Briarlides, Briarane Diterpenes from a Gorgonian *Briareum* sp.

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New briarane diterpenes, briarlides A−H (**1**−**8**), have been isolated from a gorgonian *Briareum* sp., collected at Amami Oshima, Kagoshima Prefecture. Their structures and cytotoxity toward Vero and MDCK cells are described.

The gorgonian soft corals belonging to the genus *Briareum* have been challenging targets for natural products chemists for the past decade, because they have produced many highly oxygenated briarane-type diterpenes that exhibit interesting biological activities such as cytotoxic,[1,2] anti-inflammatory,[3−5] antiviral,[3,6] insecticidal,[7,8] and antifouling activity.[9]

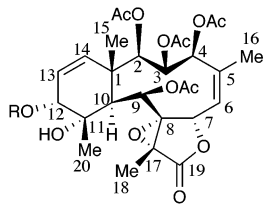
Our previous investigations of this organism, collected in the area of Bonotsu, Kagoshima Prefecture, have afforded a number of cytotoxic briarane-type diterpenes, and the relationship between the structure and cytotoxity was elucidated.[10−13]

We examined the chemical constituents of *Briareum* sp., collected at Amami Oshima in the southern region of Kagoshima Prefecture. As a result, eight new briarane-type diterpenes, **1**−**8**, which are designated as briarlides A−H, have been isolated. We report herein the isolation and structure elucidation of the new diterpenes as well as their cytotoxity toward Vero and MDCK cells.

Results and Discussion

The methanolic extract of *Briareum* sp. was partitioned between dichloromethane and water, and the organic extract was subjected to flash silica gel chromatography. Fractions eluting with 2−4% methanol−dichloromethane were purified by further silica gel chromatography and finally by C_{18} reversed-phase HPLC to yield compounds **1**−**9**.

Briarlide A (**1**) was obtained as an amorphous powder. The molecular formula of **1** was determined as $C_{30}H_{38}O_{14}$ by the HRFABMS and the NMR data (Table 1). The IR spectrum showed absorption bands due to a hydroxyl group (3545 cm^{-1}), a γ-lactone (1788 cm^{-1}), and ester carbonyls (1748 and 1229 cm^{-1}). Resonances due to four methyl protons (δ 1.16, s, 1.22, br s, 1.67, s, 2.20, d, J = 1.5 Hz, 3H each) and five acetyl protons (δ 2.02−2.31, 3H × 5, s) were observed in the ^{1}H NMR spectrum (Table 1). Nine oxygenated carbons (δ 64.7−76.7) and five acetyl carbons and a γ-lactone carbonyl carbon (δ 168.8−170.5, CO × 6, s) were observed in the ^{13}C NMR spectrum (Table 2). This suggested that briarlide A was typical of a highly oxygenated briarane-type diterpene, as often isolated from *Briareum* sp.[14] The ^{1}H NMR spectrum of **1** was similar to that of violide B (**9**),[10] except that the chemical shift of H-12 (δ 4.69, 1H, d, J = 6.6 Hz) was shifted downfield by 1.09 ppm when compared to that of **9**. In the ^{13}C NMR spectrum, resonances of C-12 (δ 73.1, d) were shifted downfield by



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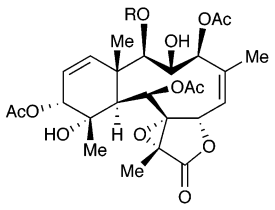

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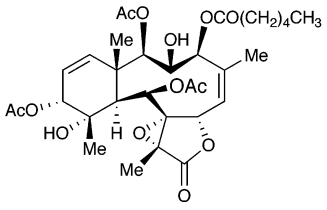

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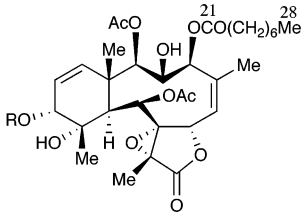

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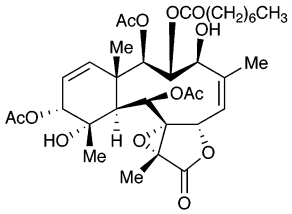

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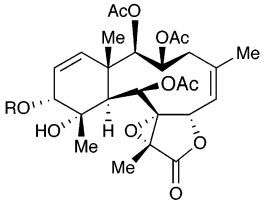

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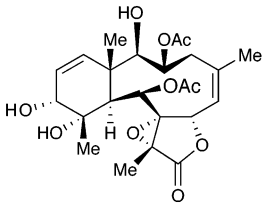

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Table 1. ^{1}H NMR Spectral Data of Compounds **1**−**8**[a]

no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
2	4.57 d (1.7)	4.64 br s	3.22 br d (8.4)	4.64 br s	4.64 br s	4.52 br s	4.67 br s	3.32 d (9.9)
3	6.09 dd (1.7, 10.3)	ca. 4.86 m	ca. 4.85 over.	4.84 br d (10.6)	4.84 br d (10.8)	5.99 br d (9.9)	5.57 dd (5.7, 12.7)	5.57 dd (5.0, 12.8)
4α	5.16 dd (0.9, 10.3)	4.88 d (10.6)	4.88 d (10.6)	4.90 d (10.6)	4.90 br d (10.8)	4.23 br dd (2.2, 9.9)	ca. 2.04 over.	2.99 br dd (5.0, 12.8)
4*β*							2.94 br dd (5.7, 12.7)	2.06 t (12.8)
6	5.60 br d (10.1)	5.51 br d (9.5)	5.46 br d (9.7)	5.50 br d (9.5)	5.51 br d (9.7)	5.61 br d (9.5)	5.47 br d (9.5)	5.38 br d (9.3)
7	5.95 d (10.1)	5.76 d (9.5)	5.71 d (9.7)	5.75 d (9.5)	5.75 d (9.7)	6.13 d (9.5)	5.73 d (9.5)	5.63 d (9.3)
9	5.97 d (4.2)	5.91 d (4.2)	5.91 over.	5.90 d (4.6)	5.90 d (4.4)	5.94 d (4.2)	5.90 d (4.2)	5.92 d (3.7)
10	2.77 d (4.2)	2.69 d (4.2)	2.48 d (4.0)	2.69 d (4.6)	2.70 d (4.4)	2.78 d (4.2)	2.73 d (4.2)	2.39 d (3.7)
12	4.69 d (6.6)	4.71 d (6.2)	4.75 d (6.2)	4.71 d (6.2)	4.71 d (6.1)	4.69 d (6.2)	4.71 d (6.0)	3.71 m
13	5.95 b dd (6.6, 10.3)	5.92 dd (6.2, 10.3)	5.91 over.	5.91 dd (6.2, 10.3)	5.91 dd (6.1, 10.4)	5.93 dd (6.2, 10.3)	5.92 dd (6.0, 10.3)	5.83 dd (6.2, 10.6)
14	5.57 d (10.3)	5.45 d (10.3)	6.02 d (10.3)	5.45 d (10.3)	5.45 d (10.4)	5.56 d (10.3)	5.51 d (10.3)	5.98 d (10.3)
15	1.16 s	1.33 s	1.20 s	1.33 s	1.33 s	1.16 s	1.15 s	1.03 s
16	2.20 d (1.5)	2.13 br s	2.04 d (1.1)	2.13 d (1.5)	2.13 br s	2.12 d (1.1)	2.01 br s	1.89 br s
18	1.67 s	1.69 s	1.69 s	1.69 s	1.69 s	1.67 s	1.68 s	1.69 s
20	1.22 br s	1.23 br s	1.23 br s	1.23 br s	1.23 br s	1.22 s	1.21 br s	1.14 b rs
*Me*CO	2.02, 2.07, 2.09, 2.16, 2.31, each s	2.07, 2.13, 2.21, 2.28 each s	2.05, 2.15, 2.26, each s	2.07, 2.20, 2.27, each s	2.07, 2.21, 2.27, each s	2.07, 2.15, 2.29, each s	2.08, 2.13, 2.13, 2.18, each s	2.10, 2.15, each s
$C_nH_{2n+1}CO$				0.88 3H t (6.8), ca. 1.29 8H m, ca. 1.62 2H over., 2.38 2H m	0.90 3H t (6.4), ca. 1.33 4H over. ca. 1.64 2H over. ca. 2.38 2H m	0.89 3H t (7.0), ca. 1.28 8H m, ca. 1.66 2H over., 2.40 2H m		

[a] Chemical shift values are in ppm from TMS, and *J* values (in Hz) are presented in parentheses.

Table 2. ^{13}C NMR Spectral Data of Compounds **1**−**8**

no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1	47.0	47.2	48.6	47.2	47.2	47.0	46.9	48.3
2	76.7	76.5	76.1	76.5	76.5[b]	77.5	77.5	77.8
3	70.8	71.2	70.8	71.3	71.3	73.3	71.4	72.3
4	76.1	76.8	77.8	76.5	76.6[b]	75.4	34.7	34.3
5	140.5	141.5	140.8	141.5	141.5	142.9	139.9	139.3
6	125.4	124.1	123.9	124.1	124.1	124.5	121.5	121.2
7	73.3	73.5	73.5	73.5	73.5	73.1	74.4	74.6
8	71.5	71.3	71.5	71.3	71.3	71.5	71.7	71.8
9	65.1	64.9	65.1	65.0	65.0	65.0	65.4	65.8
10	43.6	44.4	44.7	44.4	44.4	43.6	43.9	43.9
11	72.6	72.4	72.4	72.4	72.4	72.6	72.5	73.8
12	73.1	73.0	73.4	73.0	73.0	73.1	73.1	70.6
13	123.2	122.9	121.0	122.8	122.9	123.1	122.8	123.3
14	140.1	139.5	142.1	139.6	139.6	140.2	139.9	140.2
15	15.5	15.5	14.1	15.5	15.5	15.5	15.4	13.8
16	25.4	25.4	26.0	25.4	25.4	25.8	27.0	27.9
17	64.7	64.8	64.8	64.8	64.8	64.8	65.0	65.1
18	9.8	9.6	9.6	9.6	9.6	9.8	9.8	10.0
19	170.5	170.2	170.3	170.2	170.2	170.3	170.5	170.6
20	21.2	21.3	21.4	21.3	21.3	21.2	21.2	21.6
*Me*CO	20.5, 20.8, 20.9, 20.9, 21.3	20.8, 20.8, 21.1, 21.5	20.9, 21.0, 21.5	20.8, 20.8, 21.4	20.8, 20.8, 21.4	20.6, 20.9, 21.3	20.7, 20.8, 21.2, 21.2 168.9, 169.8	21.2, 21.2
Me*C*O	168.8, 169.7, 169.9, 169.9 170.5	168.4, 169.4, 169.7, 170.6	168.3, 169.7, 170.8	169.4, 169.4, 169.7	168.4, 169.4, 169.7	169.7, 169.8, 170.0	170.2, 170.2,	168.8, 169.2
$C_nH_{2n+1}CO$				14.1, 22.6, 24.9, 28.9, 29.0, 31.6, 34.3, 173.4	13.9, 22.3, 24.5, 31.2, 34.2, 173.4	14.0, 22.6, 25.0, 28.9, 29.1, 31.7, 34.5, 173.1		

[a] Chemical shift values for **1**−**4** and **6**−**8** are in ppm from TMS, and those for **5** from $CDCl_3$. [b] These values may be exchangeable.

3.0 ppm and those of C-11 (*δ* 72.6, s) and C-13 (*δ* 123.2, d) were shifted upfield by 1.4 and 2.2 ppm, respectively, in comparison with those of **9**. This implied that the 12-hydroxyl group was acetylated in **1**. The relative stereochemistry was elucidated by the coupling patterns in the ^{1}H NMR spectrum and NOE correlations similar to those of **9**. Thus, NOEs from H-20 (*δ* 1.22) to H-12 and H-15 (*δ* 1.16) indicated that these hydrogens were on the same

β-face. H-2 (δ 4.57, 1H, d, J = 1.7 Hz), which did not indicate correlation with H-15, was correlated with H-4 (δ 5.16, 1H, dd, J = 0.9, 10.3 Hz) and H-10 (δ 2.77, 1H, d, J = 4.2 Hz), suggesting that they were on the opposite face (α) from H-15. H-6 (δ 5.60, 1H, br d, J = 10.1 Hz) and H-16 (δ 2.20, J = 1.5 Hz) were concluded to be folded downward on the basis of NOEs from H-16 to H-4 and H-6. The β-configuration of H-7 (δ 5.95, 1H, d, J = 10.1 Hz) was evident from the large coupling constant between H-6 and H-7. H-3 (δ 6.09, 1H, dd, J = 1.7 and 10.3 Hz) was established to be α-oriented from the small coupling (J = 1.7 Hz) between H-2 and H-3 and an NOE between H-3 and H-7. The configuration of H-18 (δ 1.67) was assumed to be β from the similar chemical shifts of C-8 (δ 71.5, s), C-17 (δ 64.7, s), and C-18 (δ 9.8) in the ^{13}C NMR spectrum to those of **9**. The small coupling constant (J = 4.2 Hz) between H-9 and H-10 and NOEs from H-9 to H-15, H-18, and H-20 suggested the α-configuration of H-9. Briarlide A was, therefore, concluded to be 12-acetylviolide B.

The HRFABMS and the NMR data established the molecular formula $C_{28}H_{36}O_{13}$ for briarlide B (**2**), an amorphous solid. The IR absorption bands were indicative of hydroxyl groups (3526 cm^{-1}), a γ-lactone (1784 cm^{-1}), and ester carbonyls (1744 and 1235 cm^{-1}). The ^{1}H NMR spectrum was closely related to that of **1**, except that resonances due to an acetyl group in **1** were missing and the chemical shift of H-3 (δ ca. 4.86, 1H, m) was shifted upfield by 1.23 ppm, when compared to that of **1**. Therefore, briarlide B was elucidated as 3-deacetylbriarlide A. The presence of a hydroxyl group at C-3 was also supported by the lower-field chemical shift of H-15 (1.33, 3H, s) by 0.17 ppm in comparison with that of **1**. This shift was due to anisotropic deshielding by the C-3 hydroxyl group. The relative stereochemistry was deduced from the similar coupling patterns in the ^{1}H NMR spectrum and NOE correlations to those of **1**.

The molecular formula of briarlide C (**3**) was assigned as $C_{26}H_{34}O_{12}$ from the HRFABMS and NMR data. The ^{1}H NMR spectrum was very similar to that of **2**; however, an acetyl group was lost and the chemical shifts of H-2 and H-14 were shifted upfield by 1.42 ppm and downfield by 0.57 ppm, respectively, when compared to those of **2**. This suggested that briarlide C was 2-deacetylbriarlide B. The coupling patterns in the ^{1}H NMR spectrum and NOE correlations were identical with those of **2**.

Briarlide D (**4**), an amorphous solid, had the molecular formula $C_{34}H_{48}O_{13}$ on the basis of the HRFABMS and NMR data. The IR absorption bands indicated the presence of hydroxyl groups (3536 cm^{-1}), a γ-lactone (1784 cm^{-1}), and ester carbonyls (1744 and 1213 cm^{-1}) in the IR spectrum. The ^{1}H NMR spectrum was similar to that of **2**, except that an octanoate group (δ 0.88, 3H, t, J = 6.8 Hz; ca. 1.29, 8H, m; ca. 1.62, 2H, overlapped; 2.38, 2H, m) newly appeared and one of the acetoxyl groups in **2** disappeared. The presence of the octanoate group was also confirmed by the ^{13}C NMR spectrum (δ 14.1, q; 22.6, 24.9, 28.9, 29.0, 31.6, 34.3, each t; 173.4, s). The octanoate group was determined to be located at C-4 on the basis of the correlation of H-4 (δ 4.90, 1H, d, J = 10.6 Hz) with the ester carbonyl at C-21 (δ 173.4) in the HMBC spectrum. Moreover, the ^{1}H NMR spectrum of briarlide D was similar to that of violide A (**10**),[10] except for an additional acetyl group in **4**. The acetyl group was concluded to be positioned at C-12, since H-12 (δ 4.71, 1H, d, J = 6.2 Hz) was shifted downfield by 1.02 ppm when compared with that of **10**. From the above observations, briarlide D was assigned as 12-acetylviolide A. The relative stereochemistry was determined from the similar coupling patterns in the ^{1}H NMR spectrum and NOE correlations to those of **10**.

The molecular formula of briarlide E (**5**), an amorphous solid, was assigned as $C_{32}H_{44}O_{13}$ on the basis of HRFABMS and NMR data. It exhibited absorption bands for hydroxyl groups (3536 cm^{-1}), a γ-lactone (1784 cm^{-1}), and ester carbonyls (1744 and 1215 cm^{-1}). The ^{1}H NMR spectrum was essentially the same for **4**, except for resonances due to aliphatic protons. The molecular formula of **5** suggested that it contained a hexanoate group rather than an octanoate group. This was confirmed by the NMR data [δ_H 0.90 (3H, t, J = 6.4 Hz), ca. 1.33 (4H, overlapped), δ ca. 1.64 (2H, overlapped), ca. 2.38 (2H, m), δ_C 13.9 (q), 22.3, 24.5, 31.2, and 34.2 (each t), 173.4 (CO)]. The observation of HMBC correlation of H-4 (δ_H 4.90, 1H, d, J = 10.8 Hz) with C-21 (δ 173.4) allowed placement of the hexanoate group at the C-4 position. The relative stereochemistry was deduced from the similar coupling patterns in the ^{1}H NMR spectrum and NOE correlations to those of **4**.

Briarlide F (**6**) was an amorphous solid with the molecular formula $C_{34}H_{48}O_{13}$, deduced from the HRFABMS and the NMR data, and was isomeric with **4**. Comparison of the ^{1}H NMR spectrum of **6** with that of **4** indicated that the chemical shifts of H-3 (δ 5.99, 1H, br d, J = 9.9 Hz) were shifted downfield by 1.15, while those of H-4 (δ 4.23, 1H, br dd, J = 2.2, 9.9 Hz) were shifted upfield by 0.67 ppm, when compared to those of **4**. The remaining signals were similar to each other, suggesting that C-3 was acylated and C-4 was hydroxylated. The octanoate group was confirmed to be located at C-3 from the HMBC correlation between H-3 and C-21 (δ 173.1). The relative stereochemistry was defined on the basis of the similar coupling patterns in the ^{1}H NMR spectrum and NOE correlations to those of **2**−**5**. The structure of briarlide F was thus established as the structure **6**.

The IR spectrum of briarlide G (**7**), $C_{28}H_{36}O_{12}$, indicated the presence of a hydroxyl group (3544 cm^{-1}), a γ-lactone (1786 cm^{-1}), and ester carbonyls (1744 and 1231 cm^{-1}). The ^{1}H NMR spectrum indicated the presence of four acetyl groups (δ 2.08−2.18, 3H × 4, s). In the ^{1}H and ^{13}C NMR spectra, resonances due to the A and C rings were similar to those of **1**, **2**, and **4**−**6**, suggesting three of the four acetoxyl groups in the B ring. Comparison of the ^{1}H NMR spectrum of **7** with that of **1** showed only the difference of the absence of the acetoxyl group at C-4, since H-3 (δ 5.57, 1H, dd, J = 5.7, 12.7 Hz) was coupled to H-4 methylene protons (ca. 2.04, 1H, overlapped; 2.94, 1H, br dd, J = 5.7, 12.7 Hz). Briarlide G was, therefore, assigned as 4-deacetoxybriarlide A, or a 12-acetyl analogue of violide G (**11**).[11] On the basis of the proton−proton coupling patterns and NOE correlations, the relative stereochemistry of briarlide G was determined to have the structure **7**.

The molecular formula of briarlide H (**8**), an amorphous powder, was analyzed for $C_{24}H_{32}O_{10}$ by the HRFABMS and NMR data. The ^{1}H NMR spectrum was similar to that of **11** except that an acetyl group is missing and the chemical shifts due to H-2 and H-14 were shifted upfield by 1.28 and downfield by 0.56 ppm, respectively, as in case of briarlides B and C. This suggested that briarlide H was 2-deacetylviolide G. The relative stereochemistry was determined from the observation of the similar coupling patterns in the ^{1}H NMR spectrum and NOE correlations to those of **11**.

The structures of briarane diterpenes **1**−**8** isolated from *Briareum* sp., collected at Amami Island, are virtually the same type as those collected at Bonotus.

The inhibitory activity of **1**−**7** against Vero and MDCK

Table 3. Cytotoxic Activity (CC_{50} μg/mL) of Compounds **1**−**9**

	1	2	3	4	5	6	7	8	9
Vero	2.07	18.9	62.1	2.26	4.24	4.26	22.2	>100	9.80
MDCK	4.74	15.4	38.6	2.49	4.91	3.49	67.1	>100	28.8

cells was 2.07−62.1 and 2.49−67.1 μg/mL, respectively (Table 3). Compound **1** showed the strongest inhibitory activity among them. In essence, the tendency for activity of **1**−**7** is similar to that of the violides.[12,13] Thus, compounds **7** and **8**, without a substituent at C-4, and compounds **2**−**5**, possessing a hydroxyl group(s) at C-2 and/or C-3, were less inhibitory. Compound **4**, with a longer aliphatic chain, was more active than **5**, with a shorter chain. When the octanoyl group at C-4 was rearranged to C-3, the activity was decreased, as seen in the case of **4** and **6**. The activity of compound **2**, possessing an acetyl group at C-12, was stronger than that of **3**, with a hydroxyl group at C-12.

Experimental Section

General Experimental Procedures. Optical rotations were measured at 22 °C on a JASCO DIP-370S polarimeter. IR spectra were recorded on a MASCO FT/IR 5300. NMR spectra were recorded with a 400 MHz JEOL NMR instrument using TMS as internal standard and $CDCl_3$ as solvent. MS spectra were obtained with a JEOL JMS XD-303 instrument.

Animal Material. The *Briareum* sp. (collection no. 262) was collected at −2 m at Amami Island, Kagoshima Prefecture, and was frozen immediately after collection. The animal was compared to the type material of *Briareum* sp., and the characteristics were found to match. A voucher specimen has been deposited at the Faculty of Science, Kagoshima University.

Extraction and Isolation. The organism (wet wt, 1.7 kg) was chopped into small pieces and extracted with MeOH (20 L). The MeOH extract was suspended in H_2O and extracted with CH_2Cl_2. A portion (5.2 g) of the CH_2Cl_2 extract (15.4 g) was absorbed on silica gel and subjected to chromatography on silica gel (40 g) packed in hexane, fractions (100 mL) being collected as follows: 1/2 (hexane−CH_2Cl_2, 1:4), 3/4 (CH_2Cl_2), 5/6 (MeOH−CH_2Cl_2, 1:48), 7−11 (MeOH−CH_2Cl_2, 1:19), 12/13 (MeOH−CH_2Cl_2, 1:9), 14−17 (MeOH−CH_2Cl_2, 1:4), and 18/19 (MeOH). Fractions 5−12 (4.36 g) were chromatographed on silica gel using MeOH and CH_2Cl_2, increasing the proportion of MeOH to elute the fractions from the column. Elution with MeOH−CH_2Cl_2 (1:49) gave fractions 14/15 (2.5 g) and 19 (352 mg). The fraction 14/15 was again chromatographed on silica gel using MeOH−CH_2Cl_2 (1:49 and then 3:97). The fractions eluted with MeOH−CH_2Cl_2 (1:49) were applied to HPLC (ODS). Elution with MeOH−H_2O (13:7) afforded **5** (2.5 mg), and elution with CH_3CN−H_2O (2:3) gave **1** (4.3 mg), **3** (9.6 mg), **4** (3.0 mg), **6** (1.2 mg), and **7** (3.9 mg). Compound **2** (18.1 mg) was isolated from the fractions eluted with MeOH−CH_2Cl_2 (3:97) followed by HPLC (ODS) with MeOH−H_2O (3:2). From fraction 19, compound **8** (10.7 mg) was obtained by use of HPLC with MeOH−H_2O (3:2).

Briarlide A (1): amorphous, $[\alpha]_D$ −13° (*c* 0.23, MeOH); IR (film) ν_{max} 3545, 1788, 1748, 1229 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 645.2159 $[M + Na]^+$ (calcd for $C_{30}H_{38}O_{14}Na$, 645.2160).

Briarlide B (2): amorphous, $[\alpha]_D$ −36.8° (*c* 1.19, MeOH); IR (film) ν_{max} 3526, 1784, 1744, 1235 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 603.2083 $[M + Na]^+$ (calcd for $C_{28}H_{36}O_{13}Na$, 603.2054).

Briarlide C (3): amorphous, $[\alpha]_D$ −96° (*c* 0.13, MeOH); IR (film) ν_{max} 3503, 1784, 1744, 1233 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 539.2134 $[M + H]^+$ (calcd for $C_{26}H_{35}O_{12}$, 539.2128).

Briarlide D (4): amorphous, $[\alpha]_D$ −34° (*c* 0.13, MeOH); IR (film) ν_{max} 3536, 1784, 1744, 1213 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 665.3176 $[M + H]^+$ (calcd for $C_{34}H_{49}O_{13}$, 664.3174).

Briarlide E (5): amorphous, $[\alpha]_D$ −24° (*c* 0.12, MeOH); IR (film) ν_{max} 3536, 1784, 1744, 1215 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 635.2685 $[M - H]^+$ (calcd for $C_{32}H_{43}O_{13}$, 665.2704).

Briarlide F (6): amorphous, $[\alpha]_D$ −57° (*c* 0.05, MeOH); IR (film) ν_{max} 3526, 1786, 1744, 1215 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 665.3197 $[M + H]^+$ (calcd for $C_{34}H_{49}O_{13}$, 665.3173).

Briarlide G (7): amorphous, $[\alpha]_D$ −73° (*c* 0.20, MeOH); IR (film) ν_{max} 3544, 1786, 1744, 1231 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 587.2130 $[M + Na]^+$ (calcd for $C_{28}H_{36}O_{12}Na$, 587.2104).

Briarlide H (8): amorphous, $[\alpha]_D$ −106.4° (*c* 0.14, MeOH); IR (film) ν_{max} 3358, 1784, 1746, 1233 cm^{-1}; ^{1}H NMR (see Table 1); ^{13}C NMR (see Table 2); positive-ion HREIMS *m*/*z* 481.2079 $[M + H]^+$ (calcd for $C_{24}H_{33}O_{10}$, 481.2073).

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References and Notes

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