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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-8 α -methoxyeremophilanolide (**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}

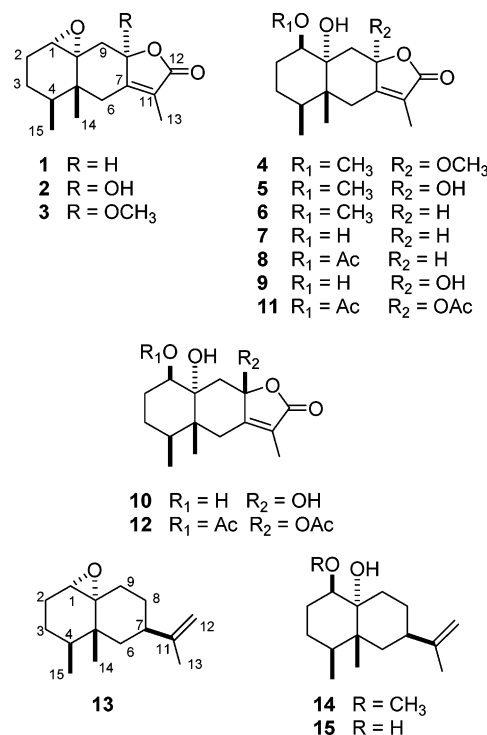
Considering the above, and in continuation of our systematic chemical research of Mexican *Senecio* species,^{11,12} we undertook a study of the roots and aerial parts of *Senecio mairetianus* D.C. This study afforded several new eremophilanolides (**1**, **2**, **4**–**7**, **9**, **10**), a new eremophilane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

Results and Discussion

The CH₃OH extract of roots was acidified and extracted with CHCl₃. The acidic aqueous solution was treated with a reductive procedure to afford the alkaloid residue, from which the known pyrrolizidine alkaloids senecionine¹⁴ and integerrimine² were obtained. The CHCl₃ extract afforded the new eremophilanolides **1** and **2** and the known 1,10-epoxy-8 α -methoxyeremophilanolide (**3**).¹³

Compound **1**, named mairetolide A (C₁₅H₂₀O₃), presented bands in the IR spectrum attributed to a conjugated γ -lactone (1747 and 1689 cm^{−1}). The ¹³C 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 sp² 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 (CH₃-13, CH₃-14, CH₃-15, 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 CH₃-14 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 CH₃-14 and CH₃-15,¹⁵ which indicated the



trans-decalin system of mairetolide A (**1**). The COSY spectrum showed cross peaks of CH₃-13 with H-6 α (δ 2.21) and H-8 (δ 4.91), which suggested dihedral angles of about 90° for H-6 α 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-6 α with H-4 and CH₃-15 and of H-6 β with CH₃-13, CH₃-14, and CH₃-15. 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, C₁₅H₂₀O₄) 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 ¹³C 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-8 α -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 (OCH₃) and 105.8 (C-8) in the ¹H and ¹³C 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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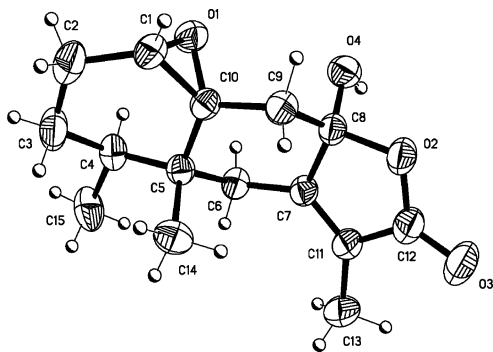


Figure 1. ORTEP projection of **2** (crystallographic numbering).

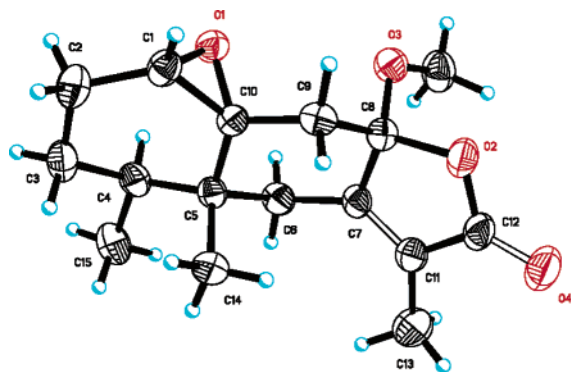


Figure 2. ORTEP projection of **3** (crystallographic numbering).

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 CH₃OH 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 senecionine¹⁴ and integerrimine² and the eremophilanolides mairetolides A, C–F, and H (**1**, **4**–**7**, and **10**) were obtained. The second portion of the CH₃OH 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**), C₁₇H₂₆O₅, 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 ¹³C 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 OCH₃ (δ 3.24) at C-1 was supported by the NOE effect between this group and CH₃-14 (δ 0.78). The *trans*-decalin system was deduced on the basis of the chemical shifts of CH₃-14 (δ 0.78) and CH₃-15 (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 OCH₃ groups were essential to the proposed structures. Mairetolides D (**5**) and E (**6**) both showed a

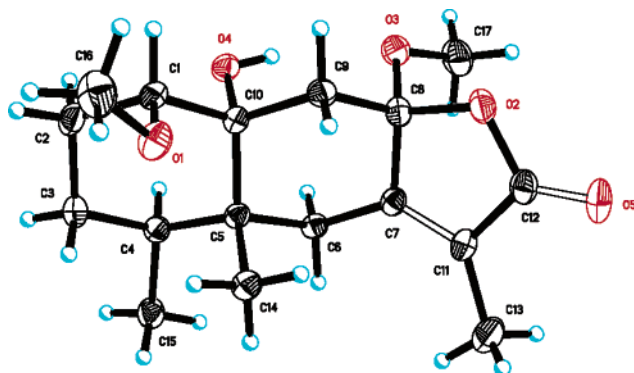


Figure 3. ORTEP projection of **4** (crystallographic numbering).

signal attributable to an OCH₃ 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 ¹³C 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 OCH₃ at C-1 of compounds **5** and **6** was deduced from the NOE effect of this group with CH₃-14. The hydroxyl group at C-1 of **7** was also β -orientated, since the NOESY spectrum of 1-*O*-acetylmairitolide F (**8**), obtained by acetylation of **7**, showed cross-peaks between the acetyl group and CH₃-14.

Mairetolides G (**9**) and H (**10**) displayed the same molecular formula, C₁₅H₂₂O₅, 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 CH₃-14 at relatively higher field (**11**: δ 0.85, **12**: δ 0.86) in relation to that of CH₃-15 (δ 0.89), which indicated the presence of a *trans*-decalin system in both compounds. The NOESY spectrum of **11** showed correlations of CH₃-14 with Ac-1 (δ 2.03) and of H-6 α (δ 2.44) with Ac-8 (δ 2.06) and H-4 (δ 2.18). Compound **12** showed cross-peaks of CH₃-14 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-epimairitolide G. An X-ray crystallographic analysis of **9** confirmed its structure (Figure 4).

Mairetin (**13**) exhibited 15 signals in the ¹³C 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 sp² carbons (C and CH₂). The signals of CH₃-13 (δ 1.80), CH₃-14 (δ 0.97), CH₃-15 (δ 0.71), and CH₂-12 (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 CH₃OH/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

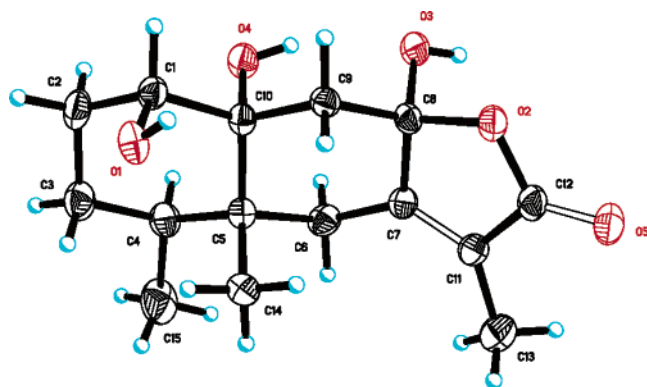


Figure 4. ORTEP projection of **9** (crystallographic numbering).

of **14** showed the coupling of H-1 with OCH₃, and in the NOESY spectrum cross-peaks of CH₃-14 with OCH₃, CH₃-13, and H-12a were observed. The above indicated that CH₃OH and H₂O 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 CH₃OH extract of the aerial parts treated with Zn/H⁺ to obtain the alkaloidal residue. These compounds, except for **1**, presented either OH or OCH₃ groups at C-1 and an OH at C-10. Structural relationships of **4**–**7** with **1**–**3** suggested that treatment of the CH₃OH extract with Zn/H⁺ induced the opening of the epoxides. To support the above assumption, compounds **1**–**3** were each dissolved in CH₃OH and treated with Zn/H₂SO₄. 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 μ A, 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-100UV₂₅₄ plates (Macherey-Nagel). X-ray crystallographic analyses were realized on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo K α 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 CH₃OH, which was evaporated until 0.5 L of solution remained. This was acidified with 2.5% aqueous H₂SO₄ and extracted with CHCl₃ 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 NH₄OH and extracted with CHCl₃ to yield 5.6 g of alkaloidal residue. This last gave, after

successive crystallizations, 204 mg of senecionine,¹⁴ mp 226–230 °C (CH₃OH), and 362 mg of integerrimine,² mp 173–175 °C (*i*-PrOH–Me₂CO). The mother liqueurs were purified by VCC (CHCl₃–CH₃OH polarity gradient) to afford 1.0 g of integerrimine. The nonalkaloidal residue was submitted to VCC (hexane–Me₂CO polarity gradient) to obtain fractions 1A–3A. Fraction 1A was purified by VCC (hexane–CHCl₃ 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 CH₃OH to yield 543 g of extract. Half of the extract (271 g) was dissolved in CH₃OH (500 mL), acidified (2.5% H₂SO₄), and treated with 85 g of Zn powder. The mixture was stirred overnight, filtered, washed with CHCl₃, basified with NH₄OH, and extracted with CHCl₃ to afford 27 g of alkaloidal residue. The latter was fractionated by VCC (CHCl₃–CH₃OH polarity gradient) to give fractions 1B–3B. Purification of fraction 1B by successive VCC (hexane–CHCl₃–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 CH₃OH extract (272 g) was fractionated by VCC (CH₂Cl₂–CH₃OH) and yielded fractions 1C–3C. Fraction 1C, after VCC (hexane–EtOAc polarity gradient), afforded fractions 1C₁–1C₅. Compound **13** (340 mg) and lupeortlandol¹⁷ (30 mg), mp 211–212 °C (Me₂CO), were obtained from fraction 1C₁ (flash chromatography, hexane–CH₂Cl₂ 9:1). Fraction 1C₂ was submitted to VCC (hexane–EtOAc 19:1) to give 250 mg of **1**. Similar treatment of fraction 1C₄ afforded 35 mg of 10 α -hydroxy-1-oxoeremophila-7(11),8(9)-dien-12,8-olide,¹⁸ mp 196–197 °C (hexane–EtOAc). Fraction 1C₃ gave 850 mg of **3** after its purification (VCC, CH₂Cl₂). Fraction 1C₅ yielded 950 mg of **2**. Fraction 2C, after successive VCC (CHCl₃–Me₂CO–CH₃OH polarity gradient, hexane–EtOAc–CH₃OH polarity gradient) gave 72 mg of **7**, 63 mg of **9**, 45 mg of quercetin,¹⁹ mp 310–312 °C (CH₃OH), and residue A. The latter was purified by VCC (CH₂Cl₂–CH₃OH, 19:1) to afford 102 mg of isorhamnetin-3 β -D-(1-*O*-acetyl) glucoside,²⁰ mp 166–167 °C (CH₃OH). Fraction 3C was fractionated by VCC (hexane–EtOAc, 3:7) into 3C₁–3C₃. From fraction 3C₁ 300 mg of quercetin 3-*O*-(6'-*O*-acetyl)- β -D-glucopyranoside,²¹ mp 245–247 °C (CH₃OH), was obtained. Purification of fraction 3C₂ (VCC, EtOAc) yielded 450 mg of the latter compound and a residue whose purification by Sephadex column (CH₃OH–H₂O gradient system) gave 180 mg of arbutin,²² mp 196–198 °C (CH₃OH), and 72 mg of isorhamnetin-3-glucoside,²³ mp 168–170 °C (CH₃OH). Fraction 3C₃ was purified by Sephadex column (CH₃OH–H₂O 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 (CH₃OH).

Mairetolide A (1): white crystals (hexane), mp 97–99 °C; [α]_D²⁰ –193.0 (*c* 0.2, CHCl₃); UV (THF) λ_{\max} (log ϵ) 219 (4.16) nm; IR (CHCl₃) ν_{\max} 1747, 1686 cm^{–1}; ¹H NMR (CDCl₃, 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-6 β), 2.21 (1H, br d, *J* = 13.5 Hz, H-6 α), 2.06 (2H, m, CH₂-2), 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, CH₃-13), 1.26 (2H, m, CH₂-3), 0.83 (3H, d, *J* = 7 Hz, CH₃-15), 0.82 (3H, s, CH₃-14); ¹³C NMR (CDCl₃, 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 (CH₂, C-9), 35.0 (CH₂, C-6), 32.5 (CH, C-4), 24.9 (CH₂, C-3), 22.2 (CH₂, C-2), 15.2 (CH₃, C-15), 14.9 (CH₃, C-14), 8.1 (CH₃, 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 C₁₅H₂₁O₃, 249.1491).

Mairetolide B (2): white crystals (hexane–EtOAc), mp 155–156 °C; [α]_D²⁰ –149.5 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{\max} (log ϵ) 220 (4.09) nm; IR (CHCl₃) ν_{\max} 3566, 1765, 1698 cm^{–1}; ¹H NMR (CDCl₃, 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-6 β), 2.43, 1.76 (each 1H, d, *J* = 14 Hz, CH₂-9), 2.38 (1H, br d, *J* = 13.5 Hz, H-6 α), 1.98 (3H, m, CH₂-2 and CH-4), 1.85 (3H, d, *J* = 1.5 Hz, CH₃-13), 1.28 (2H, m, CH₂-3), 0.84 (3H, d, *J* = 6.3 Hz, CH₃-15), 0.83 (3H, s, CH₃-14); ¹³C NMR (CDCl₃, 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 (CH₂, C-9), 39.5 (C, C-5),

33.4 (CH₂, C-6), 33.1 (CH, C-4), 24.6 (CH₂, C-3), 21.3 (CH₂, C-2), 15.2 (CH₃, C-15), 14.6 (CH₃, C-14), 8.1 (CH₃, 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 C₁₅H₂₁O₄, 265.1440).

Crystal data of 2:²⁴ C₁₅H₂₀O₄, *M_r* 264.31, monoclinic, space group *P*₂₁, *a* = 10.058(1) Å, *b* = 90.00°, *c* = 6.672(1) Å, *β* = 108.079(2)°, *V* = 10.968(1) Å³; *γ* = 90.00°, *D_c* = 699.7(1) Å³, *Z* = 2, *D_c* = 1.255 g cm⁻³, *F*(000) = 284; crystal dimensions 0.468 × 0.218 × 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 C₁₅H₂₀O₄, *M_r* 278.34, monoclinic, space group *P*₂₁, *a* = 10.402(2) Å, *b* = 6.875(1) Å, *c* = 10.640(3) Å, *β* = 106.640(3)°, *V* = 10.880(2) Å³; *γ* = 90.00°, *D_c* = 745.5(2) Å³, *Z* = 2, *D_c* = 1.240 g cm⁻³, *F*(000) = 300; crystal dimensions 0.374 × 0.152 × 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; [α]_D²⁵ –130.5 (*c* 0.2, CHCl₃); UV (CH₃OH) λ_{max} (log *ε*) 225 (4.07) nm; IR (CHCl₃) ν_{max} 3510, 1759, 1688 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.02 (1H, br s, OH-10), 3.24 (3H, s, OCH₃-1), 3.15 (3H, s, OCH₃-8), 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, CH₃-13), 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, CH₃-15), 0.78 (3H, d, *J* = 0.6 Hz, CH₃-14); ¹³C NMR (CDCl₃, 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 (CH₃, OCH₃-1), 50.1 (CH, OCH₃-8), 45.1 (C, C-5), 41.8 (CH₂, C-9), 34.6 (CH, C-4), 33.6 (CH₂, C-6), 25.7 (CH₂, C-3), 22.9 (CH₂, C-2), 15.3 (CH₃, C-15), 14.1 (CH₃, C-14), 8.3 (CH₃, 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 C₁₇H₂₇O₅, 311.1858).

Crystal data of 4:²⁴ C₁₇H₂₆O₅, *M_r* 310.38, orthorhombic, space group *P*₂₁2₁2₁, *a* = 11.573(1) Å, *b* = 11.709(1) Å, *c* = 90.00°, *V* = 12.221(1) Å³; *γ* = 90.00°, *D_c* = 1656.0(2) Å³, *Z* = 4, *D_c* = 1.245 g cm⁻³, *F*(000) = 672; crystal dimensions 0.362 × 0.150 × 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; [α]_D²⁵ –111.0 (*c* 0.2, CHCl₃); UV (CH₃OH) λ_{max} (log *ε*) 224 (3.90) nm; IR (CHCl₃) ν_{max} 3539, 3318, 1762, 1687 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.24 (3H, s, OCH₃-1), 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, CH₂-6), 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, CH₃-13), 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, CH₃-15), 0.77 (3H, s, CH₃-14); ¹³C NMR (CDCl₃, 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 (CH₃, OCH₃-1), 44.8 (C, C-5), 41.8 (CH₂, C-9), 34.7 (CH, C-4), 33.4 (CH₂, C-6), 25.6 (CH₂, C-3), 22.9 (CH₂, C-2), 15.3 (CH₃, C-15), 14.1 (CH₃, C-14), 8.1 (CH₃, 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 C₁₆H₂₅O₅, 297.1702).

Mairetolide E (6): white crystals (hexane–EtOAc), mp 165–170 °C; [α]_D²⁵ –106.5 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{max} (log *ε*) 224 (4.23) nm; IR (CHCl₃) ν_{max} 3594, 1740, 1682 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 5.08 (1H, dd, *J* = 9.7, 8.2 Hz, H-8), 3.26 (3H, s, OCH₃-1), 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, CH₃-13), 1.82 (2H, m, CH₂-2), 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, CH₃-15), 0.80 (3H, s, CH₃-14); ¹³C NMR (CDCl₃, 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 (CH₃, OCH₃-1), 43.1 (C, C-5), 40.1 (CH₂, C-9), 35.4 (CH, C-4), 34.8 (CH₂, C-6), 25.5 (CH₂, C-3), 23.4 (CH₂, C-2), 15.5 (CH₃, C-15), 14.3 (CH₃, C-14), 8.1 (CH₃, 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 C₁₆H₂₅O₄, 281.1753).

Mairetolide F (7): white crystals (hexane–EtOAc), mp 176–178 °C; [α]_D²⁵ –120.0 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{max} (log *ε*) 224 (4.20) nm; IR (CHCl₃) ν_{max} 3614, 1738, 1679 cm⁻¹; ¹H NMR (CDCl₃, 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, CH₂-6), 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, CH₃-13), 1.65 (1H, m, H-2b), 1.60 (1H, dddd, *J* = 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, CH₃-15), 0.89 (3H, s, CH₃-14); ¹³C NMR (CDCl₃, 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 (CH₂, C-9), 35.3 (CH, C-4), 35.1 (CH₂, C-6), 29.1 (CH₂, C-2), 25.3 (CH₂, C-3), 15.5 (CH₃, C-15), 14.6 (CH₃, C-14), 8.1 (CH₃, 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 C₁₅H₂₃O₄, 267.1596).

Mairetolide G (9): white crystals (hexane–Me₂CO), mp 234–238 °C; [α]_D²⁵ –95.0 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{max} (log *ε*) 224 (4.25) nm; IR (nujol) ν_{max} 3481, 3397, 1761, 1687 cm⁻¹; ¹H NMR (CH₃OH-*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, CH₃-13), 1.58 (1H, m, H-3β), 1.54 (1H, m, H-2b), 1.28 (1H, m, H-3α), 0.878 (3H, s, CH₃-14), 0.875 (3H, d, *J* = 6.7 Hz, CH₃-15); ¹³C NMR (CH₃OH-*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 (CH₂, C-9), 36.1 (CH, C-4), 34.7 (CH₂, C-6), 29.6 (CH₂, C-2), 27.0 (CH₂, C-3), 15.9 (CH₃, C-15), 15.0 (CH₃, C-14), 8.3 (CH₃, 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 C₁₅H₂₃O₅, 283.1545).

Crystal data of 9:²⁴ C₁₅H₂₂O₅, *M_r* 282.33, orthorhombic, space group *P*₂₁2₁2₁, *a* = 7.451(1) Å, *b* = 7.730(1) Å, *c* = 90.00°, *V* = 25.649(2) Å³; *γ* = 90.00°, *D_c* = 1477.3(3) Å³, *Z* = 4, *D_c* = 1.269 g cm⁻³, *F*(000) = 608; crystal dimensions 0.36 × 0.20 × 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; [α]_D²⁵ –103.0 (*c* 0.2, CH₃OH); UV (CH₃OH) λ_{max} (log *ε*) 220 (4.27) nm; IR (CHCl₃) ν_{max} 3627, 3394, 3319, 1751, 1687 cm⁻¹; ¹H NMR (CH₃OH-*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, CH₃-13), 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, CH₃-14), 0.861 (3H, d, *J* = 6.5 Hz, CH₃-15); ¹³C NMR (CH₃OH-*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 (CH₂, C-9), 36.2 (CH, C-4), 35.1 (CH₂, C-6), 29.6 (CH₂, C-2), 26.9 (CH₂, C-3), 15.7 (CH₃, C-15), 14.8 (CH₃, C-14), 8.3 (CH₃, 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 C₁₅H₂₂O₅, 282.1467).

Mairetin (13): thin needles (hexane), mp 70–71 °C; [α]_D²⁵ –77.5 (*c* 0.2, CHCl₃); IR (CHCl₃) ν_{max} 3085, 1640, 886 cm⁻¹; ¹H NMR (CDCl₃, 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, CH₃-13), 1.70 (1H, dqd, *J* = 7, 7.4 Hz, H-4), 1.57 (1H, dd, *J* = 13.5, 7 Hz, H-6α), 1.17 (2H, m, CH₂-3), 1.00 (1H, ddd, *J* = 14, 10.5, 4.5 Hz, H-9α), 0.97 (3H, s, CH₃-14),

0.86 (1H, ddd, $J = 9, 6, 3$ Hz, H-2 β), 0.71 (3H, d, $J = 7$ Hz, CH₃-15); ¹³C NMR (CDCl₃, 75 MHz) δ 149.6 (C, C-11), 108.7 (C H₂, C-12), 66.3 (C, C-10), 59.3 (CH, C-1), 38.6 (CH, C-7), 36.0 (CH₂, C-6), 36.0 (C, C-5), 34.2 (CH, C-4), 28.0 (CH₂, C-9), 24.7 (CH₂, C-8), 24.3 (CH₂, C-3), 22.5 (CH₂, C-2), 22.3 (CH₃, C-13), 15.8 (CH₃, C-14), 15.2 (CH₃, C-15); EIMS m/z 220 [M]⁺ (20), 202 (30), 110 (98), 95 (100), 81 (87); HRFABMS m/z 221.1901 (calcd for C₁₅H₂₅O, 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 (CDCl₃, 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, CH₂-6), 2.17 (1H, dd, $J = 13, 7.3$ Hz, H-9 α), 2.10 (2H, m, H-2 α and H-4), 1.82 (3H, d, $J = 1.7$ Hz, CH₃-13), 2.03 (3H, s, AcO), 1.77 (1H, dd, $J = 13, 10$ Hz, H-9 β), 1.66 (1H, dddd, $J = 15, 4, 2.3, 2.3$ Hz, H-2 β), 1.48 (1H, dddd, $J = 14, 14, 4$ Hz, H-3 β), 1.37 (1H, m, H-3 α), 0.91 (3H, d, $J = 6.8$ Hz, CH₃-15), 0.86 (3H, s, CH₃-14). Compound **11**: white crystals (hexane–EtOAc), mp 156–159 °C; ¹H NMR (CDCl₃, 300 MHz) δ 4.76 (1H, dd, $J = 3.2, 2.6$ Hz, H-1), 2.49 (1H, d, $J = 14$ Hz, H-6 β), 2.44 (1H, br d, $J = 14$ Hz, H-6 α), 2.36 (1H, d, $J = 15$ Hz, H-9 β), 2.18 (1H, m, H-4), 2.12 (1H, d, $J = 15$ Hz, H-9 α), 2.12 (1H, m, H-2 α), 2.06 (3H, s, AcO-8), 2.03 (3H, s, AcO-1), 1.88 (3H, d, $J = 0.9$ Hz, CH₃-13), 1.64 (1H, dddd, $J = 15, 4, 2.5, 2.5$ Hz, H-2 β), 1.45 (1H, dddd, $J = 14, 14, 4$ Hz, H-3 β), 1.40 (1H, m, H-3 α), 0.89 (3H, d, $J = 6.7$ Hz, CH₃-15), 0.85 (3H, s, CH₃-14). Compound **12**: colorless oil; ¹H NMR (CDCl₃, 500 MHz) δ 4.76 (1H, dd, $J = 2.5, 2.5$ Hz, H-1), 2.42 (2H, s, CH₂-6), 2.25 (1H, d, $J = 14$ Hz, H-9 β), 2.13 (2H, m, H-2 α and H-4), 2.03 (1H, d, $J = 14$ Hz, H-9 α), 2.03 (3H, s, AcO-1), 1.93 (3H, s, AcO-8), 1.87 (3H, br s, CH₃-13), 1.64 (1H, dddd, $J = 15, 4, 2, 2$ Hz, H-2 β), 1.47 (1H, dddd, $J = 14, 13.5, 13.5, 4$ Hz, H-3 β), 1.39 (1H, m, H-3 α), 0.89 (3H, d, $J = 7$ Hz, CH₃-15), 0.86 (3H, s, CH₃-14).

Methanolysis of Mairetin (13). A solution of **13** (38 mg) and concentrated H₂SO₄ (1.4 mg in 0.2 mL of H₂O) in CH₃OH (5 mL) was stirred for 4 h at room temperature. The reaction mixture was extracted with ether and purified by preparative TLC (hexane–Me₂CO, 4:1) to obtain 11 mg of **14** and 16 mg of **15**. Compound **14**: colorless oil; IR (CHCl₃) ν_{\max} 3456, 2930, 1641, 1460 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 4.93 (1H, br s, H-12a), 4.86 (1H, br q, $J = 1$ Hz, H-12b), 3.04 (3H, s, CH₃-3), 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, CH₂-8), 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, CH₃-13), 1.65 (2H, m, CH₂-6), 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, CH₃-14), 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, CH₃-15); ¹³C NMR (CDCl₃, 125 MHz) δ 150.7 (C, C-11), 108.8 (CH₂, C-12), 85.7 (CH, C-1), 75.0 (C, C-10), 57.3 (CH₃, OCH₃), 40.3 (C, C-5), 38.6 (CH, C-7), 36.4 (CH, C-4), 36.2 (CH₂, C-6), 29.9 (CH₂, C-9), 26.0 (CH₂, C-3), 24.0 (CH₂, C-2), 22.9 (CH₂, C-8), 22.4 (CH₃, C-13), 15.7 (CH₃, C-14), 15.4 (CH₃, C-15). Compound **15**: colorless oil; IR (CHCl₃) ν_{\max} 3461, 2933, 1640, 1456 cm⁻¹; ¹H NMR (CDCl₃, 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, CH₂-8), 1.79 (3H, dd, $J = 1.5, 1$ Hz, CH₃-13), 1.74 (1H, m, H-4), 1.65 (2H, br d, $J = 5.2$ Hz, CH₂-6), 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, CH₃-14), 0.77 (3H, d, $J = 7$ Hz, CH₃-15); ¹³C NMR (CDCl₃, 75 MHz) δ 150.4 (C, C-11), 108.6 (CH₂, 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 (CH₂, C-6), 29.2 (CH₂, C-9), 29.1 (CH₂, C-2), 25.1 (CH₂, C-3), 22.5 (CH₂, C-8), 22.4 (CH₃, C-13), 15.7 (CH₃, C-14), 15.2 (CH₃, 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% H₂SO₄ 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–Me₂CO, 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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