Eremophilanes from *Senecio mairetianus* and Some Reaction Products

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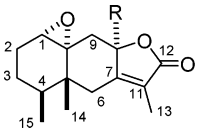
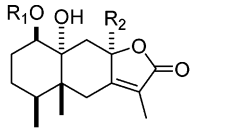
Eight new eremophilanolides (**1**, **2**, **4**−**7**, **9**, and **10**), a new eremophilane (**13**), and several known compounds were isolated from the roots and aerial parts of *Senecio mairetianus*. The chemical structures were proposed taking into consideration spectroscopic analyses and chemical transformations. X-ray diffraction analysis of **2**, **4**, and **9** confirmed their structures. The stereochemistry of 1,10-epoxy-8α-methoxyermophilanolide (**3**) was determined. Compounds **4**−**7**, **9**, and **10** are possible artifacts obtained by preparation of the alkaloidal extract.

The genus *Senecio* (Asteraceae) is considered poisonous since some of its species have been reported to be toxic to livestock and humans.[1] This toxicity has been attributed to pyrrolizidine alkaloids, which, together with eremophilanes, are the most widespread secondary metabolites reported in the genus.[1−4] Studies have shown that pyrrolizidine alkaloids of the retronecine, heliotridine, and otonecine types are carcinogenic, genotoxic, mutagenic, and teratogenic.[1,5,6] Some eremophilanes have presented antifungal, anti-inflammatory, antihyperglycemic, cytotoxic, and antimicrobial activities.[7−10]

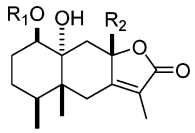
Considering the above, and in continuation of our systematic chemical research of Mexican *Senecio* species,[11,12] we undertook a study of the roots and aerial parts of *Senecio mairetianus* D.C. This study afforded several new eremophilanolides (**1**, **2**, **4**−**7**, **9**, **10**), a new eremophilane (**13**), and several known compounds. The structural elucidation of the new compounds, the stereochemistry of the known 1,10-epoxy-8α-methoxyermophilanolide (**3**),[13] and the possibility that compounds **4**−**7**, **9**, and **10** were artifacts formed during the isolation process are discussed.



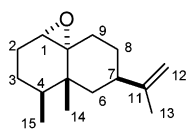
1 R = H
2 R = OH
3 R = OCH_3



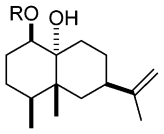
4 R_1 = CH_3 R_2 = OCH_3
5 R_1 = CH_3 R_2 = OH
6 R_1 = CH_3 R_2 = H
7 R_1 = H R_2 = H
8 R_1 = Ac R_2 = H
9 R_1 = H R_2 = OH
11 R_1 = Ac R_2 = OAc



10 R_1 = H R_2 = OH
12 R_1 = Ac R_2 = OAc



13



14 R = CH_3
15 R = H

Results and Discussion

The CH_3OH extract of roots was acidified and extracted with $CHCl_3$. The acidic aqueous solution was treated with a reductive procedure to afford the alkaloid residue, from which the known pyrrolizidine alkaloids senecionine[14] and integerrimine[2] were obtained. The $CHCl_3$ extract afforded the new eremophilanolides **1** and **2** and the known 1,10-epoxy-8α-methoxyeremophilanolide (**3**).[13]

Compound **1**, named mairetolide A ($C_{15}H_{20}O_3$), presented bands in the IR spectrum attributed to a conjugated γ-lactone (1747 and 1689 cm^{-1}). The ^{13}C NMR spectrum exhibited 15 signals, which were assigned, by HETCOR and COLOC experiments, to three methyls, four methylenes, three methines (two of them as oxymethines), one tertiary carbon bonded to an oxygen, one quaternary carbon, and three sp^2 carbons (one as a carbonyl group). The above, together with the chemical shifts and splitting pattern of the signals at δ 1.85, 0.82, and 0.83 (CH_3-13, CH_3-14, CH_3-15, respectively) in the ^1H NMR spectrum, allowed us to propose an eremophilanolide skeleton for **1**. The chemical shifts of H-1 (δ 3.06), C-1 (δ 59.9), and C-10 (δ 63.6) indicated the presence of an epoxy group. The position of the epoxide was corroborated by long-range couplings of C-10 with CH_3-14 and of H-1 with C-9, observed in the bidimensional COLOC spectrum.

The relative stereochemistry of C-5 and C-10 was deduced from the chemical shift of CH_3-14 and CH_3-15,[15] which indicated the *trans*-decalin system of mairetolide A (**1**). The COSY spectrum showed cross peaks of CH_3-13 with H-6α (δ 2.21) and H-8 (δ 4.91), which suggested dihedral angles of about 90° for H-6α and H-8 with the double bond of C-7(11), thus indicating an α-orientation for H-8. Furthermore, the NOESY spectrum showed cross-peaks of H-6α with H-4 and CH_3-15 and of H-6β with CH_3-13, CH_3-14, and CH_3-15. Therefore, mairetolide A (**1**) should contain an α-1,10-epoxide and a β-oriented γ-lactone closed to C-8.

Compound **2** (mairetolide B, $C_{15}H_{20}O_4$) presented spectroscopic data very similar to those of **1**. Eremophilanolide **2** had a hydroxyl group at C-8, which was deduced from the chemical shift of C-8 (δ 102.5) in the ^{13}C NMR spectrum and the absence of any signal attributable to H-8 in the ^1H NMR spectrum and the presence of a broad singlet at δ 4.22. An X-ray diffraction analysis of **2** corroborated the proposed structure (Figure 1).

The structural relationship of compound **3** (1,10-epoxy-8α-methoxyeremophilanolide) with **2** was evident by comparison of their spectroscopic features. The eremophilanolide **3** had a methoxy group at C-8, as shown by the signals at δ 3.20 (OCH_3) and 105.8 (C-8) in the ^1H and ^{13}C NMR spectra, respectively. On the other hand, the spectroscopic data of **3** were identical to those described for an eremophilanolide isolated from *S. gallicus*,[13] whose stere-

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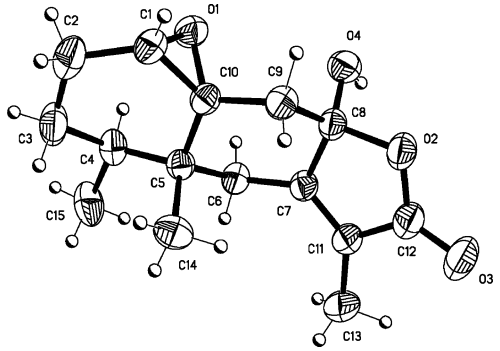

Figure 1. ORTEP projection of **2** (crystallographic numbering).

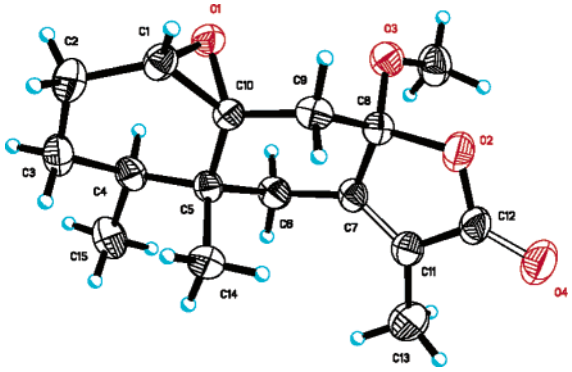

Figure 2. ORTEP projection of **3** (crystallographic numbering).

ochemistry at C-1, C-5, and C-10 was not established. Structure **3** was also proposed for an eremophilanolide isolated from *S. flavus*;[16] however, the reported physical and spectroscopic features were different from those of our compound. The ambiguity was solved when the X-ray crystallographic analysis of the eremophilanolide from *S. mairetianus* confirmed the structure **3** (Figure 2). In consequence, the stereochemistry of the lactone isolated from *S. gallicus* is that depicted in **3**, and that proposed for the eremophilanolide of *S. flavus* should be revised.

The CH_3OH extract of the aerial parts of the plant was divided in two portions; one received the usual treatment with Zn/H^+ to obtain the alkaloidal extract.[11] From this, the known alkaloids senecionine[14] and integerrimine[2] and the eremophilanolides mairetolides A, C−F, and H (**1**, **4**−**7**, and **10**) were obtained. The second portion of the CH_3OH extract gave the eremophilanolide **3**, mairetolides A, B, F, and G (**1**, **2**, **7**, and **9**), the new eremophilane mairetin (**13**), and several known compounds.

Mairetolide C (**4**), $C_{17}H_{26}O_5$, contained two carbon atoms more than **2**, but the spectroscopic data of both compounds were similar. The ^1H NMR spectrum of **4** showed two methoxy group signals (δ 3.24 and 3.15) and a triplet at δ 3.08, which was attributed to H-1. These features, together with the chemical shifts of C-1 (δ 84.6), C-8 (δ 106.2), and C-10 (δ 73.9) and the presence of two signals at δ 50.1 and 57.3 in the ^{13}C NMR spectrum, suggested that methoxy groups were present at C-1 and C-8 and that a hydroxy group was at C-10. The β-orientation of the OCH_3 (δ 3.24) at C-1 was supported by the NOE effect between this group and CH_3-14 (δ 0.78). The *trans*-decalin system was deduced on the basis of the chemical shifts of CH_3-14 (δ 0.78) and CH_3-15 (δ 0.83). Finally, the structure of **4** was confirmed by an X-ray diffraction analysis (Figure 3).

Structural relationships of mairetolides D (**5**), E (**6**), and F (**7**) with mairetolide C (**4**) were evident when their spectroscopic features were compared. A common structural characteristic was the OH group at C-10. The molecular formulas, the chemical shifts of H-1, C-1, and C-8, and the presence or absence of the H-8 signal and of those attributable to OCH_3 groups were essential to the proposed structures. Mairetolides D (**5**) and E (**6**) both showed a

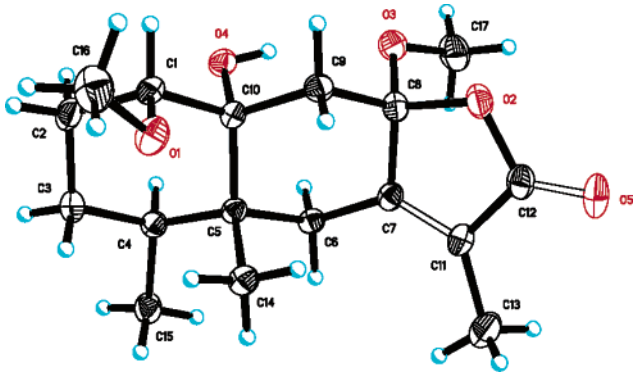

Figure 3. ORTEP projection of **4** (crystallographic numbering).

signal attributable to an OCH_3 group (δ 3.24 and 3.26, respectively). The chemical shifts of H-1 (**5**: δ 3.10, **6**: δ 3.07) and C-1 (**5**: δ 84.4, **6**: δ 85.2) were similar to those of **4**, suggesting that **5** and **6** contained a methoxy group at C-1. In the case of mairetolide F (**7**), the hydroxyl group at C-1 induced a downfield shift of H-1 ($\Delta\delta$ +0.6) and a diamagnetic shift of C-1 ($\Delta\delta$ −9.0) in comparison to those of **4**. Compounds **6** and **7** showed ^1H NMR signals at δ 5.08 and 5.11, respectively, which were assigned to H-8 of each compound. The ^1H NMR spectrum of **5** did not present any signal attributable to H-8. Its ^{13}C NMR spectrum showed the C-8 signal with a diamagnetic shift ($\Delta\delta$ −3) in comparison to that of **4**, but similar to that of **2**. In consequence, an OH group was proposed at C-8 for compound **5**. The β-orientation of OCH_3 at C-1 of compounds **5** and **6** was deduced from the NOE effect of this group with CH_3-14. The hydroxyl group at C-1 of **7** was also β-orientated, since the NOESY spectrum of 1-*O*-acetylmairetolide F (**8**), obtained by acetylation of **7**, showed cross-peaks between the acetyl group and CH_3-14.

Mairetolides G (**9**) and H (**10**) displayed the same molecular formula, $C_{15}H_{22}O_5$, and almost identical spectroscopic data. The only significant differences were the chemical shifts of C-8 (**9**: δ 105.2, **10**: δ 96.0), the specific rotations (**9**: −95, **10**: −103), and the melting points (**9**: 234−238 °C, **10**: 150−156 °C). The H-1, C-1, and C-10 signals of both compounds presented chemical shifts similar to those of **7**; then, OH groups at C-1 and C-10 were proposed for both compounds. In order to establish the stereochemistry of **9** and **10**, the respective diacetyl derivatives **11** and **12** were obtained. The ^1H NMR spectra showed CH_3-14 at relatively higher field (**11**: δ 0.85, **12**: δ 0.86) in relation to that of CH_3-15 (δ 0.89), which indicated the presence of a *trans*-decalin system in both compounds. The NOESY spectrum of **11** showed correlations of CH_3-14 with Ac-1 (δ 2.03) and of H-6α (δ 2.44) with Ac-8 (δ 2.06) and H-4 (δ 2.18). Compound **12** showed cross-peaks of CH_3-14 with the two acetyl groups. The above results led us to propose that the AcO at C-8 was α-oriented in **11** and β-oriented in **12**. Therefore, mairetolide G (**9**) should have an α-OH at C-8 and mairetolide H (**10**) should correspond to 8-epimairetolide G. An X-ray crystallographic analysis of **9** confirmed its structure (Figure 4).

Mairetin (**13**) exhibited 15 signals in the ^{13}C NMR spectrum, which, on the basis of the DEPT, HMQC, and HMBC spectra, were attributed to three primary carbons, six secondary carbons (one of them attached to oxygen), three tertiary carbons (one of them attached to oxygen), one quaternary carbon, and two sp^2 carbons (C and CH_2). The signals of CH_3-13 (δ 1.80), CH_3-14 (δ 0.97), CH_3-15 (δ 0.71), and CH_2-12 (δ 4.83 and 4.89) in the ^1H NMR spectrum were in agreement with the profile of an eremophilane with a double bond at C-11. The epoxide group at C-1 and C-10 was deduced from the chemical shifts of H-1 (δ 2.91), C-1 (δ 59.3), and C-10 (δ 66.3). Treatment of **13** with CH_3OH/H^+ opened the epoxide, affording **14** and **15**, whose structures were deduced from the chemical shifts of H-1, C-1, and C-10. The HMBC spectrum

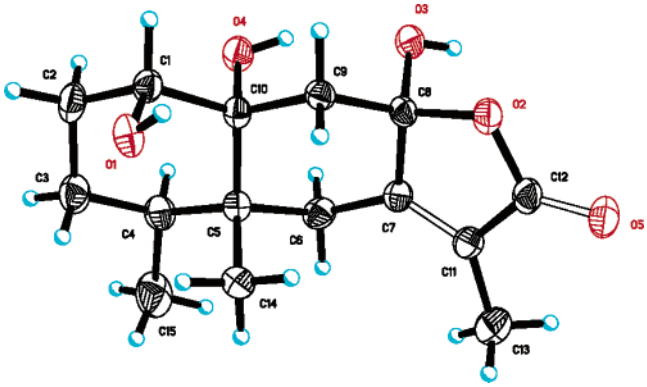

Figure 4. ORTEP projection of **9** (crystallographic numbering).

of **14** showed the coupling of H-1 with OCH_3, and in the NOESY spectrum cross-peaks of CH_3-14 with OCH_3, CH_3-13, and H-12a were observed. The above indicated that CH_3OH and H_2O added to C-1 of **13** from the β-face. Therefore,**13** should have the epoxide group α-oriented.

On the other hand, the eremophilanolides of *S. mairetianus*, **1**, **4**−**7**, and **10**, were isolated from the CH_3OH extract of the aerial parts treated with Zn/H^+ to obtain the alkaloidal residue. These compounds, except for **1**, presented either OH or OCH_3 groups at C-1 and an OH at C-10. Structural relationships of **4**−**7** with **1**−**3** suggested that treatment of the CH_3OH extract with Zn/H^+ induced the opening of the epoxides. To support the above assumption, compounds **1**−**3** were each dissolved in CH_3OH and treated with Zn/H_2SO_4. Mairetolide A (**1**) afforded mairetolide F (**7**), mairetolide B (**2**) gave mairetolides D (**5**) and G (**9**), and compound **3** yielded mairetolide C (**4**). We conclude that the conditions used to obtain the alkaloidal concentrate caused the transformation of **1**−**3** into **4**−**7**. Considering the above, the hypothetical 8-epimairetolide B should be the precursor of **10**.

Experimental Section

General Experimental Procedures. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 343 polarimeter. UV and IR spectra were recorded on Shimadzu UV 160U and Bruker Tensor 27 spectrophotometers, respectively. 1D and 2D NMR spectra were obtained on an Eclipse JEOL 300 MHz or a Varian-Unity Inova 500 MHz spectrometer with TMS as internal standard. EIMS (70 eV, ionization current 100 μA, ionization chamber at 250 °C, direct inlet) were obtained on a JEOL JMS-AX505HA mass spectrometer, and HRFABMS data were measured with a JEOL JMS-SX102A mass spectrometer. Vacuum column chromatography (VCC) was carried out with Merck silica gel G 60. Flash chromatography was performed with silica gel 60 (230−400 mesh, Macherey-Nagel). Preparative thin-layer chromatography (TLC) was carried out using precoated Sil G-100UV_{254} plates (Macherey-Nagel). X-ray crystallographic analyses were realized on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXS. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms, except for those bonded to oxygen atoms, were included at calculated positions and were not refined.

Plant Material. Roots and aerial parts of *Senecio mairetianus* D.C. were collected near the first crater of the Nevado de Toluca, State of Mexico, Mexico, in October 2000. A voucher specimen (MEXU 1045508) was deposited at the Herbario Nacional, Instituto de Biología, UNAM.

Extraction and Isolation. Dried and ground roots (577 g) were exhaustively extracted with CH_3OH, which was evaporated until 0.5 L of solution remained. This was acidified with 2.5% aqueous H_2SO_4 and extracted with $CHCl_3$ to afford 10.5 g of a nonalkaloidal residue. The acid part was treated with Zn powder (57 g), stirred overnight, and filtered. The filtrate was basified with NH_4OH and extracted with $CHCl_3$ to yield 5.6 g of alkaloidal residue. This last gave, after successive crystallizations, 204 mg of senecionine,[14] mp 226−230 °C (CH_3OH), and 362 mg of integerrimine,[2] mp 173−175 °C (*i*-PrOH−Me_2CO). The mother liqueurs were purified by VCC ($CHCl_3$−CH_3-OH polarity gradient) to afford 1.0 g of integerrimine. The nonalkaloidal residue was submitted to VCC (hexane−Me_2CO polarity gradient) to obtain fractions 1A−3A. Fraction 1A was purified by VCC (hexane−$CHCl_3$ polarity gradient) followed of preparative TLC (hexane−EtOAc, 4:1) to yield 12 mg of **1** and 21 mg of **2**. Compound **3**[13] (44 mg) was isolated after purification of fraction 3A by VCC (hexane−EtOAc polarity gradient).

Dried and ground aerial parts (3.77 kg) of *S. mairetianus* were extracted with CH_3OH to yield 543 g of extract. Half of the extract (271 g) was dissolved in CH_3OH (500 mL), acidified (2.5% H_2SO_4), and treated with 85 g of Zn powder. The mixture was stirred overnight, filtered, washed with $CHCl_3$, basified with NH_4OH, and extracted with $CHCl_3$ to afford 27 g of alkaloidal residue. The latter was fractionated by VCC ($CHCl_3$−CH_3OH polarity gradient) to give fractions 1B−3B. Purification of fraction 1B by successive VCC (hexane−$CHCl_3$−EtOAc polarity gradient) yielded 21 mg of **1**, 64 mg of **4**, 76 mg of **5**, and 15 mg of **6**. Fraction 2B was submitted to consecutive VCC (hexane−EtOAc polarity gradient) to give 316 mg of **7** and 70 mg of **10**. Fraction 3B yielded by crystallization 3.7 mg of senecionine and 550 mg of integerrimine.

The remaining half of the CH_3OH extract (272 g) was fractionated by VCC (CH_2Cl_2−CH_3OH) and yielded fractions 1C−3C. Fraction 1C, after VCC (hexane−EtOAc polarity gradient), afforded fractions $1C_1$−$1C_5$. Compound **13** (340 mg) and lupeportlandol[17] (30 mg), mp 211−212 °C (Me_2CO), were obtained from fraction $1C_1$ (flash chromatography, hexane−CH_2Cl_2 9:1). Fraction $1C_2$ was submitted to VCC (hexane−EtOAc 19:1) to give 250 mg of **1**. Similar treatment of fraction $1C_4$ afforded 35 mg of 10α-hydroxy-1-oxoeremophila-7(11),8(9)-dien-12,8-olide,[18] mp 196−197 °C (hexane−EtOAc). Fraction $1C_3$ gave 850 mg of **3** after its purification (VCC, CH_2Cl_2). Fraction $1C_5$ yielded 950 mg of **2**. Fraction 2C, after successive VCC ($CHCl_3$−Me_2CO−CH_3-OH polarity gradient, hexane−EtOAc−CH_3OH polarity gradient) gave 72 mg of **7**, 63 mg of **9**, 45 mg of quercetin,[19] mp 310−312 °C (CH_3-OH), and residue A. The latter was purified by VCC (CH_2Cl_2−CH_3-OH, 19:1) to afford 102 mg of isorhamnetin-3β-D-(1-*O*-acetyl) glucoside,[20] mp 166−167 °C (CH_3OH). Fraction 3C was fractionated by VCC (hexane−EtOAc, 3:7) into $3C_1$−$3C_3$. From fraction $3C_1$ 300 mg of quercetin 3-*O*-(6″-*O*-acetyl)-β-D-glucopyranoside,[21] mp 245−247 °C (CH_3OH), was obtained. Purification of fraction $3C_2$ (VCC, EtOAc) yielded 450 mg of the latter compound and a residue whose purification by Sephadex column (CH_3OH−H_2O gradient system) gave 180 mg of arbutin,[22] mp 196−198 °C (CH_3OH), and 72 mg of isorhamnetin-3-glucoside,[23] mp 168−170 °C (CH_3OH). Fraction $3C_3$ was purified by Sephadex column (CH_3OH−H_2O gradient system) to yield 250 mg of quercetin 3-*O*-(6″-*O*-acetyl)-β-D-glucopyranoside and 280 mg of quercetin 3-*O*-glucoside,[19] mp 220−222 °C (CH_3OH).

Mairetolide A (1): white crystals (hexane), mp 97−99 °C; $[\alpha]^{28}_D$ −193.0 (*c* 0.2, $CHCl_3$); UV (THF) λ_{max} (log ϵ) 219 (4.16) nm; IR ($CHCl_3$) ν_{max} 1747, 1686 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.91 (1H, br dd, J = 9, 9 Hz, H-8), 3.06 (1H, d, J = 3.5 Hz, H-1), 2.76 (1H, d, J = 13.5 Hz, H-6β), 2.21 (1H, br d, J = 13.5 Hz, H-6α), 2.06 (2H, m, CH_2-2), 2.02 (1H, d, J = 13 Hz, H-9a), 1.91 (1H, m, H-4), 1.86 (1H, d, J = 13 Hz, H-9b), 1.85 (3H, dd, J = 1.8, 1.2 Hz, CH_3-13), 1.26 (2H, m, CH_2-3), 0.83 (3H, d, J = 7 Hz, CH_3-15), 0.82 (3H, s, CH_3-14); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.6 (C, C-12), 160.4 (C, C-7), 122.3 (C, C-11), 77.4 (CH, C-8), 63.7 (C, C-10), 59.9 (CH, C-1), 38.8 (C, C-5), 38.5 (CH_2, C-9), 35.0 (CH_2, C-6), 32.5 (CH, C-4), 24.9 (CH_2, C-3), 22.2 (CH_2, C-2), 15.2 (CH_3, C-15), 14.9 (CH_3, C-14), 8.1 (CH_3, C-13); EIMS *m*/*z* 248 $[M]^+$ (7), 233 (7), 230 (7), 219 (6), 215 (4), 174 (4), 163 (4), 152 (8), 137 (26), 125 (25), 110 (100), 95 (56), 91 (8), 82 (12), 81 (9), 67 (6), 55 (6), 53 (8), 43 (7), 41 (9); HRFABMS *m*/*z* 249.1491 (calcd for $C_{15}H_{21}O_3$, 249.1491).

Mairetolide B (2): white crystals (hexane−EtOAc), mp 155−156 °C; $[\alpha]^{29}_D$ −149.5 (*c* 0.2, CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 220 (4.09) nm; IR ($CHCl_3$) ν_{max} 3566, 1765, 1698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.22 (1H, br s, OH-8), 3.06 (1H, d, J = 3.9 Hz, H-1), 2.66 (1H, d, J = 13.5 Hz, H-6β), 2.43, 1.76 (each 1H, d, J = 14 Hz, CH_2-9), 2.38 (1H, br d, J = 13.5 Hz, H-6α), 1.98 (3H, m, CH_2-2 and CH-4), 1.85 (3H, d, J = 1.5 Hz, CH_3-13), 1.28 (2H, m, CH_2-3), 0.84 (3H, d, J = 6.3 Hz, CH_3-15), 0.83 (3H, s, CH_3-14); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.7 (C, C-12), 158.1 (C, C-7), 123.9 (C, C-11), 102.4 (C, C-8), 63.9 (C, C-10), 59.6 (CH, C-1), 42.4 (CH_2, C-9), 39.5 (C, C-5),

33.4 (CH_2, C-6), 33.1 (CH, C-4), 24.6 (CH_2, C-3), 21.3 (CH_2, C-2), 15.2 (CH_3, C-15), 14.6 (CH_3, C-14), 8.1 (CH_3, C-13); EIMS *m/z* 264 $[M]^+$ (8), 247 (13), 218 (13), 139 (18), 126 (40), 121 (100), 105 (13), 98 (13), 95 (32), 93 (16), 79 (13), 55 (13), 43 (17), 41 (19); HRFABMS *m/z* 265.1445 (calcd for $C_{15}H_{21}O_4$, 265.1440).

Crystal data of 2:[24] $C_{15}H_{20}O_4$, M_r 264.31, monoclinic, space group $P2_1$, $a = 10.058(1)$ Å, $\alpha = 90.00°$, $b = 6.672(1)$ Å, $\beta = 108.079(2)°$, $c = 10.968(1)$ Å; $\gamma = 90.00°$, $V = 699.7(1)$ Å^3, $Z = 2$, $D_c = 1.255$ g cm^{-3}, $F(000) = 284$; crystal dimensions $0.468 \times 0.218 \times 0.218$ mm. Reflections collected 8303, independent reflections 2201. Number of parameters refined 178; final *R* indices (observed data) $R_1 = 4.21\%$, $wR^2 = 9.74\%$; *R* indices (all data) $R = 4.71\%$, $wR^2 = 9.95\%$.

Crystal data of 3:[24] $C_{16}H_{22}O_4$, M_r 278.34, monoclinic, space group $P2_1$, $a = 10.402(2)$ Å, $\alpha = 90.00°$, $b = 6.875(1)$ Å, $\beta = 106.640(3)°$, $c = 10.880(2)$ Å; $\gamma = 90.00°$, $V = 745.5(2)$ Å^3, $Z = 2$, $D_c = 1.240$ g cm^{-3}, $F(000) = 300$; crystal dimensions $0.374 \times 0.152 \times 0.058$ mm. Reflections collected 7233, independent reflections 3440. Number of parameters refined 185; final *R* indices (observed data) $R_1 = 6.67\%$, $wR^2 = 10.36\%$; *R* indices (all data) $R = 12.25\%$, $wR^2 = 11.89\%$.

Mairetolide C (4): white crystals (hexane−EtOAc), mp 165−169 °C; $[\alpha]^{28}_D$ −130.5 (*c* 0.2, $CHCl_3$); UV (CH_3OH) λ_{max} (log ϵ) 225 (4.07) nm; IR ($CHCl_3$) ν_{max} 3510, 1759, 1688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.02 (1H, br s, OH-10), 3.24 (3H, s, OCH_3-1), 3.15 (3H, s, OCH_3-8), 3.08 (1H, t, $J = 2.6$ Hz, H-1), 2.47 (1H, d, $J = 14.3$ Hz, H-9β), 2.40 (1H, d, $J = 13$ Hz, H-6β), 2.25 (1H, br d, $J = 13$ Hz, H-6α), 2.15 (1H, dqd, $J = 12.3$, 7, 4 Hz, H-4), 2.06 (1H, d, $J = 14.3$ Hz, H-9α), 1.88 (3H, d, $J = 1.5$ Hz, CH_3-13), 1.88 (1H, dddd, $J = 14.3$, 13.5, 4.3, 2.6 Hz, H-2α), 1.75 (1H, dddd, $J = 14.3$, 4.4, 2.6, 2.3 Hz, H-2β), 1.40 (1H, dddd, $J = 13.5$, 13.5, 12.5, 4.4 Hz, H-3β), 1.28 (1H, m, H-3α), 0.83 (3H, d, $J = 7$ Hz, CH_3-15), 0.78 (3H, d, $J = 0.6$ Hz, CH_3-14); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3 (C, C-12), 157.0 (C, C-7), 126.4 (C, C-11), 106.2 (C, C-8), 84.6 (CH, C-1), 73.9 (C, C-10), 57.3 (CH_3, OCH_3-1), 50.1 (CH, OCH_3-8), 45.1 (C, C-5), 41.8 (CH_2, C-9), 34.6 (CH, C-4), 33.6 (CH_2, C-6), 25.7 (CH_2, C-3), 22.9 (CH_2, C-2), 15.3 (CH_3, C-15), 14.1 (CH_3, C-14), 8.3 (CH_3, C-13); EIMS *m/z* 311 $[M + H]^+$ (5), 310 $[M]^+$ (3), 278 (100), 260 (19), 246 (35), 228 (17), 218 (12), 155 (88), 127 (48), 124 (20), 95 (70), 83 (6), 71 (19), 69 (15), 55 (10), 53 (10), 43 (8), 41 (14); HRFABMS *m/z* 311.1862 (calcd for $C_{17}H_{27}O_5$, 311.1858).

Crystal data of 4:[24] $C_{17}H_{26}O_5$, M_r 310.38, orthorhombic, space group $P2_12_12_1$, $a = 11.573(1)$ Å, $\alpha = 90.00°$, $b = 11.709(1)$ Å, $\beta = 90.00°$, $c = 12.221(1)$ Å; $\gamma = 90.00°$, $V = 1656.0(2)$ Å^3, $Z = 4$, $D_c = 1.245$ g cm^{-3}, $F(000) = 672$; crystal dimensions $0.362 \times 0.150 \times 0.086$ mm. Reflections collected 16 649, independent reflections 3800. Number of parameters refined 207; final *R* indices (observed data) $R_1 = 4.37\%$, $wR^2 = 5.71\%$; *R* indices (all data) $R = 7.47\%$, $wR^2 = 6.15\%$.

Mairetolide D (5): white crystals (hexane−EtOAc), mp 170−173 °C; $[\alpha]^{29}_D$ −111.0 (*c* 0.2, $CHCl_3$); UV (CH_3OH) λ_{max} (log ϵ) 224 (3.90) nm; IR ($CHCl_3$) ν_{max} 3539, 3318, 1762, 1687 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.24 (3H, s, OCH_3-1), 3.10 (1H, dd, $J = 2.6$, 2.3 Hz, H-1), 2.47 (1H, d, $J = 14.3$ Hz, H-9β), 2.40 (2H, br s, CH_2-6), 2.12 (1H, dqd, $J = 12$, 7, 4 Hz, H-4), 2.05 (1H, d, $J = 14.3$ Hz, H-9α), 1.85 (1H, dddd, $J = 14.3$, 13, 4.5, 2.6 Hz, H-2α), 1.79 (3H, d, $J = 0.6$ Hz, CH_3-13), 1.78 (1H, m, H-2β), 1.41 (1H, dddd, $J = 13.5$, 13, 12, 4 Hz, H-3β), 1.28 (1H, br ddd, $J = 13.5$, 7, 4.5 Hz, H-3α), 0.84 (3H, d, $J = 7$ Hz, CH_3-15), 0.77 (3H, s, CH_3-14); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.5 (C, C-12), 159.8 (C, C-7), 123.5 (C, C-11), 103.6 (C, C-8), 84.4 (CH, C-1), 74.5 (C, C-10), 57.4 (CH_3, OCH_3-1), 44.8 (C, C-5), 41.8 (CH_2, C-9), 34.7 (CH, C-4), 33.4 (CH_2, C-6), 25.6 (CH_2, C-3), 22.9 (CH_2, C-2), 15.3 (CH_3, C-15), 14.1 (CH_3, C-14), 8.1 (CH_3, C-13); EIMS *m/z* 296 $[M]^+$ (3), 278 (42), 260 (15), 246 (25), 228 (10), 155 (80), 127 (52), 124 (24), 123 (23), 95 (100), 71 (40), 69 (25), 55 (14), 43 (16), 41 (19); HRFABMS *m/z* 297.1709 (calcd for $C_{16}H_{25}O_5$, 297.1702).

Mairetolide E (6): white crystals (hexane−EtOAc), mp 165−170 °C; $[\alpha]^{29}_D$ −106.5 (*c* 0.2, CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 224 (4.23) nm; IR ($CHCl_3$) ν_{max} 3594, 1740, 1682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.08 (1H, dd, $J = 9.7$, 8.2 Hz, H-8), 3.26 (3H, s, OCH_3-1), 3.07 (1H, dd, $J = 2.3$, 2 Hz, H-1), 2.47 (1H, d, $J = 13.3$ Hz, H-6β), 2.40 (1H, br d, $J = 13.3$ Hz, H-6α), 2.12 (1H, dd, $J = 13.2$, 8.2 Hz, H-9β), 2.07 (1H, dd, $J = 13.2$, 9.7 Hz, H-9α), 1.94 (1H, dqd, $J = 12$, 6.8, 3.5 Hz, H-4), 1.87 (3H, br s, CH_3-13), 1.82 (2H, m, CH_2-2), 1.46 (1H, br ddd, $J = 13.5$, 12, 7, Hz, H-3β), 1.29 (1H, br ddd, $J = 13.5$, 7, 3.5 Hz, H-3α), 0.88 (3H, d, $J = 6.8$ Hz, CH_3-15), 0.80 (3H, s, CH_3-14); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.3 (C, C-12), 162.0 (C, C-7), 121.5 (C, C-11), 85.2 (CH, C-1), 79.2 (CH, C-8), 75.9 (C, C-10), 57.6 (CH_3, OCH_3-1), 43.1 (C, C-5), 40.1 (CH_2, C-9), 35.4 (CH, C-4), 34.8 (CH_2, C-6), 25.5 (CH_2, C-3), 23.4 (CH_2, C-2), 15.5 (CH_3, C-15), 14.3 (CH_3, C-14), 8.1 (CH_3, C-13); EIMS *m/z* 281 $[M + H]^+$ (17), 280 $[M]^+$ (7), 262 (98), 248 (13), 230 (97), 174 (31), 152 (15), 139 (45), 137 (48), 125 (59), 110 (100), 95 (86), 83 (32), 71 (65), 55 (34), 53 (36), 43 (39), 41 (50); HRFABMS *m/z* 281.1753 (calcd for $C_{16}H_{25}O_4$, 281.1753).

Mairetolide F (7): white crystals (hexane−EtOAc), mp 176−178 °C; $[\alpha]^{28}_D$ −120.0 (*c* 0.2, CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 224 (4.20) nm; IR ($CHCl_3$) ν_{max} 3614, 1738, 1679 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.11 (1H, dd, $J = 10$, 7.6 Hz, H-8), 3.67 (1H, dd, $J = 2.3$, 2.3 Hz, H-1), 2.46 (2H, s, CH_2-6), 2.19 (1H, dd, $J = 13$, 7.6 Hz, H-9β), 2.05 (1H, dd, $J = 13$, 10 Hz, H-9α), 2.04 (1H, m, H-2a), 1.99 (1H, m, H-4), 1.81 (3H, br s, CH_3-13), 1.65 (1H, m, H-2b), 1.60 (1H, dddd, $J = 13.5$, 13.5, 13.5, 4 Hz, H-3β), 1.34 (1H, br ddd, $J = 13.5$, 8, 3.5 Hz, H-3α), 0.90 (3H, d, $J = 7$ Hz, CH_3-15), 0.89 (3H, s, CH_3-14); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.5 (C, C-12), 162.4 (C, C-7), 121.4 (C, C-11), 79.4 (CH, C-8), 75.7 (C, C-10), 75.6 (CH, C-1), 42.9 (C, C-5), 39.9 (CH_2, C-9), 35.3 (CH, C-4), 35.1 (CH_2, C-6), 29.1 (CH_2, C-2), 25.3 (CH_2, C-3), 15.5 (CH_3, C-15), 14.6 (CH_3, C-14), 8.1 (CH_3, C-13); EIMS *m/z* 267 $[M + H]^+$ (7), 248 (100), 230 (59), 209 (15), 202 (15), 188 (9), 174 (17), 163 (64), 137 (29), 135 (18), 125 (84), 110 (73), 95 (69), 83 (40), 69 (27), 55 (35), 43 (38), 41 (37); HRFABMS *m/z* 267.1600 (calcd for $C_{15}H_{23}O_4$, 267.1596).

Mairetolide G (9): white crystals (hexane−Me_2CO), mp 234−238 °C; $[\alpha]^{29}_D$ −95.0 (*c* 0.2, CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 224 (4.25) nm; IR (nujol) ν_{max} 3481, 3397, 1761, 1687 cm^{-1}; ^{1}H NMR (CH_3OH-d_4, 300 MHz) δ 3.54 (1H, dd, $J = 2.9$, 2.4 Hz, H-1), 2.48 (1H, d, $J = 13.2$ Hz, H-6β), 2.40 (H, d, $J = 13.2$ Hz, H-6α), 2.39 (1H, d, $J = 14$ Hz, H-9β), 2.14 (2H, m, H-2α and H-4), 1.96 (1H, d, $J = 14$ Hz, H-9α), 1.81 (3H, d, $J = 1.2$ Hz, CH_3-13), 1.58 (1H, m, H-3β), 1.54 (1H, m, H-2b), 1.28 (1H, m, H-3α), 0.878 (3H, s, CH_3-14), 0.875 (3H, d, $J = 6.7$ Hz, CH_3-15); ^{13}C NMR (CH_3OH-d_4, 75 MHz) δ 174.2 (C, C-12), 161.5 (C, C-7), 124.4 (C, C-11), 105.2 (C, C-8), 75.9 (CH, C-1), 75.6 (C, C-10), 46.1 (C, C-5), 43.1 (CH_2, C-9), 36.1 (CH, C-4), 34.7 (CH_2, C-6), 29.6 (CH_2, C-2), 27.0 (CH_2, C-3), 15.9 (CH_3, C-15), 15.0 (CH_3, C-14), 8.3 (CH_3, C-13); EIMS *m/z* 282 $[M]^+$ (2), 264 (18), 243 (9), 227 (17), 219 (18), 218 (17), 179 (8), 163 (5), 151 (11), 141 (23), 139 (14), 124 (100), 113 (32), 95 (44), 83 (11), 69 (14), 55 (13), 43 (21), 41 (13); HRFABMS *m/z* 283.1548 (calcd for $C_{15}H_{23}O_5$, 283.1545).

Crystal data of 9:[24] $C_{15}H_{22}O_5$, M_r 282.33, orthorhombic, space group $P2_12_12_1$, $a = 7.451(1)$ Å, $\alpha = 90.00°$, $b = 7.730(1)$ Å, $\beta = 90.00°$, $c = 25.649(2)$ Å; $\gamma = 90.00°$, $V = 1477.3(3)$ Å^3, $Z = 4$, $D_c = 1.269$ gcm^{-3}, $F(000) = 608$; crystal dimensions $0.36 \times 0.20 \times 0.08$ mm. Reflections collected 14 768, independent reflections 3374. Number of parameters refined 193; final *R* indices (observed data) $R_1 = 5.04\%$, $wR^2 = 5.37\%$; *R* indices (all data) $R = 8.81\%$, $wR^2 = 5.86\%$.

Mairetolide H (10): white crystals (hexane−EtOAc), mp 150−156 °C; $[\alpha]^{28}_D$ −103.0 (*c* 0.2, CH_3OH); UV (CH_3OH) λ_{max} (log ϵ) 220 (4.27) nm; IR ($CHCl_3$) ν_{max} 3627, 3394, 3319, 1751, 1687 cm^{-1}; ^{1}H NMR (CH_3OH-d_4, 500 MHz) δ 3.52 (1H, dd, $J = 3.5$, 2.5 Hz, H-1), 2.48 (1H, d, $J = 13$ Hz, H-6β), 2.35 (1H, br d, $J = 13$ Hz, H-6α), 2.33 (1H, d, $J = 14$ Hz, H-9β), 2.14 (1H, m, H-4), 2.09 (1H, dddd, $J = 13.5$, 13.5, 5, 3.5 Hz, H-2α), 1.89 (1H, d, $J = 14$ Hz, H-9α), 1.79 (3H, d, $J = 1.5$ Hz, CH_3-13), 1.57 (1H, dddd, $J = 13.5$, 13.5, 13.5, 6.5 Hz, H-3β), 1.54 (1H, m, H-2β), 1.27 (1H, m, H-3α), 0.864 (3H, d, $J = 1$ Hz, CH_3-14), 0.861 (3H, d, $J = 6.5$ Hz, CH_3-15); ^{13}C NMR (CH_3OH-d_4, 125 MHz) δ 174.9 (C, C-12), 162.5 (C, C-7), 124.5 (C, C-11), 96.0 (C, C-8), 75.8 (CH, C-1), 75.1 (C, C-10), 46.2 (C, C-5), 43.5 (CH_2, C-9), 36.2 (CH, C-4), 35.1 (CH_2, C-6), 29.6 (CH_2, C-2), 26.9 (CH_2, C-3), 15.7 (CH_3, C-15), 14.8 (CH_3, C-14), 8.3 (CH_3, C-13); EIMS *m/z* 281 $[M - H]^+$ (38), 264 (36), 253 (89), 246 (14), 237 (15), 219 (20), 218 (18), 198 (14), 174 (30), 165 (26), 164 (31), 151 (26), 138 (32), 124 (100), 96 (36), 95 (33), 81 (44), 69 (22), 55 (28), 53 (16), 43 (23), 41 (38); HRFAB *m/z* 282.1466 (calcd for $C_{15}H_{22}O_5$, 282.1467).

Mairetin (13): thin needles (hexane), mp 70−71 °C; $[\alpha]^{25}_D$ −77.5 (*c* 0.2, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3085, 1640, 886 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.83 (1H, br s, H-12a), 4.79 (1H, br q, $J = 1.5$ Hz, H-12b), 2.91 (1H, br d, $J = 4.5$ Hz, H-1), 2.43 (1H, br t, $J = 5.5$ Hz, H-7), 2.36 (1H, ddd, $J = 14$, 9.5, 5.5 Hz, H-9β), 1.94 (1H, m, H-2α), 1.93 (1H, m, H-8β), 1.86 (1H, m, H-8α), 1.83 (1H, dd, $J = 13.5$, 5.5 Hz, H-6β), 1.80 (3H, s, CH_3-13), 1.70 (1H, dqd, $J = 7$, 7,4.5 Hz, H-4), 1.57 (1H, dd, $J = 13.5$, 7 Hz, H-6α), 1.17 (2H, m, CH_2-3), 1.00 (1H, ddd, $J = 14$, 10.5, 4.5 Hz, H-9α), 0.97 (3H, s, CH_3-14),

0.86 (1H, ddd, $J = 9, 6, 3$ Hz, H-2β), 0.71 (3H, d, $J = 7$ Hz, CH_3-15); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.6 (C, C-11), 108.7 (C H_2, C-12), 66.3 (C, C-10), 59.3 (CH, C-1), 38.6 (CH, C-7), 36.0 (CH_2, C-6), 36.0 (C, C-5), 34.2 (CH, C-4), 28.0 (CH_2, C-9), 24.7 (CH_2, C-8), 24.3 (CH_2, C-3), 22.5 (CH_2, C-2), 22.3 (CH_3, C-13), 15.8 (CH_3, C-14), 15.2 (CH_3, C-15); EIMS *m*/*z* 220 $[M]^+$ (20), 202 (30), 110 (98), 95 (100), 81 (87); HRFABMS *m*/*z* 221.1901 (calcd for $C_{15}H_{25}O$, 221.1905).

Acetylation of Mairetolides F (7), G (9), and H (10). Compounds **7** (119 mg), **9** (67 mg), and **10** (48.5 mg) were acetylated, independently, in the usual manner, to give 40 mg of **8**, 25.6 mg of **11**, and 30.9 mg of **12**, respectively. Compound **8**: white crystals (hexane−EtOAc), mp 165−168 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.10 (1H, dd, $J = 10$, 7.3 Hz, H-8), 4.82 (1H, dd, $J = 3$, 2.6 Hz, H-1), 2.51 (2H, br s, CH_2-6), 2.17 (1H, dd, $J = 13$, 7.3 Hz, H-9α), 2.10 (2H, m, H-2α and H-4), 1.82 (3H, d, $J = 1.7$ Hz, CH_3-13), 2.03 (3H, s, AcO), 1.77 (1H, dd, $J = 13$, 10 Hz, H-9β), 1.66 (1H, dddd, $J = 15$, 4, 2.3, 2.3 Hz, H-2β), 1.48 (1H, dddd, $J = 14$, 14, 14, 4 Hz, H-3β), 1.37 (1H, m, H-3α), 0.91 (3H, d, $J = 6.8$ Hz, CH_3-15), 0.86 (3H, s, CH_3-14). Compound **11**: white crystals (hexane−EtOAc), mp 156−159 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.76 (1H, dd, $J = 3.2$, 2.6 Hz, H-1), 2.49 (1H, d, $J = 14$ Hz, H-6β), 2.44 (1H, br d, $J = 14$ Hz, H-6α), 2.36 (1H, d, $J = 15$ Hz, H-9β), 2.18 (1H, m, H-4), 2.12 (1H, d, $J = 15$ Hz, H-9α), 2.12 (1H, m, H-2α), 2.06 (3H, s, AcO-8), 2.03 (3H, s, AcO-1), 1.88 (3H, d, $J = 0.9$ Hz, CH_3-13), 1.64 (1H, dddd, $J = 15$, 4, 2.5, 2.5 Hz, H-2β), 1.45 (1H, dddd, $J = 14$, 14, 14, 4 Hz, H-3β), 1.40 (1H, m, H-3α), 0.89 (3H, d, $J = 6.7$ Hz, CH_3-15), 0.85 (3H, s, CH_3-14). Compound **12**: colorless oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.76 (1H, dd, $J = 2.5$, 2.5 Hz, H-1), 2.42 (2H, s, CH_2-6), 2.25 (1H, d, $J = 14$ Hz, H-9β), 2.13 (2H, m, H-2α and H-4), 2.03 (1H, d, $J = 14$ Hz, H-9α), 2.03 (3H, s, AcO-1), 1.93 (3H, s, AcO-8), 1.87 (3H, br s, CH_3-13), 1.64 (1H, dddd, $J = 15$, 4, 2, 2 Hz, H-2β), 1.47 (1H, dddd, $J = 14$, 13.5, 13.5, 4 Hz, H-3β), 1.39 (1H, m, H-3α), 0.89 (3H, d, $J = 7$ Hz, CH_3-15), 0.86 (3H, s, CH_3-14).

Methanolysis of Mairetin (13). A solution of **13** (38 mg) and concentrated H_2SO_4 (1.4 mg in 0.2 mL of H_2O) in CH_3OH (5 mL) was stirred for 4 h at room temperature. The reaction mixture was extracted with ether and purified by preparative TLC (hexane−Me_2-CO, 4:1) to obtain 11 mg of **14** and 16 mg of **15**. Compound **14**: colorless oil; IR ($CHCl_3$) ν_{max} 3456, 2930, 1641, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.93 (1H, br s, H-12a), 4.86 (1H, br q, $J = 1$ Hz, H-12b), 3.04 (3H, s, CH_3O), 2.66 (1H, br t, $J = 2.5$ Hz, H-1), 2.55 (1H, ddd, $J = 14$, 10.5, 6 Hz, H-9a), 2.39 (1H, br quint, $J = 6$ Hz, H-7), 1.92 (2H, m, CH_2-8), 1.87 (1H, m, H-2a), 1.81 (1H, dqd, $J = 13.5$, 7,3.5 Hz, H-4), 1.74 (3H, ddd, $J = 2$, 1, 1 Hz, CH_3-13), 1.65 (2H, m, CH_2-6), 1.62 (1H, m, H-2b), 1.54 (1H, dddd, $J = 14$, 13.5, 13.5, 4 Hz, H-3a), 1.19 (3H, d, $J = 1.5$ Hz, CH_3-14), 1.15 (1H, br d, $J = 13$ Hz, H-3b), 0.91 (1H, ddd, $J = 14$, 6, 4.5 Hz, H-9b), 0.79 (3H, d, $J = 7$ Hz, CH_3-15); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.7 (C, C-11), 108.8 (CH_2, C-12), 85.7 (CH, C-1), 75.0 (C, C-10), 57.3 (CH_3, OCH_3), 40.3 (C, C-5), 38.6 (CH, C-7), 36.4 (CH, C-4), 36.2 (CH_2, C-6), 29.9 (CH_2, C-9), 26.0 (CH_2, C-3), 24.0 (CH_2, C-2), 22.9 (CH_2, C-8), 22.4 (CH_3, C-13), 15.7 (CH_3, C-14), 15.4 (CH_3, C-15). Compound **15**: colorless oil; IR ($CHCl_3$) ν_{max} 3461, 2933, 1640, 1456 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.87 (1H, dq, $J = 1.8$, 1 Hz, H-12a), 4.79 (1H, dq, $J = 3$, 1.5 Hz, H-12b), 3.50 (1H, dd, $J = 3.6$, 2.4 Hz, H-1), 2.41 (1H, ddd, $J = 14$, 9.6, 7 Hz, H-9a), 2.40 (1H, m, H-7), 2.15 (2H, m, H-2a and 3a), 1.95 (2H, m, CH_2-8), 1.79 (3H, dd, $J = 1.5$, 1 Hz, CH_3-13), 1.74 (1H, m, H-4), 1.65 (2H, br d, $J = 5.2$ Hz CH_2-6), 1.58 (1H, m, H-2b), 1.26 (1H, m, H-3b), 1.17 (1H, dt, $J = 14$, 4.8 Hz, H-9b), 1.06 (3H, s, CH_3-14), 0.77 (3H, d, $J = 7$ Hz, CH_3-15); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.4 (C, C-11), 108.6 (CH_2, C-12), 75.8 (CH, C-1), 75.0 (C, C-10), 39.8 (C, C-5), 38.0 (CH, C-7), 36.1 (CH, C-4), 35.9 (CH_2, C-6), 29.2 (CH_2, C-9), 29.1 (CH_2, C-2), 25.1 (CH_2, C-3), 22.5 (CH_2, C-8), 22.4 (CH_3, C-13), 15.7 (CH_3, C-14), 15.2 (CH_3, C-15).

Treatment of Mairetolides A (1) and B (2) and Compound 3 with Zn. Zn powder (2 mg) and a drop of 2.5% H_2SO_4 aqueous solution were added to a methanolic solution (1 mL) of **1** (50 mg). The reaction mixture was stirred overnight at room temperature. The solvent was eliminated with an air flux and the residue purified by preparative TLC (hexane−Me_2CO, 4:1) to give 18 mg of **1** and 12 mg of **7**. The same treatment was applied to compounds **2** and **3**. Thus, **2** afforded 27 mg of recovered product, 7 mg of **5**, and 15 mg of **9**, and compound **3** gave 31 mg of recovered product and 5 mg of **4**.

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Supporting Information Available: Copies of the ^1H NMR spectra of mairetolides A−H (**1**, **2**, **4**−**7**, **9**, and **10**) and mairetin (**13**) are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(24) Crystallographic data for the structures reported in this paper (Nos. CCDC 619392, 619393, 619394, and 619395) have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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