and an epoxy function at C-4, respectively. The presence of two broadened one-proton singlets at δ3.60 (H-2) and 3.29 (H-3) suggested the attachment of oxygens at C-2 and C-3 as in canin [5] and

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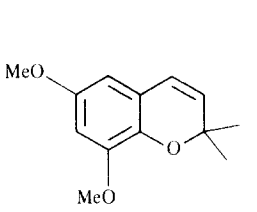

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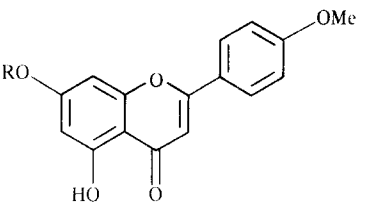
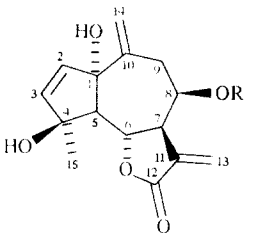
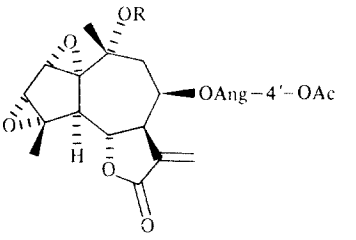


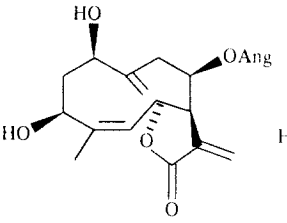
2 R = Me
3 R = H

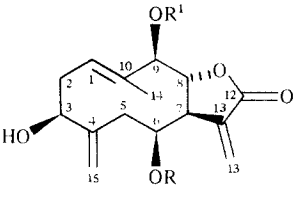


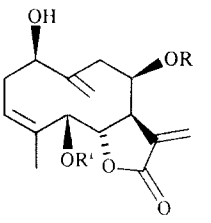
4a R = Ang–4'–OAc
4b R = iso-butyrate



5 R = H
6 R = Cl_3C—C(=O)—NH—C(=O)—



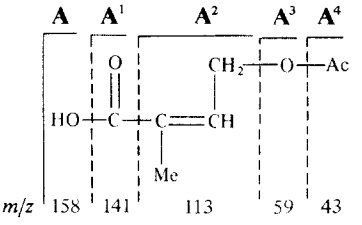


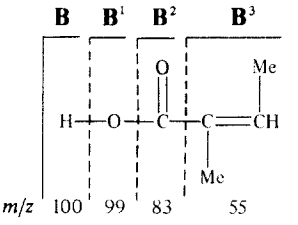


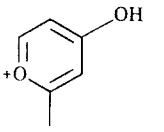
7a R = angelate
7b R = tiglate

8a R^1 = Ang, R = Ac or reverse

8b







C m/z 111

artecanin [6]. The small coupling constant ($J_{2,3} \sim 1$ Hz) indicated a *cis*-arrangement of these protons, and from the chemical shift of H-5 (δ2.86), which is comparable with the one of artecanin [6] and shifted towards lower fields with respect to the H-5 of canin [5], we concluded that the 2,3-epoxide group had to be α-oriented as in artecanin [6]. Comparison of the chemical shift of H-6 in compound **5** with the one in artecanin [6], also suggested an α-orientation for the hydroxyl group at C-10, since a β-hydroxy group would cause deshielding of H-6. Further corroboration of this conclusion was obtained by *in situ* acylation of **5** with trichloroacetyl isocyanate [7]. The ^{1}H NMR spectrum of the trichloroacetyl carbamate derivative (**6**) of jamaicolide B (**5**) showed one NH signal at δ8.53 providing further evidence for the presence of one hydroxyl group in compound **5**. The ^{1}H NMR signals of **6** were assigned by double irradiation experiments as shown in Table 1. The paramagnetic acylation shift of the C-10 methyl group signals (H-14) from δ1.13 in **5** to 1.41 in **6** ($\Delta\delta = 0.28$) indicated the presence of a tertiary hydroxyl group at C-10 [7]. The absence of a paramagnetic shift of H-6 in **6**, when compared with the H-6 of **5**, corroborated the stereochemistry at C-10 with an α-oriented hydroxyl group. On the basis of the above spectroscopic evidence we propose for jamaicolide B a stereo-structure as shown in **5**.

Table 1. ^{1}H NMR spectral data* of compounds **4a**, **5**, **6** and **7a** (200 MHz in $CDCl_3$ [C_6D_6])

	4a	**5**	**6**	**7a**
H-1	—	—	—	4.09 *dd* (11.0; 3.6)
H-2a	5.63 [5.34] *d* (6.7)	3.60 *br*	3.76 *br*	2.38 *ddd* (11.0; 11.0; 2.5)
H-2b				2.05–2.10
H-3	5.99 [5.80] *d* (6.7)	3.29 *br*	3.37 *br*	4.51 *dd* (6.8; 2.5)
H-5	2.51 [2.42] *d* (11.0)	2.86 *d* (11.2)	2.35 *d*	5.31 *br dd* (9.8; 1.8)
H-6	4.68 [4.70] *dd* (11.0; 9.2)	4.68 *t* (11.2)	4.71 *t*	6.37 *dd* (9.8; 2.5)
H-7	3.63 [3.32] *m*	3.77 *dq* (11.2; 3.0)	3.39 *dq*	3.13 *m*
H-8	5.67 [5.45] *m*	5.65 *dt* (9.0; 3.0)	5.70 *dt*	5.22 *m*
H-9a	3.23 [3.10] *dd* (15.0; 4.0)	2.38 *dd* (16.0; 9.0)	2.81 *dd*	2.92 *dd* (15.0; 7.5)
H-9b	2.45 [2.31] *dd* (15.0; 2.5)	1.86 *dd* (16.0; 3.0)	1.99 *dd*	2.58 *dd* (15.0; 4.0)
H-13a	6.31 [6.21] *d* (3.5)	6.26 *d* (3.0)	6.42 *d*	6.34 *d* (2.5)
H-13b	5.65 [5.23] *d* (3.0)	5.46 *d* (3.0)	5.52 *d*	5.77 *d* (2.0)
H-14a	5.64 *s*	1.13 *s* (Me)	1.41 *s* (Me)	5.51 *br s*
	[4.68] *br*			
H-14b	5.61 *s*			5.12 br s
H-15(Me)	1.37 [1.34] *s*	1.58 *s*	1.57 *s*	1.77 *d* (1.8)
OR	6.03 [5.77] *tq* (5.8; 1.8)	6.02 *tq* (6.0; 2.0)	6.06 *tq*	6.11 *qq* (7.0; 1.8)
	4.94 [5.07] *br dd* (5.8; 1.8)	4.99 *dq* (6.0; 2.0)	4.99 *dq*	1.96 *dq* (7.0; 1.8)
	1.85 [1.61] *s* (1.8)	1.90 *br d* (2.0)	1.91 *brd*	1.81 *d* (1.8)
OAc	2.07 [1.66] *s*	2.08 *s*	2.08 *s*	—
NH	—	—	8.53 *s*	—

*Spectra were run at ambient temperature and TMS was used as internal standard. Chemical shifts are recorded in ppm relative to TMS. Coupling constants (J) are given in parentheses.

Jamaicolide C (**7a**), $C_{20}H_{26}O_6$, was a gum. Its IR bands indicated the presence of hydroxyl group(s) (3500 and 3405 cm^{-1}), a γ-lactone (1755 cm^{-1}), an unsaturated ester (1710 cm^{-1}) and double bond(s) (1650 cm^{-1}). The presence of an α-methylene-γ-lactone in **7a** was corroborated by diagnostic ^{1}H NMR signals (Table 1). The unsaturated ester side chain was assigned an angelate group on the basis of typical ^{1}H NMR signals (Table 1), together with strong mass spectral fragments at m/z 83 [$\mathbf{B}^2$] and 55 [$\mathbf{B}^3$]. Assignments of all the ^{1}H NMR signals were deduced from double irradiation experiments, the results being summarized in Table 1.

Comparison of the ^{1}H NMR spectrum of **7a** with the data of calbertolide C (**7b**), a lactone previously isolated from *Calea berteriana* [8], showed significant differences only for the signals corresponding to the side chain. We therefore conclude that jamaicolide C has the same configurations at C-1, C-3, C-6, C-7 and C-8 as calbertolide C (**7b**) [8], and we propose stereo-structure **7a** for this new lactone.

Jamaicolide D (**8a**), $C_{22}H_{28}O_7$, was a gum, the IR spectrum of which exhibited absorptions at 3480 (broad, OH), 1765 (γ-lactone), 1730 (saturated ester), 1710 (unsaturated ester) and 1650 cm^{-1} (double bonds). Portions of the ^{1}H NMR spectrum of the new compound showed broad and uncharacteristic signals when run at room temperature, suggesting an equilibrium between conformational isomers which is typical for certain germacranolide rings [9]. Two one-proton doublets at δ6.24 (H-13a) and 5.48 (H-13b), which collapsed to singlets upon irradiation of a broad signal at δ3.46 (H-7) confirmed the presence of an α-methylene-γ-lactone moiety. An IR band at 1730 cm^{-1}, a three-proton singlet at δ2.08 and a strong mass spectral peak at m/z 43 indicated an acetate and the presence of an angelate group was derived from typical ^{1}H NMR signals (a broadened one-proton quartet at δ6.13, a three-proton doublet of quartets at δ1.97, and a three-proton broad singlet at δ1.84) and diagnostic mass spectral fragments at m/z 83 [$\mathbf{B}^2$] and 55 [$\mathbf{B}^3$].

Exhaustive spin decoupling experiments in deuterobenzene at 107° and in $CDCl_3$ at 67° and −40° allowed the assignment of all skeletal proton signals (Table 2). The numbering shown in structure **8a** was used for the following discussion. The ^{1}H NMR spectrum of jamaicolide D in $CDCl_3$ at 67° exhibited, besides the signals corresponding to the side chains, two sets of vinylic methylene proton signals (two doublets at δ6.24 and 5.48 due to H-13a and 13b and two broadened one-proton singlets at δ5.34 and 4.93 caused by exocyclic methylene protons at C-4 or C-10). Besides a vinylic methyl signal (δ1.87), allylically coupled to an olefinic proton (δ5.17), the spectrum showed one proton due to a carbon bearing a hydroxyl group (δ4.30), two protons on carbons bearing the ester side chains (δ5.91 and 5.45), and the lactonic signal at δ4.97. Since the proton signals were strongly broadened at room temperature, and the chemical shifts did not change significantly when the spectra were run at elevated temperature (Table 2), the ^{1}H NMR spectral discussion below refers to data obtained at high temperature (107°) in deuterobenzene. Double irradiation of the multiplet at δ2.92 (H-7) collapsed the doublets at δ6.17 (H-13a) and 5.23 (H-13b), simplified the multiplet at δ5.78 to a doublet of doublets, and reduced the triplet at δ4.87 to a doublet. On the basis of chemical shift arguments, the triplet at δ4.87 was assigned a lactonic proton, and the multiplet at 5.78 to a proton on a carbon bearing an ester side chain. The appearance of broad ^{1}H NMR signals at ambient temperature and their drastic sharpening at higher temperature suggested that jamaicolide D possibly represents a 12,8-germacranolide [10–14]. Using struc-

Table 2. ^{1}H NMR spectral data* for jamaicolide D (**8a**) at 200 MHz

	$CDCl_3$, −40°	$CDCl_3$, 67°	C_6D_6, 107°
H-1	5.05 *br d* (9.0)	5.17 *dd* (9.0; 4.5)	5.11 *dd* (9.0; 4.5)
H-2a,b	1.90–2.10†	1.85–2.10†	1.87–2.10†
H-3	4.38 *br t* (7.5)	4.30 *br t* (7.5)	3.85 *br t* (7.5)
H-5a	2.66 *br dd* (16; 5)	2.63 *br d*	2.39 *br dd* (16.0; 5.5)
H-5b	2.05–2.20†	1.90–2.10†	2.01 *br dd* (16.0; 10.0)
H-6	5.92 *br t* (7)	5.91 *br m*	5.78 *m*
H-7	3.48 *br m*	3.38 *br m*	2.92 *m*
H-8	4.98 *t* (9.5)	4.97 *t* (9.5)	4.87 *t* (9.5)
H-9	5.41 *d* (9.5)	5.45 *d* (9.5)	5.15 *d* (9.5)
H-13a	6.22 *d* (3.0)	6.24 *d* (3.0)	6.17 *d* (3.0)
H-13b	5.44 *d* (3.0)	5.48 *d* (3.0)	5.23 *d* (3.0)
H-14	1.77 *br*	1.87 *br*	1.61 *br s*
H-15a	5.34 *br s*	5.34 *br s*	4.84 *br s*
H-15b	4.90 *br s*	4.93 *br s*	4.51 *br s*
OAng	6.12 *br q* (7.0)	6.10 *qq* (7.0; 1.8)	5.74 *qq* (7.0; 1.8)
	1.91 *br dq* (7.0)	1.95 *dq* (7.0; 1.8)	1.85 *dq* (7.0; 1.8)
	1.88 *br*	1.84 *br*	1.72 *br*
OAc	2.07 *s*	2.06 *s*	1.71 *s*

*Chemical shifts are recorded in ppm relative to TMS. Figures in parentheses are coupling constants or line separations in Hz.

†Obscured by other signals.

ture **8a** as a tentative working model, we assigned the triplet at δ4.87 to the lactonic H-8 and the multiplet at δ5.78 to H-6. The coupling constant $J_{7,8} = 9.5$ Hz indicated an antiperiplanar arrangement of H-7 and H-8, suggesting a 12,8α-lactone. Spin decoupling of the lactonic proton (H-8) collapsed the broad H-7 multiplet to a narrow multiplet, and reduced the doublet at δ5.15 (δ5.45 in $CDCl_3$) to a singlet, which on the basis of chemical shift arguments should correspond to the proton on the carbon bearing the second ester side chain (H-9). The coupling constant $J_{8,9} = 9.5$ Hz indicated an antiperiplanar arrangement for H-8 and H-9 and therefore a β-orientation for the ester side chain at C-9. Spin decoupling of H-6 sharpened the H-7 multiplet at δ2.92, and collapsed the two broadened doublet of doublets at δ2.39 (H-5a) and δ2.01 (H-5b) to broad doublets. In return, double irradiation of either of the C-5 protons, besides reducing the H-6 multiplet at δ5.78, sharpened the broadened singlets at δ4.84 (H-15a) and 4.51 (H-15b), while irradiation of either of the two C-15 protons sharpened both broadened H-5 doublet of doublets at δ5.11 representing an olefinic relationship of the C-5 protons and the C-15 methylene protons. The remaining downfield signals to be assigned were a broad triplet at δ3.85, which corresponds to a proton on a carbon bearing a hydroxyl group, and a doublet of doublets at δ5.15 representing an olefinic proton. Spin decoupling at δ3.85 changed the region between δ1.9–2.1, and sharpened both broad H-15 singlets at δ4.84 and 4.51, showing the allylic position of this proton with the C-15 protons, identifying it as H-3. Spin decoupling at δ1.94 (H-2's) collapsed the H-3 triplet at δ3.85 to a broadened singlet, and reduced the doublet of doublets at δ5.11 to a broad singlet. On this basis, the olefinic doublet of doublets at δ5.11 was assigned H-1. Further corroboration of its olefinic character was obtained by double irradiation: besides the changes in the δ1.9–2.1 region, it also sharpened the broadened olefinic methyl signal at δ1.61 (H-14).

At ambient temperature in $CDCl_3$, portions of the jamaicolide D spectrum exhibited strongly broadened signals which sharpened when the spectrum was run at higher temperature (67°) or at −40°. At low temperature (−40°) only one set of signals could be detected, suggesting that one major conformation (> 95%) must be present in the conformational equilibrium mixture. The fact that only proton signals of the lower half (H-3, H-5a,b, H-6 and H-7) gave strongly broadened signals at ambient temperature suggested conformational changes in this region of the molecule, possibly involving rotation of the C-4 methylene group between the α- and β-face of the medium ring.

Based on the above ^{1}H NMR spectral evidence structures **8a** or **8b** could be proposed for jamaicolide D, exclusive of stereochemistry. Configurational and conformational assignments were performed by the extensive use of NOE difference spectroscopy in $CDCl_3$ and benzene-d_6, using the numbering of **8a** for the following discussion. The configuration of the endocyclic medium ring double bond was assigned as *trans* (*E*) on the basis of the absence of an NOE-effect between H-1 and the C-10 methyl group. A clear NOE was exhibited between the C-10 methyl group and the lactonic H-8 which must be β-oriented, since $J_{7,8} = 9.5$ Hz suggests an antiperiplanar orientation of the two protons, assuming an H-7α as in all lactones from higher plants. Interaction between H-9 and H-7 and H-1 and H-9 supports the configurational assignment (*E*) of the 1(10)-double bond and also suggests an α-configuration of H-9. An NOE between H-1 and H-3 and an interaction between H-3 and the olefinic H-15a allowed the stereochemical assignment of H-3 as α and an orientation of the exocyclic methylene group at C-4 below the plane of the medium ring. Finally, strong interaction between H-6 and H-13b as well as H-15b suggested an α-orientation of H-6 which was supported by the absence of an NOE between H-6 and H-8. An alternate structure with the C-4 methylene group above the plane of the

medium ring and H-3 and H-6 being β-oriented would have not allowed interaction between H-6 and H-13b. Therefore, we propose the configurational structure **8a** for jamaicolide D and a conformation in which the C-10 methyl group is oriented above and the C-15 methylene below the plane of the medium ring. The attachments of the side chains in **8a** remain open.

EXPERIMENTAL

Calea jamaicensis L. was collected on 4 December 1979 in St. Thomas Parish, Jamaica, 4 miles east of Kingston on St. Thomas Road (L. E. Urbatsch, No. 3401, voucher deposited at L.S.U., Baton Rouge, U.S.A.), and recollected for the present chemical study in January 1984 (J. D. Connolly, *S.n.*). The air-dried plant material (1.48 kg) was extracted with CH_2Cl_2 (3 l.) providing 50.7 g of a gummy material. Treatment of 20 g of this gummy residue with $Pb(OAc)_2$ as described before [15], yielded 6.4 g of the crude terpenoid extract. CC of the crude syrup on silica gel with $CHCl_3$–Me_2CO mixtures of increasing polarity yielded 95 fractions of 175 ml each.

Fractions 1–2 (90 mg) were purified by prep. TLC on silica gel with Et_2O–hexane (1:1), giving 31 mg of prunichromene B (**1**). Fractions 3–5 (190 mg) yielded 140 mg of *O*-methylacacetin (**2**), while fractions 15–18 (102 mg) gave 96 mg of acacetin (**3**) as a yellow powder. Fractions 19–20 (52 mg) were purified by repeated prep. TLC on silica gel with $CHCl_3$–Me_2CO (9:1) giving 17 mg of jamaicolide D (**8a**). Fraction 23 (38 mg) was rechromatographed on silica gel with $CHCl_3$–Me_2CO (9:1) yielding 9 mg of jamaicolide B (**5**), and fractions 31–40 (380 mg) provided 41 mg of jamaicolide C (**7a**). Fractions 41–60 (710 mg) yielded 63 mg of jamaicolide A (**4a**) after repeated purification by prep. TLC on silica gel with $CHCl_3$–Me_2CO (85:15).

Jamaicolide A (**4a**). $C_{22}H_{26}O_8$, gum; UV λ^{MeOH} nm: end absorption; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3360 (br, OH), 1755 (γ-lactone), 1730 (satd ester), 1710 (unsatd ester), 1645 (double bond); EIMS (probe) *m/z* (rel. int.): 403 $[M-Me]^+$ (5.6), 376 $[M-CH_2CO]^+$ (0.3), 358 $[M-HOAc]^+$ (0.6), 343 $[M-HOAc-Me]^+$ (6.3), 260 $[M-A]^+$, (5.5), 245 $[M-A-Me]^+$ (6.5), 243 $[M-A-H-H_2O]^+$ (18.4), 242 $[M-A-H_2O]^+$ (28.8), 227 $[M-A-Me-H_2O]^+$ (8.1), 225 $[M-A-H-2H_2O]^+$ (8.1), 224 $[M-A-2H_2O]^+$ (13.6), 99 $[A-A^3]^+$ (100.0), 82 $[A^1-A^3]^+$ (42.8), 43 $[A^4]^+$ (38.1).

Jamaicolide B (**5**). $C_{22}H_{26}O_9$, gum; UV λ^{MeOH} nm: end absorption; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3490 (br, OH), 1760 (γ-lactone), 1740 (acetate), 1705 (unsatd ester), 1650 (double bond); EIMS (probe) *m/z* (rel. int.): 392 $[M-CH_2CO]^+$ (0.3), 375 $[M-OAc]^+$ (0.1), 293 $[M-A^1]^+$ (0.1), 276 $[M-A]^+$ (0.2), 259 $[M-A-H-H_2O]^+$ (0.9), 258 $[M-A-H_2O]^+$ (0.2), 231 $[M-A-H-H_2O-CO]^+$ (0.7), 230 $[M-A-H_2O-CO]^+$ (0.3), 111 $[C_6H_7O_2]^+$ (100.0), 99 $[A-A^3]^+$ (20.8), 82 $[A^1-A^3]^+$ (9.7), 43 $[A^4]^+$ (11.5).

absorption; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 3405 (OH), 1755 (γ-lactone), 1710 (unsatd ester), 1650 (double bond); EIMS (probe) *m/z* (rel. int.): 344 $[M-H_2O]^+$ (0.3), 263 $[M-B^1]^+$ (2.5), 262 $[M-B]^+$ (1.2), 245 $[M-B^1-H_2O]^+$ (1.8), 244 $[M-B-H_2O]^+$ (2.1), 227 $[M-B^1-2H_2O]^+$ (2.3), 226 $[M-B-2H_2O]^+$ (1.1), 217 $[M-B^1-H_2O-CO]^+$ (3.2), 216 $[M-B-H_2O-CO]^+$ (2.9), 199 $[M-B^1-2H_2O]^+$ (4.4), 198 $[M-B-2H_2O-CO]^+$ (1.4), 83 $[B^2]^+$ (100.0), 55 $[B^3]^+$ (19.8).

Jamaicolide D (**8a**). $C_{22}H_{28}O_7$, gum; UV λ^{MeOH} nm; end absorption; IR $\nu_{max}^{CDCl_3}$ cm^{-1}: 3480 (br, OH), 1765 (γ-lactone), 1715 (unsatd ester), 1650 (double bonds); EIMS (probe) *m/z* (rel. int.): 362 $[M-CH_2CO]^+$ (0.3), 344 $[M-HOAc]^+$ (0.2), 304 $[M-B]^+$ (0.2), 286 $[M-B-H_2O]^+$ (0.1), 262 $[M-CH_2CO-B]^+$ (0.7), 244 $[M-HOAc-B]^+$ (1.8), 216 $[M-HOAc-B-CO]^+$ (1.2), 83 $[B^2]^+$ (100.0), 55 $[B^3]^+$ (56.9), 43 $[Ac]^+$ (54.0).

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