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GRANDILOBALIDES A, B AND C, SESQUITERPENES FROM THE LIVERWORT *PORELLA GRANDILOBA*

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Key Word Index—*Porella grandiloba*; Hepaticae; pinguisane; grandilobalide; bryopterin B; perrottetianals; caespitenone; secoswartzianin A.

Abstract—Three new pinguisane-type sesquiterpenes, named grandilobalide A, B, and 6α-hydroxy-4,8-dimethoxycarbonyl-pinguis-11,6-olide, and a new rearranged pinguisane-type, named grandilobalide C, together with six known sesqui- and diterpenes, have been isolated from the liverwort *Porella grandiloba* grown in the field. Their structures have been elucidated on the basis of spectroscopic evidence and chemical correlation.
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INTRODUCTION

Pinguisane-type and rearranged pinguisane-type sesquiterpenes are widely distributed in liverworts [1–3]. In a previous paper, we have reported the structures and biosynthesis of pinguisane-type sesquiterpenes produced by axenic cultures of *Aneura pinguis* [4–6]. In our continuous study of pinguisane-type sesquiterpenes, we examined *Porella grandiloba* grown in the field. *P. grandiloba* is distributed in Far Eastern Asia, including deciduous broad-leaved forests in middle to northern Japan, and usually grows on rocks or bark in shaded places [7]. In earlier work, norpinguisone methyl ether (**6**), and perrottetianal A (**9**) have been isolated from *P. grandiloba* [8]. We report herein the isolation and the structural elucidation of four new sesquiterpenes, **1**–**4**, together with four known sesquiterpenes and two known diterpenes from *P. grandiloba*.

RESULTS AND DISCUSSION

The diethyl ether extracts of gametophytes of *P. grandiloba* grown in the field were separated into three fractions by column chromatography on Sephadex LH-20. Fr. 2 was further separated by the combination of vacuum liquid chromatography and HPLC (SiO_2, *n*-hexane–EtOAc or pentane-Et_2O mixtures as solvent systems) to afford grandilobalide A (**1**), 6α-hydroxy-4,8-dimethoxycarbonyl-pinguis-11,6-olide (**2**), grandilobalide B (**3**), and C (**4**), together with known, bryopterin B (**5**), norpinguisone methyl ester (**6**), caespitenone (**7**), secoswartzianin A (**8**), perrottetianal A (**9**) and perrottetianal B (**10**). Compounds **5**–**10** were identified by a direct comparison with their authentic data [9–14] (^1H and ^{13}C NMR spectra, and EIMS, $[\alpha]_D$ and mp data).

The molecular formula, $C_{15}H_{18}O_5$, of grandilobalide A (**1**) was determined by the EI-HR mass spectrum (246.1255, $[M]^+$; calcd 246.1256). The UV spectrum (225 nm) and IR spectrum (1720 cm^{-1}), together with ^{13}C NMR spectrum (δ_C 171.0), suggested the presence of a δ-lactone ring. The ^1H NMR spectrum displayed a singlet methyl (δ_H 1.34), a doublet methyl (δ_H 1.16), a singlet methine (δ_H 3.50), and two vinylic protons (δ_H 6.33, 7.28) with nine other protons. The ^{13}C NMR spectrum contained signals of two methyls, four methylenes, four methines and five quaternary carbons indicating two double bonds (δ_C 109.2, 113.7, 141.6, and 149.6) and one carboxyl group (δ_C 171.0). These observations and the seven double bond equivalents suggested **1** was a tetracyclic sesquiterpene. A ^1H-^1H COSY experiment established the sequences $C(3)H_2$-$C(2)H_2$-C(1)H-C(13)H_3. As followed from the ^1H and ^{13}C NMR data of **1**, this compound differed from bryopterin B (**5**) [9] by the presence of an additional methylene (δ_C 78.1), the absence of two methyls (δ_C 51.54, 51.8) and the absence of one carboxyl carbon signal. Additionally, the resonance of two methyl protons found in the ^1H NMR spectrum of **5** were replaced by two new doublet signals at δ_H 4.42 and 4.72. Thus, compound **1** has an ester linkage between C-15 and C-12 or between C-15 and C-14. However, the structure of **1** could not be resolved by ^1H-^{13}C

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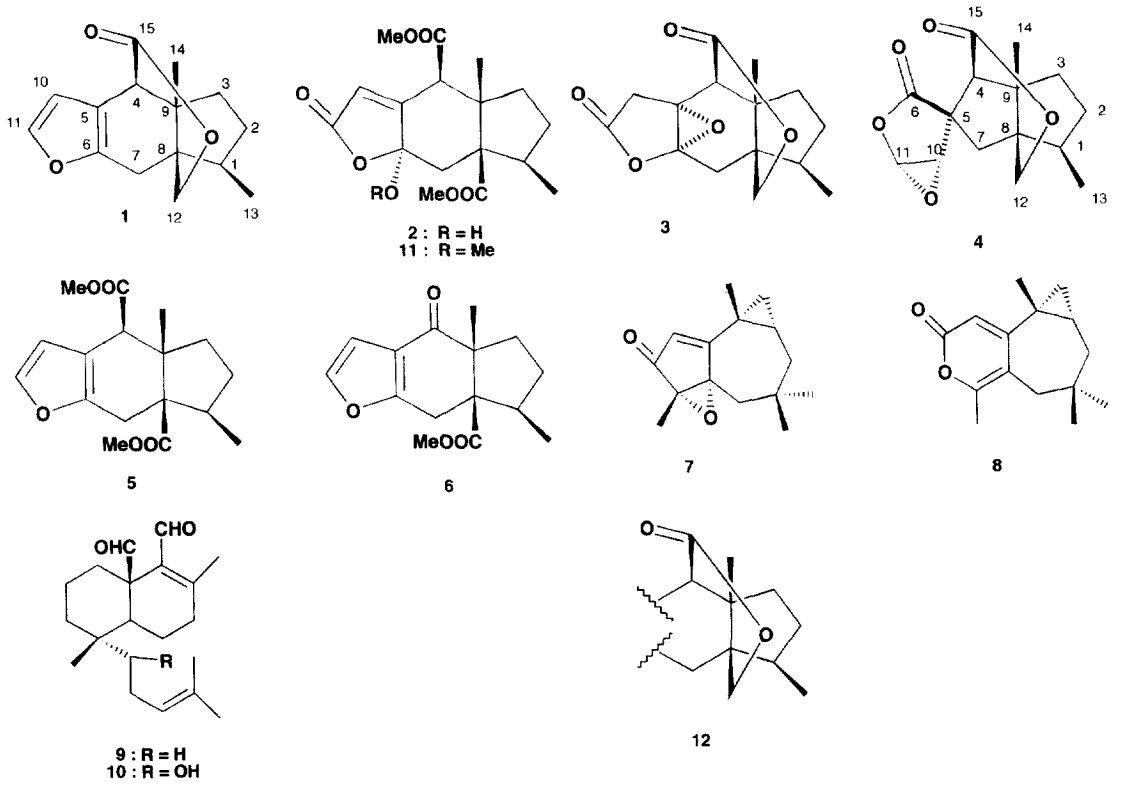

COSY and COLOC. The structure elucidation of **1** was finally completed by the NOE experiment and observed W letter coupling. The proton-proton NOE between H-7β (δ_H 2.92) and the signal at δ_H 4.42, and the W letter coupling between H-7α (δ_H 2.68) and the signal at δ_H 4.72 indicated that **1** is the 15,12-olide as shown in Fig. 1.

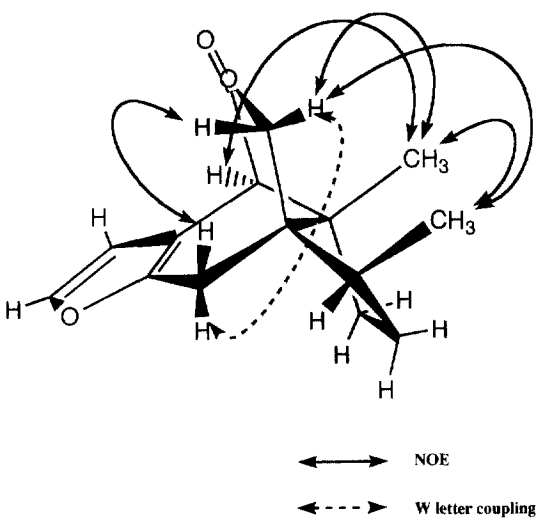

Fig. 1. NOEs and W letter couplings detected for grandilobalide A (**1**).

Compound **2** was an oil with a molecular formula, $C_{17}H_{22}O_7$ from its EI-HR mass spectrum (*m/z* 338.1390, $[M]^+$; calcd 338.1366). The UV spectrum (225 nm) and IR spectrum (1760, 1736 and 1650 cm^{-1}) together with ^{13}C NMR spectrum (δ_C 172.9, 169.8, and 169.5) suggested the presence of three carboxyl groups. The ^{13}C NMR spectrum also showed the signals indicating one conjugated double bond (δ_C 163.6 and 117.2) and one hemiacetal carbon (δ_C 103.6). The comparison of ^1H and ^{13}C NMR data of **2** with those for **5** allowed that compound **2** should be an analogous compound of **5** where the furan ring has been replaced by a 6-hydroxy-11,6-γ-butenolide moiety. The complete structure of **2** was achieved by following through ^1H (Table 1) and ^{13}C NMR (Table 2) assignment with ^1H–^1H COSY, ^1H–^{13}C COSY, ^1H–^1H homodecoupling, COLOC and NOESY. The α,β-conjugated γ-lactone ring of **2** was confirmed by H–H coupling (H-10 with H-4) observed by ^1H–^1H COSY and ^1H–^{13}C long range couplings (H-10 to C-6, C-11, and C-15; H-15 to C-5) by COLOC. The long range coupling between H-7α and H-10 resulted in a broad doublet of H-7α, showing that this hydrogen is equatorial. Proton-proton NOEs between H-7α and H-12, between H-7α and H-13, between H-7β and H-12, and between H-12 and H-13, were observed by NOESY. These observations indicated that the hydroxy group at C-6 was in the axial α-position. The oxidation of **5** with *m*-CPBA gave further confirmation of the structural relationship between **2** and **5**. Subsequent methy-

Table 1. ^{1}H NMR Data for compounds **1–4**

H-	1	2	3	4	4(C_6D_6, Δ)
1	2.23 *m*	3.02 *m*	2.13 *m*	2.28 *m*	1.55 *m* (0.73)
2α	2.40 *m*	2.11 *m*	1.74 *m*	2.45 *m*	1.80 *m* (0.65)
2β	1.41 *m*	1.66 *m*	1.64 *m*	1.75 *m*	0.97 *m* (0.78)
3α	1.70 *m*	1.73 *m*	2.40 *m*	1.91 *m*	1.16 *m* (0.83)
3β	1.56 *m*	1.73 *m*	1.36 *m*	1.79 *m*	0.96 *m* (0.83)
4	3.50 *s*	3.72 *d*, *J* = 2.0 Hz	3.21 *s*	3.25 *s*	3.25 *s* (0.00)
6					
7α	2.68 *d*, *J* = 17.8 Hz	2.55 *d*, *J* = 15.5 Hz	2.19 *dd*, *J* = 1.3, 16.1 Hz	1.99 *d*, *J* = 14.2 Hz	1.05 *d*, *J* = 14.2 Hz (0.94)
7β	2.92 *d*, *J* = 17.8 Hz	2.55 *d*, *J* = 15.5 Hz	2.75 *d*, *J* = 16.1 Hz	2.40 *d*, *J* = 14.2 Hz	1.79 *d*, *J* = 14.2 Hz (0.61)
10α	6.33 *s*	6.17 *d*, *J* = 2.0 Hz	3.23 *dd*, *J* = 1.0, 19.1 Hz	3.80 *d*, *J* = 2.1 Hz	2.70 *d*, *J* = 3.2 Hz (1.67)
10β			2.74 *d*, *J* = 19.1 Hz		
11	7.28 *d*, *J* = 1.6 Hz			5.59 *d*, *J* = 2.1 Hz	4.71 *d*, *J* = 2.3 Hz (0.88)
12a	4.42 *d*, *J* = 11.5 Hz		4.26 *d*, *J* = 12.1 Hz	4.51 *d*, *J* = 10.9 Hz	3.85 *d*, *J* = 10.9 Hz (0.66)
12b	4.72 *d*, *J* = 11.5 Hz		4.56 *d*, *J* = 12.1 Hz	4.55 *d*, *J* = 10.9 Hz	3.98 *dd*, *J* = 1.7, 10.9 Hz (0.57)
13	1.16 *dd*, *J* = 1.3, 7.6 Hz	0.93 *d*, *J* = 7.0 Hz	1.11 *d*, *J* = 7.6 Hz	1.04 *d*, *J* = 7.3 Hz	0.46 *d*, *J* = 4.6 Hz (0.58)
14	1.34 *s*	0.92 *s*	1.19 *d*, *J* = 0.7 Hz	1.29 *s*	0.81 *s* (0.48)
-OMe		3.67 *s*			
		3.79 *s*			

* 270 MHz in $CDCl_3$ and C_6D_6; solvent peaks as the int. standard.
^{1}H connectivities were determined by means of ^{1}H-^{1}H COSY and homodecoupling.

Table 2. ^{13}C NMR Data for compounds **1–4**

C-No.	1	2	3	4
1	41.2	37.1	42.1	38.2
2	31.5	29.0	30.9	33.5
3	31.6	35.0	32.2	34.6
4	49.4	48.2	50.2	62.3
5	113.7	163.6	58.0	53.3
6	149.6	103.6	85.7	178.5
7	39.0	36.9	37.4	47.3
8	43.8	54.3	44.6	53.0
9	45.5	61.7	41.9	54.0
10	109.2	117.9	38.6	59.1
11	141.6	172.9	172.1	77.7
12	78.1	169.8	76.0	75.3
13	19.6	15.2	19.8	19.3
14	23.8	17.5	23.7	19.8
15	171.0	169.5	165.5	169.2
-OMe		51.5		
		52.2		

* 67.5 MHz in $CDCl_3$, solvent peaks at the int. standard.
Bond types were distinguished by DEPT.
One-bond and long-range heteronuclear ^{1}H-^{13}C connectives were determined by ^{1}H-^{13}C COSY and COLOC, respectively.

lation of **2** with methanolic hydrogen chloride afforded **11** confirming the stereochemistry at the C-6 position by the observation of NOE between 6-OMe and H-7α in **11**.

Grandilobalide B (**3**) was a colorless oil with a molecular formula, $C_{15}H_{18}O_5$ from the EI-HR mass spectrum (*m/z* 278.1163, $[M]^+$; $C_{15}H_{18}O_5$, calcd 278.1154). ^{1}H NMR spectrum displayed one singlet methyl (δ_H 1.19), one doublet methyl (δ_H 1.11, *J* = 7.6 Hz), one singlet methine (δ_H 3.21), and three pairs of doublet signals which showed large geminal coupling constants (δ_H 2.19, 2.75, *J* = 16.1 Hz; δ_H 2.74, 3.23, *J* = 19.1 Hz; δ_H 4.26, 4.56, *J* = 12.1 Hz). The ^{13}C NMR spectrum displayed the signals of two methyls, five methylenes, two methines, and six quaternary carbons. These spectra were similar to those of **1** except for the furan ring moiety. The UV spectrum (218 nm) and IR spectrum (1810, 1740 cm^{-1}), together with ^{13}C NMR spectrum (δ_C 166.0, 172.5), suggested the presence of two carboxyl groups. Then, a remaining oxygen should be an epoxide due to seven double bond equivalents. The resonance of olefinic carbons found in the ^{13}C NMR spectrum of **1** which were assigned to a furan ring were replaced by new signals at δ_C 39.0 (CH_2), 58.5 (C), 86.2 (C), and 172.5 (C) in **3**. The ^{1}H NMR spectrum also showed the absence of olefinic protons H-10 and H-11, and the presence of new signals at δ_H 2.74 and 3.23 in **3**. Thus, the furan ring in **1** should be replaced by a 3,4-epoxy-γ-lactone ring in **3**. The complete structure of **3** was achieved through ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) assignments with ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, ^{1}H-^{1}H homodecoupling, COLOC and NOESY. The long range coupling between H-7α and H-10α resulted in a broad doublet showing that they were equatorial. Proton-proton NOEs between H-4 and H-7α, between H-7β and H-10β, between H-7β and H-12a, and between H-10β and Me-15 were observed by NOESY. From these observations, together with the low-field

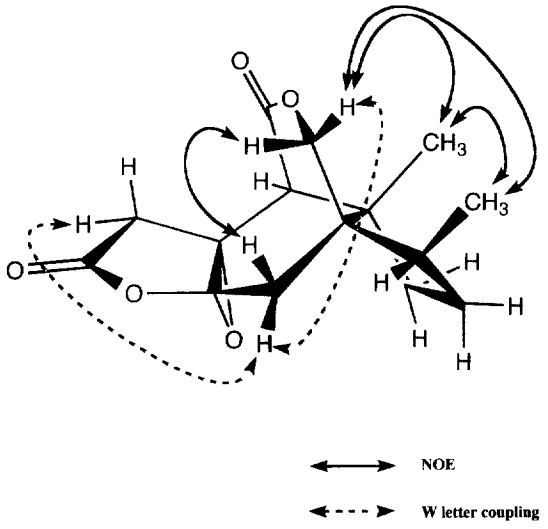

Fig. 2. NOEs and W letter couplings detected for grandilobalide B (**2**).

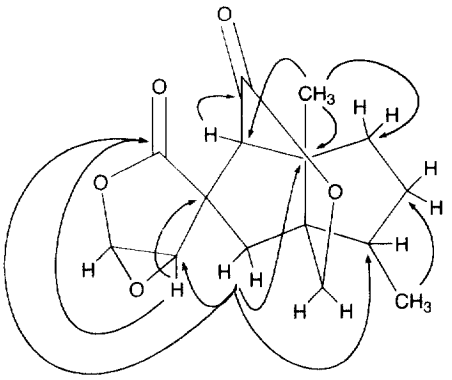

Fig. 3. Long-range correlation for grandilobalide C (**4**) detected by the COLOC spectrum.

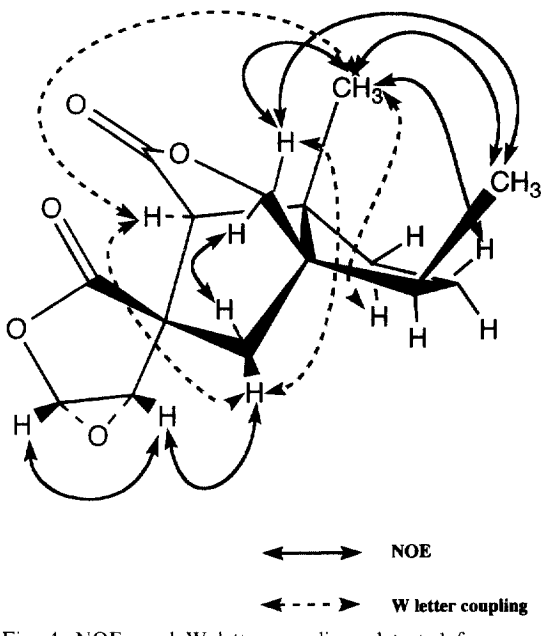

Fig. 4. NOEs and W letter couplings detected for grandilobalide C (**4**).

shift of H-7α and H-10α, the inspection of a model required the proposed configuration with the epoxide at C-5 and C-6 in the α-position (Fig. 2).

Grandilobalide C (**4**) was a colorless oil with a molecular formula, $C_{15}H_{18}O_5$ from EI-HRMS (*m/z* 279.1223 $[M+1]^+$ calcd 279.1233). The ^1H NMR and ^{13}C NMR spectra of **4** were also similar to those of **1** except for the signals due to the furan ring moiety. The ^{13}C NMR spectrum displayed the signals of two methyls, four methylenes, four methines and five quaternary carbons. ^1H–^1H COSY and ^1H–^{13}C COSY experiments suggested the partial structure **12**. The presence of a γ-lactone (1790 cm^{-1}) and a δ-lactone ring (1730 cm^{-1}), and the absence of hydroxyl or additional carbonyl groups, were evident from the IR spectrum. Thus, the remaining oxygen should constitute an ether linkage. This was further confirmed by the presence of the methine signals at δ_H 3.80 (δ_C 59.1) and δ_H 5.59 (δ_C 77.7) which were coupled with each other ($J = 2.1$ Hz). From these observations, compound **2** should be a rearranged pinguisane-type sesquiterpene having a spiro lactone moiety.

Furthermore, long range couplings between the methylene protons at C-7 and the carbons at C-6 and C-10, the proton at C-10 and the carbons at C-5 and C-6, observed by COLOC, revealed the structure of **4** (Fig. 3). Its stereochemistry was determined by W letter couplings and NOEs. The NOEs between H-10 and H-11, between H-10 and H-7α, between H-7β and H-12a, and between H-12b and H-13 and H-14 were observed. W letter couplings between H-4 and H-7α and between H-7α and H-12b were observed. From these observations, the inspection of a model of **4** required the proposed configurations as illustrated in Fig. 4. Comparison of ^1H NMR spectra of **4** in $CDCl_3$ and C_6D_6 indicated that the signals except for H-4 were all shifted substantially upfield in C_6D_6 relative to $CDCl_3$, while H-4 was virtually unchanged. This supported the suggestion that only H-4 was on the opposite face of γ-lactone ring from the epoxide hydrogens [15].

Porella species of liverworts produce various sesqui- and diterpenes [1]. An earlier work on *P. grandiloba* reported the isolation of norpinguisone methyl ester (**6**) and perrottetianal A (**9**), and the identification of α-pinene, camphene, α-phellandrene, β-elemene, and β-caryophyllene by GC-MS [8]. Recently, several new pinguisane-type sesquiterpenes have been isolated from members of the Porellaceae [1]. Our results showed that *P. grandiloba* produces not only known sesqui- and diterpenes, but also new pinguisane- and rearranged pinguisane-type sesquiterpenes which have a highly oxygenated structure.

EXPERIMENTAL

General

Optical rotations were measured in $CHCl_3$. UV spectra were measured in EtOH. NMR spectra were recorded in $CDCl_3$ soln using a 270 MHz instrument (H; 270 MHz; C: 67.5 MHz) relative to $CHCl_3$ at δ_H 7.26 and $CDCl_3$ at δ_C 77.0, respectively. ^{13}C multiplicities were determined using the DEPT pulse sequence. IR: KBr pellet.

Plant materials

Porella grandiloba Lindb. was collected in June 1995 halfway up Poroshiri Mt., Japan, and identified by Dr T. Furuki. A voucher specimen was deposited at the Department of Bioresource Chemistry, Obihiro University of Agriculture and Veterinary Medicine, Japan.

Extraction and isolation

The air-dried ground material (74.6 g) of *P. grandiloba* was extracted with Et_2O and the extracts (1.43 g) were separated into three fractions by chromatography on a Sephadex LH-20 column (10 mm i.d. × 50 cm) with CH_2Cl_2–MeOH (1:1) as the eluent. Fr. 2 (1.045 g) was subjected to vacuum liquid chromatography (VLC) on silica gel eluted with *n*-hexane containing various concns of EtOAc to give six fractions: A (*n*-hexane–EtOAc 19:1) (317.5 mg), B (9:1) (220.6 mg), C (4:1) (194.4 mg), D (7:3) (80.0 mg), E (3:2) (63.4 mg), and F (2:3) (337.5 mg). A combination of VLC on silica gel (pentane–Et_2O) and HPLC (silica gel) (*n*-hexane–EtOAc, 9:1) of fr. A, resulted in the isolation of **5** (8.4 mg), **6** (29.3 mg), **7** (39.1 mg), and **9** (1.9 mg). A combination of VLC on silica gel (pentane–Et_2O) and HPLC (silica gel) (*n*-hexane–EtOAc, 9:1) of fr. B resulted in the isolation of **1** (16.0 mg) and **8** (1.3 mg). A combination of VLC on silica gel (pentane–Et_2O) and HPLC (silica gel) (*n*-hexane–EtOAc, 4:1) of fr. C resulted in the isolation of **10** (3.2 mg). A combination of VLC on silica gel (pentane–Et_2O) and HPLC (silica gel) *n*-hexane–EtOAc, 7:3) of fr. D resulted in the isolation of **2** (4.2 mg). A combination of VLC on silica gel (pentane–Et_2O) and HPLC (silica gel) (*n*-hexane–EtOAc, 3:2) of fr. E resulted in the isolation of **3** (5.0 mg). A combination of VLC on silica gel (pentane–Et_2O) and HPLC (silica gel) (*n*-hexane–EtOAc, 2:3) of fr. F resulted in the isolation of **4** (2.7 mg).

Grandilobalide A (**1**). $[\alpha]_D$ −84.0 (*c* 0.91 $CHCl_3$); EI-HRMS *m/z* 246.1255, $[M]^+$; $C_{15}H_{18}O_3$, calcd 246.1256. EIMS *m/z* (rel. int.): 246 (70.1), 218 (14.3), 202 (7.7), 187 (32.5), 159 (11.7), 145 (100), 131 (42.1), 107 (11.7), 91 (15.7), 77 (6.9), 41 (5.9). UV λ_{max} nm (log ε): 225 (3.79); IR ν_{max} cm^{-1}: 2900, 1720, 1190, 1180, 1090, 730. ^1H NMR and ^{13}C NMR: see Tables 1 and 2, respectively.

6α-Hydroxy-4,8-dimethoxycarbonyl-pinguis-11,6-olide (**2**). $[\alpha]_D$ −140.0 (*c* 0.21 $CHCl_3$). EI-HRMS *m/z* 338.1390, $[M]^+$; $C_{17}H_{22}O_7$, calcd 338.1365. EIMS *m/z* (rel. int.): 338 (22.3), 306 (33.3), 278 (62.7), 260 (95.8), 246 (53.4) 219 (31.9), 201 (100), 173 (38.7), 153 (77.9), 121 (41.0), 109 (39.3), 93 (65.0), 70 (16.6), 67 (14.4), 59 (12.7), 43 (8.3). UV λ_{max} nm (log ε): 225 (3.54). IR ν_{max} cm^{-1}: 3400, 2950, 1760, 1736, 1650, 1430, 1200, 1170, 730. ^1H NMR and ^{13}C NMR: see Tables 1 and 2, respectively.

Grandilobalide B (**3**). $[\alpha]_D$ −88.0 (*c* 0.25 $CHCl_3$). EI-HRMS *m/z* 278.1163, $[M]^+$; $C_{15}H_{18}O_5$, calcd 278.1154; EIMS *m/z* (rel. int.): 278 (7.1), 260 (23.8), 232 (15.1), 201 (31.3), 188 (29.9), 160 (100), 145 (26.6), 121 (22.6), 107 (88.8), 91 (49.0), 79 (26.7), 77 (20.6) 55 (17.3), 43 (16.4). UV λ_{max} nm (log ε): 218 (3.45). IR ν_{max} cm^{-1}: 2950, 1810, 1740, 1730, 1280, 1240, 1180, 1030, 1010, 840, 760. ^1H NMR and ^{13}C NMR: see Tables 1 and 2, respectively.

Grandilobalide C (**4**). $[\alpha]_D$ −93.3 (*c* 0.135 $CHCl_3$). EI-HRMS *m/z* 279.1233, $[M+1]^+$; $C_{15}H_{19}O_5$, calcd 279.1232; EIMS *m/z* (rel. int.): 279 (5.7), 249 (2.6), 235 (1.3), 205 (11.9), 190 (30.9), 175 (35.1), 148 (71.9), 122 (62.1), 105 (100), 91 (79.3), 79 (39.0), 41 (46.8). UV λ_{max} nm (log ε): 204 (2.87), 260 (1.69). IR ν_{max} cm^{-1}: 2950, 1790, 1730, 1400, 1250, 1150, 1080, 1050, 850. ^1H NMR and ^{13}C NMR: see Tables 1 and 2, respectively.

Oxidation of compound **1**. Compound **1** (5.7 mg) was oxidized with *m*-chloroperbenzoic acid (14.4 mg) in CH_2Cl_2 at 30° for 1 h. The reaction mixture was washed with 5% $NaHCO_3$, and dried over Na_2SO_4. The resultant solution was evaporated *in vacuo* to dryness and then chromatographed on a silica gel column (3 mm × 3 cm), followed by HPLC (silica gel, 4.6 mm i.d. × 250 mm) with *n*-hexane–EtOAc (60:40) to afford compound **2** (3.6 mg).

Methylation of compound **2**. Compound **2** (3.6 mg) was dissolved in 1 ml of 3% HCl/MeOH at room temp. After 1 h, the reaction mixture was diluted with 10 ml of H_2O, and then extracted (× 3) with Et_2O (10 ml). The Et_2O extract was dried over dry Na_2SO_4 overnight, evaporated *in vacuo* to dryness to afford compound **11** (2.2 mg).

6α-Methoxy-4,8-dimethoxycarbonyl-pinguis-11,6-olide (**11**). $[\alpha]_D$ −136 (*c* 0.10 $CHCl_3$). EI-HRMS *m/z* 352.1525, $[M]^+$; $C_{18}H_{24}O_7$, calcd 352.1522. UV λ_{max} nm (log ε): 226 (4.50), 260 (3.80). IR ν_{max} cm^{-1}: 3000, 1760, 1740, 1720, 1440, 1240, 1170, 920. ^1H NMR ($CDCl_3$): δ 0.93 (3H, *d*, *J* = 7.3 Hz, H-13), 0.94 (3H, *s*, H-14), 1.66 (1H, *m*, H-2α), 2.01 (1H, *m*, H-3β), 2.06 (1H, *m*, H-2β), 2.09 (1H, *m*, H-3α), 2.19 (1H, *d*, *J* = 15.3 Hz, H-7β), 2.59 (1H, *d*, *J* = 15.3 Hz, H-7α), 2.92 (1H, *m*, H-1), 3.17 (3H, *s*, 6-OMe), 3.48 (1H, *d*, *J* = 1.7 Hz, H-4), 3.66 (3H, *s*, 12-OMe), 3.79 (3H, *s*, 13-OMe), 6.29 (1H, *d*, *J* = 2.0 Hz, H-10). ^{13}C NMR: δ 15.4 (C-13), 17.4 (C-14), 29.0 (C-2), 35.0 (C-3), 36.0 (C-7), 37.2 (C-1), 48.3 (C-4), 50.6 (OMe), 51.5 (OMe), 52.3 (OMe), 54.2 (C-8), 61.8 (C-9), 106.3 (C-6), 119.2

(C-10), 161.8 (C-5), 169.3 (C-15), 169.4 (C-12), 172.9 (C-11).

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