New Isomalabaricane Derivatives from a New Species of *Jaspis* Sponge Collected at the Vanuatu Islands

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Six new cytotoxic isomalabaricane-type triterpenoids and nortriterpenoids with a 3α-acetoxy group were isolated, along with the known globostellatic acids B (**1**) and C (**2**), from the marine sponge *Jaspis* sp. collected at Vanuatu Island. The structures were determined by 2D NMR data and by comparison with spectral data of known related compounds.

Although sponges represent a remarkable source of new sesquiterpenes, diterpenes, and sesterterpenes, only few reports of triterpene derivatives from sponges have appeared in the literature. Among these, isomalabaricane triterpenes appear to be confined to sponges belonging to the genera *Jaspis*[1−3] and *Stelletta*[4−8] (order Choristidae). Significant examples are jaspiferals A−G from the Okinawan marine sponge *J. stellifera*[3] and the globostellatic acids A−D from *S. globostellata*.[6]

During our continuing study on marine sponges collected at the Vanuatu Islands and, in particular, on sponges of the genus *Jaspis*,[9,10] we were intrigued by a sponge whose taxonomic classification was not straightforward. This sponge showed spiculation characteristic of a *Jaspis* sponge but with the growth form of a *Geodia* sponge. Whereas the morphological analysis of this sponge did not allow its unambiguous classification, the chemical analysis indicated that our sponge represents a new *Jaspis* species restricted to the Western Pacific. In fact, the chemical investigation of the sponge extracts resulted in the isolation of known globostellatic acids B and C,[6] together with a new isomalabaricane triterpenoid and five new isomalabaricane nortriterpenes as their methyl ester derivatives **1**−**8** (Chart 1).

Results and Discussion

Kupchan solvent partitioning[10] of the methanolic extract afforded four extracts of increasing polarity (*n*-hexane, CCl_4, $CHCl_3$, and butanol). The more cytotoxic $CHCl_3$ extract (IC_{50} 5.2 μg/mL) was fractionated by SiO_2 flash chromatography (0−10% MeOH/CH_2Cl_2), and the intensely yellow fractions were treated with diazomethane. The separation of these methylated fractions by normal-phase HPLC afforded the methyl esters of known globostellatic acids B (**1**) and C (**2**), and of new isomalabaricane derivatives globostellatic acid E (**3**), 3-*O*-acetyljaspiferal B (**4**), 3-*O*-acetyljaspiferal D (**5**), 3-*O*-acetyljaspiferal G (**6**), and the dimethyl esters of jaspiferoic acids A (**7**) and B (**8**).

NMR data of **1** and **2** were superimposable with those reported by the Fusetani group for the methyl esters of globostellatic acids B and C.[6] In the original paper, a 13-*Z* geometry was suggested for these compounds on the basis of a NOESY cross-peak between 28-CH_3 and 26-CH_3. However, in the ROESY spectrum performed on our sample, the above cross-peak was absent, whereas a correlation between H-15/CH_3-26 was observed. This indicated a 13-*E* geometry. This alternative stereochemistry was also supported by NMR data; in fact, all the ^{1}H and ^{13}C NMR data for the side chain nuclei were in agreement with a 13-*E* stereochemistry, according to the values reported for stelleferins A−F[2] and jaspiferals A−G.[3] It should be noted that all the isomalabaricane-type terpenoids readily undergo a photoisomerization of the side chain double bonds during the isolation and characterization steps. This isomerization mainly occurs at the C-13 double bond. All compounds described in this paper were isolated as geometrical pure isomers (13-*E* configuration), but some isomerization was observed during storage.

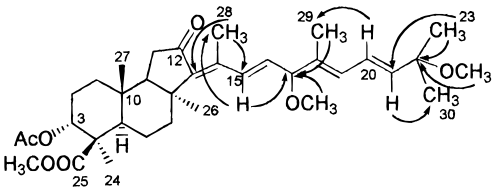

Figure 1. Key HMBC of globostellatic acid E methyl ester (**3**).

The ^{1}H and ^{13}C NMR spectra of globostellatic acid E methyl ester (**3**) [*m*/*z* 584, EIMS] indicated that this compound shared the same isomalabaricane tricyclic portion of globostellatic acid derivatives, while significant differences were observed for all nuclei belonging to the polyene side chain. The conjugated system in **3** was shorter than in globostellatic acids B and C as revealed by UV data [λ_{max} 235 and 340 nm]. Analysis of the ^{1}H−^{1}H COSY of **3** showed the connectivities from H-15 to H-17 and from H-19 to H-21. Linkage of the nonprotonated olefinic carbon C-18 to C-19 followed from the long-range COSY between the allylic methyl protons at δ_H 1.70 (H-29) and the olefinic proton at δ_H 6.11 (H-19). A methoxy group was placed at C-17 on the basis of HMBC correlations between the methoxy protons at δ_H 3.30 and C-17 at δ_C 86.7. A second methoxy group, apparent from the ^{1}H NMR spectrum (δ_H 3.16, s), was placed at the dimethyl-bearing oxygenated quaternary carbon (C-22) on the basis of the key HMBC correlations OCH_3/C-22, H-23/C-22, H-23/C-21. The complete gross structure of the polyene chain of globostellatic acid E (**3**) was inferred by key HMBC correlations depicted in Figure 1.

3-*O*-Acetyljaspiferal B methyl ester (**4**) showed the molecular ion in the EIMS at *m*/*z* 496. The molecular formula $C_{30}H_{40}O_6$ was established by HREIMS (*m*/*z* 496.2856, Δ 3.1 mmu). The UV absorption at λ_{max} 268 (log

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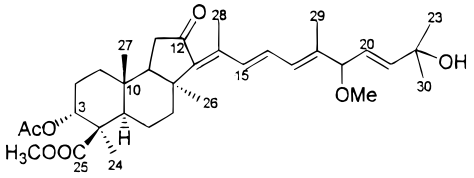
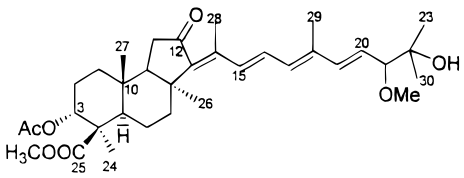
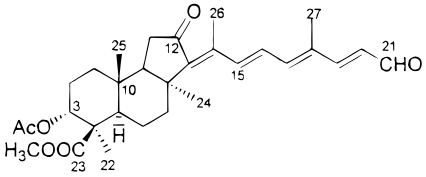
Chart 1



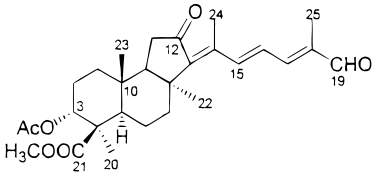
Globostellatic acid B methyl ester (**1**)



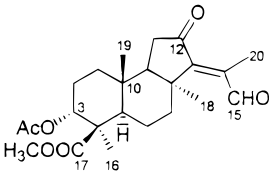
Globostellatic acid C methyl ester (**2**)



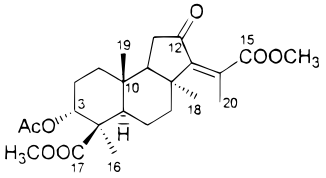
3-O-acetyl-Jaspiferal B methyl ester (**4**)



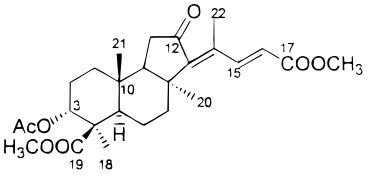
3-O-acetyl-Jaspiferal D methyl ester (**5**)



3-O-acetyl-Jaspiferal G methyl ester (**6**)



Jaspiferoic acid A dimethyl ester (**7**)



Jaspiferoic acid B dimethyl ester (**8**)

ϵ 3.1) and 363 (log ϵ 3.8) was indicative of the presence of a conjugated polyene chromophore. A detailed analysis of NMR data, including COSY and HMBC spectra, clearly indicated a close analogy with jaspiferal B.[3] In the ^{1}H NMR spectrum the only significant differences between the two compounds were the absence of the signal at δ_H 4.07, assigned to the hydroxymethine at C-3 in jaspiferal B, with its replacement by a broad singlet a δ_H 5.33, and the presence of an additional methyl singlet a δ_H 2.09. The HMBC spectrum showed connectivity from the methyl proton signal at δ_H 2.09 to an ester carbonyl at δ_C 172.0, which was found to be coupled to the oxymethine signal at δ_H 5.33, indicating that an acetoxy group was present at C-3.

The EIMS spectrum of 3-*O*-acetyljaspiferal D methyl ester (**5**) showed a molecular ion at *m*/*z* 470. This ion was measured to be 470.2689 by HREIMS, which corresponds to a molecular formula $C_{28}H_{38}O_6$ (Δ 2.1 mmu). A trienal side chain was inferred by UV absorption at λ_{max} 339 nm and NMR data. ^{1}H and ^{13}C NMR analysis (see Experimental Section) clearly indicated that **5** was the 3-*O*-acetyl derivative of jaspiferal D.[3]

The molecular formula $C_{23}H_{32}O_6$ was inferred for 3-*O*-acetyljaspiferal G methyl ester (**6**) by HREIMS data (*m*/*z* 404.2157, Δ − 4.2 mmu). NMR data of **6** were superimposable on those of jaspiferal G, except for the presence of a broad singlet at δ_H 5.44, indicating that compound **6** is the 3-*O*-acetyl derivative of jaspiferal G.

The molecular formula $C_{24}H_{34}O_7$ was deduced for jaspiferoic acid A dimethyl ester (**7**) by HREIMS calculation on the molecular ion at *m*/*z* 434.2347 (Δ 2.2 mmu). NMR data indicated the presence of the same tricyclic core of the above compounds, whereas the signals related to the polyene chain were missing. The ^{1}H NMR spectrum contained proton signals due to an olefinic methyl group at δ_H 1.99 and to an additional methoxy group at δ_H 3.80.

In the HMBC spectrum the olefinic vinyl protons at δ_H 1.99 were found to correlate with two olefinic carbon signals at δ_C 146.5 (C-13) and 134.2 (C-14) and to an ester carbonyl group (δ_C 171.7). These data indicated that a carbomethoxy group was attached to C-14 in a structural situation similar to jaspiferal G. The 13-*Z* geometry was deduced by a NOE observed between the CH_3-20 and the CH_3-18.

Jaspiferoic acid B dimethyl ester (**8**) possesses two methine carbons more than **7** (HREIMS, *m*/*z* 460.2424, $C_{26}H_{36}O_7$, Δ −3.7 mmu). The ^{1}H NMR spectrum of jaspiferoic acid B methyl ester showed a pair of mutually coupled olefinic protons (δ_H 7.76, d, J = 16.1 Hz and 6.23, d, J = 16.1 Hz) and an additional methoxy group at δ_H 3.80. The UV adsorption at λ_{max} 304 (log ϵ 4.5) is compatible with the presence of a dienone system conjugated further with a carboxylic acid methyl ester. The structure was also secured by key HMBC correlations: CH_3-22/C-13, CH_3-22/C-14, CH_3-22/C-15, H-15/C-17, and OCH_3/C-17. The value of the coupling constant $J_{15,16}$ = 16.1 Hz indicated a 15-*E* geometry, whereas the chemical shifts of CH_3-22 (δ_H 2.27, δ_C 14.3) and H-15 (δ_H 7.76) were consistent with a 13-*E* geometry. Although these new malabaricane derivatives exhibited a weak cytotoxicity against L1220 cells (IC_{50} > 3.3 μg/mL), the photolability of these compounds hampered further biological evaluations.

Experimental Section

General Experimental Procedures. NMR spectra were obtained on a Bruker AMX-500 NMR spectrometer (^{1}H at 500 MHz, ^{13}C at 125 MHz), δ (ppm), J in hertz, spectra referred to $CHCl_3$ as internal standards. Mass spectra were run on a VG PROSPEC instrument equipped with an EI source. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. UV spectra were recorded on a Beckman DU70 spectrophotometer. IR spectra were taken on a IFS 48 Bruker instrument. HPLC was performed on a Macherey-Nagel Nucleosil column (30 cm × 3.9 mm i.d.; flow rate 5 mL min^{-1}), particle size 7 μm, pore size 50 Å, using a Waters model 6000 A pump equipped with U6K injector and a differential refractometer, model 401.

Animal Material. The sponge was collected at Emae in the Vanuatu Islands in 1996, and identified as *Jaspis* sp. (order Choristidae, family Jaspidae) by John Hooper of Queensland Museum, South Brisbane, Australia. A voucher specimen has been deposited at the Queensland Museum (accession number G 306893).

Extraction and Isolation. The animals were freeze-dried, and the lyophilized material (300 g) was extracted with methanol (3 × 2.5 L) and filtered. The extracts were combined and partitioned according to the modified Kupchan[11] procedure as follows. The methanol extract (72 g) was dissolved in a mixture of MeOH/H_2O containing 10% H_2O and partitioned against *n*-hexane. The water content (% v/v) of the MeOH extract was adjusted to 20% and 40%, and partitioned against CCl_4 and $CHCl_3$, respectively. The aqueous phase was concentrated to remove MeOH and then extracted with *n*-BuOH. The bioactive chloroform extract (6.6 g) was chromatographed by Si MPLC (Merck Kiesegel 60, 230−400 mesh, 20 g) eluting with 0−5% MeOH/CH_2Cl_2. The bright yellow fractions that eluted with 2% MeOH/CH_2Cl_2 were treated with an excess of ethereal diazomethane at room temperature for 30 min. The mixtures of methyl esters were further purified by Si HPLC. Less polar fractions were purified using 96% hexane/2-propanol as eluent to yield the methyl ester of 3-*O*-acetyljaspiferal B (**4**) (13.3 mg, 4.3 × 10^{-3}%, t_R = 20.8 min), the methyl ester of 3-*O*-acetyljaspiferal D (**5**) (23.2 mg, 7.7 × 10^{-3}%, t_R = 13.6 min), the methyl ester of 3-*O*-acetyljaspiferal G (**6**) (4.4 mg, 1.4 × 10^{-3}%, t_R = 9.1 min), the dimethyl ester of jaspiferoic acid A (**7**) (7.1 mg, 2.3 × 10^{-3}%, t_R = 16.7 min), and the methyl ester of globostellatic acid E (**3**) (2.2 mg, 7.3 × 10^{-4}%, t_R = 10.8 min). More polar fractions were purified using 94% hexane/2-propanol as eluent to yield the methyl esters of globostellatic acid B (**1**) (32 mg, 1.1 × 10^{-2}%, t_R = 16.8 min) and of globostellatic acid C (**2**) (24.8 mg, 8.2 × 10^{-3}%, t_R = 13.1 min) and the dimethyl ester of jaspiferoic acid B (**8**) (3.0 mg, 1.0 × 10^{-3}%, t_R = 7.6 min).

Methyl ester of globostellatic acid E (3): yellow amorphous solid; $[\alpha]^{25}_D$ −23.8° (*c* 0.4, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 235 (4.1), 340 (4.8) nm; IR (KBr) ν_{max} 1735, 1685 cm^{-1}; ^{1}H ($CDCl_3$, 500 MHz) δ 6.66 (1H, d, J = 15.7 Hz, H-15), 6.37 (1H, dd, J = 14.8, 10.5 Hz, H-20), 6.11 (1H, d, J = 10.5 Hz, H-19), 6.04 (1H, dd, J = 15.7, 5.7 Hz, H-16), 5.71 (1H, d, J = 14.8 Hz, H-21), 5.42 (1H, br s, H-3), 4.18 (1H, d, J = 5.7 Hz, H-17), 3.60 (3H, s, 26-OCH_3), 3.30 (3H, s, 17-OCH_3), 3.18 (3H, s, 22-OCH_3), 2.40 (1H, m, H-5), 2.32 (1H, m, H-11a), 2.26 (3H, s, H-28), 2.24 (1H, m, H-2a), 2.20 (1H, m, H-11b), 2.17 (2H, m, H-7), 2.14 (1H, m, H-2a), 2.09 (3H, s, *CH*$_3$COO), 1.87 (1H, m, H-9), 1.84 (1H, m, H-6a), 1.77 (1H, m, H-6b), 1.74 (1H, m, H-2b), 1.74 (1H, m, H-1a), 1.70 (3H, s, H-29), 1.42 (3H, s, H-26), 1.30 (6H, s, H-23 and H-30), 1.19 (1H, m, H-1b), 1.19 (3H, s, H-24), 0.82 (3H, s, H-27); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 208.0 (s, C-12), 176.5 (s, C-25), 173.1 (s, O*C*OCH_3), 148.0 (s, C-13), 141.5 (s, C-14), 139.7 (s, C-21), 135.9 (d, C-16), 130.6 (d, C-15), 127.1 (d, C-19), 124.2 (d, C-20),86.7 (d, C-17), 76.2 (s, C-22), 73.3 (d, C-3), 56.2 (q, 17-OCH_3), 51.0 (q, 25-OCH_3), 50.2 (q, 22-OCH_3), 49.8 (s, C-4), 49.1 (d, C-9), 45.6 (s, C-8), 41.4 (d, C-5), 39.2 (t, C-7), 37.9 (s, C-10), 36.4 (t, C-11), 29.3 (t, C-1), 25.3 (q's, C-23, C-26, and C-30), 24.8 (t, C-2), 22.9 (q, C-24), 21.0 (q, OCO*C*H_3), 19.8 (t, C-6), 19.4 (q, C-27), 14.2 (q, C-28), 11.9 (q, C-29); HREIMS, 584.3728 (calcd for $C_{35}H_{52}O_7$, 584.3713).

Methyl ester of 3-*O*-acetyljaspiferal B (4): yellow amorphous material; $[\alpha]^{25}_D$ −30.8° (*c* 0.8, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 268 (3.1), 363 (3.8), 385 (sh) nm; IR (KBr) ν_{max} 1710, 1670 cm^{-1}; ^{1}H (CD_3OD, 500 MHz) δ 9.62 (1H, d, J = 7.2 Hz, H-21), 7.46 (1H, d, J = 15.2 Hz, H-19), 7.19 (1H, dd, J = 15.6, 10.6 Hz, H-16), 7.04 (1H, d, J = 15.6 Hz, H-15), 6.87 (1H, d, J = 10.6 Hz, H-17), 6.32 (1H, dd, J = 15.2, 7.2 Hz, H-20), 5.33 (1H, br s, H-3), 3.60 (3H, s, OCH_3), 2.50 (1H, m, H-5), 2.40 (3H, s, H-26), 2.32 (1H, m, H-11a), 2.24 (1H, m, H-2a), 2.18 (1H, m, H-11b), 2.06 (3H, s, H-27), 2.09 (3H, s, AcO), 2.00 (2H, m, H-7), 1.96 (1H, m, H-9), 1.94 (2H, m, H-6), 1.74 (1H, m, H-2b), 1.72 (1H, m, H-1a), 1.52 (3H, s, H-24), 1.24 (1H, m, H-1b), 1.23 (3H, s, H-22), 1.05 (3H, s, H-25); ^{13}C NMR (CD_3OD, 125 MHz) δ 209.4 (s, C-12), 196.0 (d, C-21), 176.5 (s, C-23), 172.0 (s, O*C*OCH_3), 158.2 (s, C-19), 152.0 (s, C-13), 143.1 (s, C-14), 142.0 (s, C-18), 141.3 (d, C-17), 138.1 (d, C-15), 136.4 (d, C-20), 130.8 (d, C-16), 74.1 (d, C-3), 51.8 (q, OCH_3), 50.8 (d, C-9), 50.2 (s, C-4), 45.8 (s, C-8), 43.4 (d, C-5), 40.6 (t, C-7), 37.0 (s, C-10), 36.4 (t, C-11), 30.3 (t, C-1), 25.4 (q, C-24), 24.9 (t, C-2), 24.5 (t, C6), 23.2 (q, C-22), 21.7 (q, OCO*C*H_3), 19.8 (q, C-25), 15.8 (q, C-26), 12.4 (q, C-27); HREIMS, *m*/*z* 496.2856 (calcd for $C_{30}H_{40}O_6$, 496.2825).

Methyl ester of 3-*O*-Acetyljaspiferal D (5): yellow amorphous material; $[\alpha]^{25}_D$ −198.4° (*c* 1, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 288 (3.1), 339 (3.8), 385 (sh) nm; IR (KBr) ν_{max} 1710, 1670 cm^{-1}; ^{1}H ($CDCl_3$, 500 MHz) δ 9.51 (1H, s, H-19), 7.06 (1H, d, J = 15.4 Hz, H-15), 7.02 (1H, dd, J = 15.4, 10.8 Hz, H-16), 6.98 (1H, d, J = 15.4 Hz, H-17), 5.43 (1H, br s, H-3), 3.65 (3H, s, OCH_3), 2.43 (1H, br d, J = 10.5 Hz, H-5), 2.35 (3H, s, H-25), 2.30 (1H, m, H-11), 2.18 (1H, m, H-11a), 2.17 (2H, m, H-7), 2.10 (1H, m, H-2a), 2.09 (3H, s, AcO), 2.06 (3H, s, H-26), 1.93 (3H, s, H-25), 1.83 (1H, m, H-9), 1.81 (1H, m, H-1a), 1.76 (2H, m, H-6), 1.73 (1H, m, H-2b), 1.47 (3H, s, H-22), 1.18 (3H, s, H-20), 1.25 (1H, m, H-1b), 0.83 (3H, s, H-23); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.8 (s, C-12), 198.2 (d, C-19), 179.8 (s, C-21), 172.5 (s, O*C*OCH_3), 150.3 (s, C-13), 149.5 (d, C-17), 142.5 (s, C-18), 141.4 (s, C-15), 138.9 (s, C-14), 130.5 (d, C-16), 74.8 (d, C-3), 52.5 (q, OCH_3), 50.3 (d, C-9), 48.1 (s, C-4), 45.1 (s, C-8), 42.5 (d, C-5), 37.4 (t, C-11), 37.1 (t, C-7), 36.4 (s, C-10), 29.4 (t, C-1), 25.4 (t, C-2), 25.1 (q, C-22), 24.5 (t, C6), 23.2 (q, C-20), 22.0 (q, OCO*C*H_3), 20.4 (t, C-6), 19.8 (q, C-23), 14.3 (q, C-24), 10.4 (q, C-25); HREIMS, *m*/*z* 470.2689 (calcd for $C_{28}H_{38}O_6$, 470.2668).

Methyl ester of 3-*O*-Acetyljaspiferal G (6): yellow amorphous material; $[\alpha]^{25}_D$ −46.8° (*c* 0.4, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 207 (3.8), 260 (4.0) nm; IR (KBr) ν_{max} 1730, 1700,

1680 cm^{-1}; ^1H ($CDCl_3$, 500 MHz) δ 10.2 (1H, s, H-15), 5.44 (1H, br s, H-3), 3.65 (3H, s, OCH_3), 2.43 (1H, br d, $J = 10.5$ Hz, H-5), 2.20 (2H, m, H-7), 2.15 (2H, m, H-11), 2.10 (1H, m, H-2a), 2.07 (3H, s, AcO), 2.05 (3H, s, H-20), 1.87 (1H, m, H-9), 1.81 (1H, m, H-1a), 1.76 (2H, m, H-6), 1.71 (1H, m, H-2b), 1.58 (3H, s, H-18), 1.25 (3H, s, H-16), 1.15 (1H, m, H-1b), 0.85 (3H, s, H-19); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.4 (s, C-12), 195.2 (d, C-15), 176.8 (s, C-17), 172.6 (s, O*C*OCH$_3$), 157.7 (s, C-13), 138.5 (s, C-14), 74.8 (d, C-3), 51.0 (q, OCH_3), 50.3 (d, C-9), 48.1 (s, C-4), 45.1 (s, C-8), 41.5 (d, C-5), 37.4 (t, C-11), 37.1 (t, C-7), 36.4 (s, C-10), 29.4 (t, C-1), 27.0 (q, C-18), 25.4 (t, C-2), 21.5 (q, OCO*C*H$_3$), 20.4 (t, C-6), 19.8 (q, C-19), 11.1 (q, C-20); HREIMS, *m/z* 404.2157 (calcd for $C_{23}H_{32}O_6$, 404.2199).

Dimethyl ester of jaspiferoic acid A (7): yellow amorphous material; $[\alpha]^{25}_D$ −30.1° (*c* 0.6, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 208 (3.6), 240 (4.2) nm; IR (KBr) ν_{max} 1730, 1690 cm^{-1}; ^1H ($CDCl_3$, 500 MHz) δ 5.40 (1H, br s, H-3), 3.80 (3H, s, 15-OCH_3), 3.65 (3H, s, 17-OCH_3), 2.43 (1H, br d, $J = 10.5$ Hz, H-5), 2.20 (2H, m, H-7), 2.15 (2H, m, H-11), 2.10 (1H, m, H-2a), 2.07 (3H, s, AcO), 1.99 (3H, s, H-20), 1.87 (1H, m, H-9), 1.81 (1H, m, H-1a), 1.76 (2H, m, H-6), 1.71 (1H, m, H-2b), 1.36 (3H, s, H-18), 1.25 (3H, s, H-16), 1.15 (1H, m, H-1b), 0.81 (3H, s, H-19); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.7 (s, C-12), 176.7 (s, C-17), 171.7 (s, C-15), 169.9 (s, O*C*OCH$_3$), 146.5 (s, C-13), 134.2 (s, C-14), 73.3 (d, C-3), 51.7 (q, 15-OCH_3), 50.8 (q, 18-OCH3), 49.5 (d, C-9), 46.7 (s, C-4), 42.6 (s, C-8), 41.2 (d, C-5), 37.5 (t, C-11), 36.5 (t, C-7), 35.8 (s, C-10), 28.9 (t, C-1), 24.9 (t, C-2), 21.7 (q, OCO*C*H$_3$), 20.4 (t, C-6), 25,2 (q, C-18), 18.8 (q, C-19), 10.8 (q, C-20); HREIMS, *m/z* 434.2347 (calcd for $C_{24}H_{34}O_7$, 434.2305).

Dimethyl ester of jaspiferoic acid B (8): yellow amorphous material; $[\alpha]^{25}_D$ −38.4° (*c* 0.8, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 215 (3.6), 304 (4.5) nm; IR (KBr) ν_{max} 1730, 1700, 1680 cm^{-1}; ^1H ($CDCl_3$, 500 MHz) δ 7.76 (1H, d, $J = 16.1$ Hz, H-15), 6,23 (1H, d, $J = 16.1$ Hz, H-16), 5.42 (1H, br s, H-3), 3,80 (3H, s, OCH_3), 3.66 (3H, s, OCH_3), 2.35 (1H, br d, $J = 10.5$ Hz, H-5), 2.27 (3H, s, H-22), 2.24 (2H, m, H-7a), 2.22 (2H, m, H-7b), 2.20 (2H, m, H-11), 2.14 (1H, m, H-2a), 2.09 (3H, s, AcO), 2.05 (3H, s, H-15), 1.89 (1H, m, H-9), 1.77 (1H, m, H-1a), 1.76 (2H, m, H-6), 1.75 (1H, m, H-2b), 1.45 (3H, s, H-20), 1.18 (3H, s, H-18), 1.15 (1H, m, H-1b), 0.81 (3H, s, H-21); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 203.7 (s, C-12), 177.2 (s, C-19), 169.4 (s, O*C*OCH$_3$), 167.1 (s, C-17), 151.7 (s, C-13), 144.3 (d, C-15), 137.6 (s, C-14), 122.8 (d, C16), 72.8 (d, C-3), 51.7 (q, 17-OCH_3), 50.9 (q, 19-OCH3), 49.0 (d, C-9), 46.8 (s, C-4), 41.2 (d, C-5), 39.8 (s, C-8), 37.5 (t, C-11), 36.7 (t, C-7), 35.3 (s, C-10), 29.2 (t, C-1), 25.8 (q, C-20), 24.9 (t, C-2), 23.2 (q, C-18), 21.4 (t, C-6), 21.0 (q, OCO*C*H$_3$), 19.3 (q, C-21), 14.3 (q, C-22); HREIMS, *m/z* 460.2421 (calcd for $C_{26}H_{36}O_7$, 460.2461).

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