New Xenia Diterpenes Isolated from the Soft Coral, *Xenia florida*

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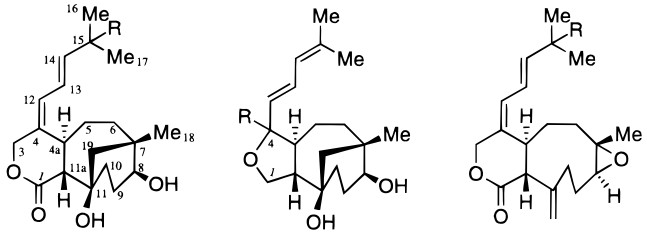
Seven new xenia diterpenes have been isolated from the soft coral, *Xenia florida*. Four of them possess a bicyclic [4.3.1] ring system. The three others, which contained a cyclononane skeleton with an epoxide, seem to be precursors for diterpenes with a bicyclic [4.3.1] ring system.

Soft corals belonging to the genus *Xenia* (subclass Octocorallia, order Alcyonacea, family Xeniidae) are rich sources of xenicane-type monocarbocyclic diterpenes, containing a cyclononane skeleton.[1] The methanol extract of *X. florida* (Lesson, 1826) has yielded nine new tricarbocyclic and dicarbocyclic diterpenes, possessing a bicyclic [4.3.1] ring system.[2] Further investigation of *X. florida* has resulted in seven new xenia diterpenes. Four of them, named florlides A (**1**) and B (**2**) and florethers A (**3**) and B (**4**), were dicarbocyclic diterpenes with a bicyclic [4.3.1] ring system. The three others, florlides C (**6**), D (**5**), and E (**7**), containing a cyclononane skeleton with an epoxide, were monocarbocyclic. These latter compounds could be precursors for diterpenes with a bicyclic [4.3.1] ring system.



1 R=OH **3** R=β-^{3}CH$_2$OH **5** R=H

2 R=H **4** R=α-CH$_2$OH **6** R=OH

7 R=OOH

Results and Discussion

Florlide A (**1**) showed a UV maximum at 245 nm, suggesting a conjugated diene system. The IR spectrum indicated absorption bands due to hydroxyl (3450 cm^{-1}), ester carbonyl (1720 cm^{-1}), and conjugated double-bond (1660 cm^{-1}) functionalities. The molecular formula for florlide A (**1**), $C_{20}H_{30}O_5$, obtained by the HREIMS and ^{13}C NMR data (Table 1), indicated six equivalents of unsaturation, two of which are accounted for as double bonds [four olefinic carbons δ 121.9 (d), 129.0 (d), 137.7 (c), and 146.5 (d)] and a third as an ester [δ 176.8 (s)]. This implied that florlide A was tricyclic. The ^{1}H NMR spectral data of the A ring and the side chain were similar to those in xeniolide B.[3] Resonances due to two methyl protons on a carbon carrying a hydroxyl group at δ 1.29 (3H, s) and 1.30 (3H each, s,) were assigned to H-16 and H-17. The resonance due to H-13 (δ 6.29, 1H, dd, J = 11.4, 15.0 Hz) showed that H-13 was coupled to H-12 (δ 6.11, 1H, br d, J = 11.4 Hz) and H-14 (1H, δ 5.95, d, J = 15.0 Hz). An AB system at δ 4.42 (1H, br d, J = 11.7 Hz) and 5.01 (1H, d, J = 11.7 Hz) was due to H-3. The presence of the bicyclic [4.3.1] ring system, containing two hydroxyl groups at C-8 and C-11, was assumed from the resonances due to methyl protons at C-18 (δ 1.03, 3H, s), isolated methylene protons at C-19 (δ 1.66, 1H, br d, J = 13.9 Hz, δ.1.82, 1H, d, J = 13.9 Hz), and a broad singlet at C-8 (δ 3.35, 1H).[2] The *E* geometry of the double bond at C-13 was determined by the coupling constant (J = 15.0 Hz) between H-13 and H-14. The geometry of the olefinic bond between C-4 and C-12 was concluded to be *E* on the basis of a strong NOE from H-4a (δ 2.78, m) to H-13. The stereochemistry of all chiral centers was elucidated from NOE experiments on **1**. NOEs from H-19 (δ 1.66) to H-11a (ca. δ 2.82, 1H, overlapped) and H-18 and from H-11a to H-3 (δ 5.01) showed that these protons occur on the same face of the ring system (β). The large coupling constant (J = 12.5 Hz) between H-4a and H-11a (δ 2.62, d) in $CDCl_3$ suggested that the configuration of H-4a was α-oriented. The α-configuration of H-8 was assumed from the signal pattern (broad singlet) as for floridicins.[2] Therefore, the structure of florlide A was assigned as **1** on the basis of the above results.

Florlide B (**2**) was isolated as an oil with a molecular formula $C_{20}H_{30}O_4$, indicating that **2** had one less oxygen than **3**. The ^{1}H NMR spectrum was similar to that of **1**, except that the hydroxyl group at C-15 in **1** was replaced with hydrogen: H-14 (δ 5.82, 1H, dd, J = 7.0, 14.5 Hz), H-15 (δ ca. 2.40, 1H, m), H-16, and H-17 (δ 1.03, 3H × 2, d, J = 6.6 Hz). The ^{13}C NMR spectrum was also very similar to that of **1**, except for C-13 to C-17. Thus, florlide B (**2**) was concluded to be 15-dehydroxyflorlide A.

The ^{13}C NMR spectral data due to the bicyclic [4.3.1] ring system in florether B (**3**), $C_{20}H_{32}O_4$, were similar to those of florlide A (**1**), except that resonances assigned to C-4a and C-5 were shifted downfield and upfield, respectively (Table 1). The presence of a tetrahydrofuran ring with a hydroxymethyl group and a 4-methyl-1,3 pentadiene moiety were deduced by comparing the NMR data with those of xeniaethers A and B.[4] H-1 oxymethylene protons (δ 3.86, 1H, dd, J = 7.7, 11.5 Hz and δ 4.17, 1H, t, J = 7.7 Hz) in the ^{1}H NMR were coupled to H-11a (δ 2.39, 1H, br dt, J = 7.7, 11.5 Hz), which in turn was coupled to H-4a (δ 1.91, 1H, overlapped). An AB system at δ 3.47 and 3.59 (J = 11.0 Hz) was assigned to oxymethyl protons at C-4. Resonances due to the 4-methyl-1,3 pentadiene moiety were as follows: δ 1.80 (3H × 2, s, H-16 and H-17), δ 5.56 (1H, d, J = 15.2 Hz, H-12), 5.84 (1H, br d, J = 11.0 Hz, H-14), and δ 6.55 (1H, dd, J = 11.0, 15.2 Hz, H-13). The β-configuration of the hydroxymethyl group was determined by NOE experiments of **3** in which irradiation of H-11a produced peak enhancements of the signals of H-1β (δ 4.16), H-3, and H-19 (δ 1.71, d, J = 14.7 Hz). The configurations of H-8 (δ 3.37, 1H, br s) and H-18 (δ 1.06,

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Table 1. ^{13}C NMR Spectral Data for **1**−**7** in CD_3OD

C	1	2	3	4	5	6	7
1	176.8	176.9	69.3	69.2	176.0	175.9	175.9
3	72.6	72.5	65.2	65.9	72.7	72.6	72.5
4	137.7	136.1	88.2	89.5	137.7	139.3	140.2
4a	38.3	38.3	51.6	45.3	37.2	37.3	37.2
5	35.7	35.5	25.2	26.4	36.9	37.1	37.1
6	39.2	39.2	38.9	39.0	40.0	39.9	39.9
7	38.2	38.3	39.5	39.0	61.3	61.3	61.3
8	74.7	74.7	75.0	75.2	65.6	65.5	65.6
9	28.9	28.7	26.9[a]	27.0[a]	28.5	28.5	28.5
10	28.4	28.4	29.1[a]	28.9[a]	29.5	29.6	29.4
11	72.6	72.6	72.7	72.9	145.2	145.2	145.0
11a	58.6	58.6	59.0	57.0	58.3	58.3	58.3
12	129.0	129.6	126.1[b]	125.9	129.7	129.1	129.0
13	121.9	123.1	126.3[b]	129.2[b]	123.6	122.6	156.0
14	146.5	146.8	133.5	130.0[b]	146.8	146.4	142.5
15	71.4	32.7	135.9	135.7	32.6	71.4	82.5
16, **17**	29.9, 30.0	22.6, 22.6	26.1, 18.4	26.1, 18.3	22.5, 22.6	29.9, 30.0	24.9, 25.2
18	31.2	31.2	31.6	31.6	19.0	19	19.1
19	43.7	43.7	45.6	45.5	120.8	120.8	121.0

[a,b] These values may be interchangeable in any vertical column.

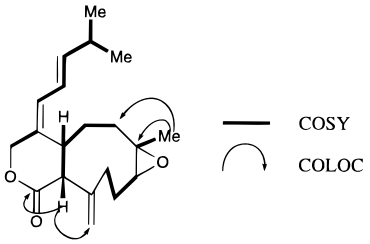

Figure 1. $^1H-^1H$ COSY and COLOC correlations of **5**.

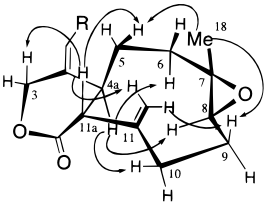

Figure 2. NOE correlations of **5**.

3H, s) were elucidated to be β on the basis of the NOEs from H-18 to H-8 and H-19 and the signal patterns of H-8, as observed for **1** and xeniaethers A and B.

The close resemblance of the ^1H and ^{13}C NMR data of florether B (**4**), $C_{20}H_{32}O_4$, to those of **3** led us to the assumption that **4** might be a C-4 epimer of **3**. The β-orientation of the diene at C-4 was determined by the observation of NOEs from H-13 (δ 6.51, 1H, dd, J = 11.4, 15.0 Hz) to H-1 (δ 4.12, t, J = 8.0 Hz) and H-11a (δ ca. 2.16, 1H, overlapped). Therefore, the structure of florether B was shown to be **4**. This is the second isolation of xenia diterpenes containing a tetrahydrofuran ring.[4]

The molecular formula $C_{20}H_{28}O_3$ of florlide D (**5**) indicated seven olefinic bond equivalents. The ^{13}C NMR spectrum showed the presence of an epoxide (δ 59.4, s and δ 64.1, d), three double bonds (δ 120.8, t; δ 123.6, d; δ 129.7, d; δ 137.7, s; δ 145.2, s; δ 146.8, d), and a lactone carbonyl (δ 175.0, s), suggesting that **5** was tricyclic. The ^1H NMR data of **5** were similar to those of **2**, except that resonances due to the bicyclic [4.3.1] ring system were missing. Resonances due to methyl protons (δ 1.21, 3H, s) on the epoxide and to end methylene protons (δ 5.15, 1H, br s and δ 5.19, 1H, br s) were observed. The gross structure was assigned by the use of the NMR techniques including $^1H-^1H$ COSY, $^{13}C-^1H$ COSY, and COLOC experiments (Figure 1). The presence of two isolated spin systems from H-11a to H-6 through H-4a and from H-8 to H-10 was elucidated by the $^1H-^1H$ COSY spectrum. H-11a (δ 3.22, 1H, d, J = 9.9 Hz) was coupled to H-4a (δ 3.07, 1H, m), which in turn was coupled to H-5 (δ 1.77, 1H, m; δ 1.94, 1H, m). The H-5 was further coupled to H-6 (δ 1.39, 1H, m; δ ca. 2.11, 1H, m). The connectivity of C-18 and C-7 resulted from cross peaks from H-18 (δ 1.21, 3H, s) to C-6 (δ 38.9, t) and C-7 (59.4, s). Resonances due to an epoxide proton (δ 3.03, 1H, dd, J = 2.7, 11.4 Hz, H-8) were coupled to H-9 (δ 1.48, 1H, dt, J = 4.3, 11.9 Hz, δ ca. 2.22, 1H, overlapped), which in turn were coupled to H-10 (δ ca. 2.11, 1H, overlapped, δ 2.84, 1H, br d, J = 14.7 Hz). Thus, the above results and the biogenetic considerations suggested that the epoxide and the terminal methylene group must be located between C-7 and C-8 and at C-11, respectively.

The stereochemistry was established mainly from NOE experiments (Figure 2). NOEs from H-11a to H-3 (δ 4.90, 1H, d, J = 12.1 Hz) and H-5 (δ 1.77) showed that these protons occurred on the same face on the ring system (β). The coupling constant (J = 9.9 Hz) between H-4a and H-11a suggested a trans ring junction, which implied that H-4a was α-oriented. NOEs from H-4a to H-6 (δ ca. 1.39), H-8, and H-10 (δ 2.11) suggested that these protons were on the face (α) opposite H-11a. The β-configuration of H-18 was determined by the observation of NOEs between H-18 and H-5β.

The ^1H NMR spectra of florlides C (**6**), $C_{20}H_{28}O_4$, and E (**7**), $C_{20}H_{28}O_5$, were similar to that of **5**, except that resonances due to H-15 were missing. In the case of **6**, the molecular formula of which had one more oxygen than **5**, H-14 appeared as a doublet (δ 5.98, 1H, J = 15.0 Hz) and H-16 and H-17 as singlets (δ 1.29 and 1.30, 3H each, s). Thus, the H-15 proton in **5** must be replaced by a hydroxyl group. As for **7**, the ^1H NMR signal patterns were almost the same of those of **6**; however, the chemical shift (δ 82.5) of C-15 in the ^{13}C NMR spectrum was shifted downfield by 11.1 ppm in comparison with that of **6**. Therefore, the results and the molecular formula suggested a hydroperoxyl group was located at C-15. The stereochemistry of the H-18, epoxides, ring junctions, and olefinic bonds between C-4 and C-12 and at C-13 in **6** and **7** was determined on the basis of results similar to those of **5** obtained from NOEs and J values.

Diterpenes containing a cyclononane skeleton with an epoxide between C-7 and C-8, such as **5** and **6**, could be precursors for diterpenes possessing a bicyclic [3.2.1] ring system, such as **1** and **2**, as shown in Figure 3.

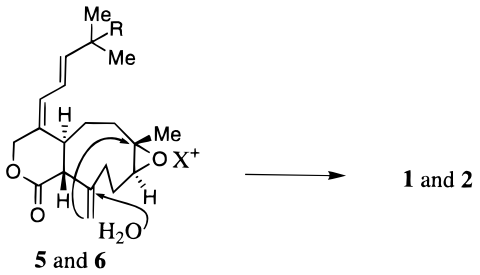

Figure 3. Possible biogenetic pathway for **1** and **2**.

Antibacterial activity tests were performed on compounds **2**−**6** using the paper disk method. Compounds **2** and **5** had antibacterial activity at 100 μg/disk against *Staphylococcus aureus* and *Aeromonas salmonisida*, respectively.

Experimental Section

Extraction and Isolation. The organism (wet wt 12 kg) was immersed in MeOH (50 L). The MeOH extract was partitioned between CH_2Cl_2 and H_2O. The CH_2Cl_2-soluble portion (12.2 g) was absorbed on Si gel and subjected to a column chromatography of Si gel (Merck 60H, 60 g) packed in hexane, and fractions (100 mL) were collected as follows: 1−4 (hexane), 5−8 (CH_2Cl_2−hexane, 3:7), 9−12 (CH_2Cl_2−hexane, 1:1), 13−16 (CH_2Cl_2−hexane, 4:1), 17−20 (CH_2Cl_2), 21−23 (MeOH−CH_2Cl_2, 1:99), 24−36 (MeOH−CH_2Cl_2, 1:19), 37−41 (CH_2Cl_2−MeOH, 1:9). Fractions 24−36 (10.2 g) were again chromatographed on Si gel using CH_2Cl_2−hexane, MeOH−CH_2Cl_2, and MeOH-ether as solvent systems. Elution with CH_2Cl_2−hexane (4:1) to MeOH−CH_2Cl_2 (1:99) gave a residue, which was applied to HPLC (ODS) with MeOH−H_2O (7:3) to afford **5** (20 mg) and **7** (3.4 mg), as well as floridicin (300 mg) and 2-*O*-methylfloridicin (13 mg). Elution with MeOH−CH_2Cl_2 (1:99 to 1:49) afforded a residue from which **2** (2.3 mg) and **3** (4.0 mg) were separated by use of Si gel chromatography with ether−hexane (4:1) and HPLC with MeOH−H_2O (7:3). Compound **1** (24 mg) was isolated from the residue by Si gel chromatography with ether and by HPLC with MeOH−H_2O (17:1). From fractions 37−41, compounds **3** (2.7 mg) and **4** (2.0 mg) were obtained by Si gel chromatography with MeOH−ether (1:49 to 1:26) and by HPLC with MeOH−H_2O (7:3).

Florlide A (1): amorphous white solid; $[\alpha]_D$ +95.5° (*c* 0.33, MeOH); UV (MeOH) λ_{max} (log ϵ) 246 (4.19) nm; IR (KBr) ν_{max} 3450, 1720, 1660, 980, 940 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.03 (3H, s, H-18), 1.29 and 1.30 (3H each, s, H-16 and H-17), 1.54 (1H, m, H-6β), 1.65−1.74 (2H, overlapped, H-6α and H-9), 1.66 (1H, br d, J = 13.9 Hz, H-19), 1.82 (1H, d, J = 13.9 Hz, H-19), ca. 1.89 (1H, m, H-10), 1.97 (1H, m, H-5), 2.09−2.16 (1H, m, H-9), 2.40−2.44 (1H, m, H-10), ca. 2.82 (2H, overlapped, H-4a and H-11a), 3.35 (1H, br s, H-8), 4.42 (1H, d, J = 11.7 Hz, H-3α), 5.01 (1H, br d, J = 11.7 Hz, H-3β), 5.95 (1H, d, J = 15.0 Hz, H-14), 6.11 (1H, br d, J = 11.4 Hz, H-12), 6.29 (1H, dd, J = 11.4, 15.0 Hz, H-13); LREIMS m/z 332 [M − 18]$^+$; HREIMS m/z 332.1986 ([M − 18]$^+$, calcd for $C_{20}H_{28}O_4$, 332.1986).

Florlide B (2): amorphous white solid; $[\alpha]_D$ +150° (*c* 0.08, MeOH); UV (MeOH) λ_{max} (log ϵ) 245 nm (4.25); IR (KBr) ν_{max} 3450, 1720, 1650, 970, 940 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.03 (6H, d, J = 6.6 Hz, H-16 and H-17), 1.40−1.52 (1H, m, H-6), 1.64−1.75 (2H, overlapped, H-6 and H-8), 1.65 (1H, br d, J = 13.2 Hz, H-19), 1.78−1.96 (2H, overlapped, H-5 and H-9), 1.81 (1H, d, J = 13.2 Hz, H-19), ca. 1.96 (1H, m, H-5), 2.04−2.11 (1H, m, H-8), 2.36−2.44 (2H, overlapped, H-9 and H-15), ca. 2.79 (2H, overlapped, H-4a and H-11a), 3.36 (1H, br s, H-8), 4.40 (1H, d, J = 11.9 Hz, H-3α), 5.00 (1H, br d, J = 11.9 Hz, H-3β), 5.82 (1H, dd, J = 7.0, 14.5 Hz, H-14), 6.00 (1H, dd, J = 11.2, 14.5 Hz, H-13), 6.08 (1H, br d, J = 11.2 Hz, H-12); LREIMS m/z 334 [M]$^+$, 318 [M − 18]$^+$; HREIMS m/z 334.2177 ([M]$^+$, calcd for $C_{20}H_{30}O_4$, 334.2144).

Florether A (3): amorphous white solid; $[\alpha]_D$ +52.3° (*c* 0.11, MeOH); UV (MeOH) λ_{max} (log ϵ) 244 nm (4.12); IR (KBr) ν_{max} 3400, 1655, 995, 960, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06 (3H, s, H-18), 1.71 (1H, br d, J = 14.7 Hz, H-19), 1.80 (3H × 2, s, H-16 and H-17), 2.04 (1H, m, H-9), 2.39 (1H, dt, J = 7.7, 11.5 Hz, H-11a), 3.37 (1H, br s, H-8), 3.47 and 3.59 (1H each, br d, J = 11.0 Hz, H-3), 3.86 (1H, dd, J = 7.7, 11.5 Hz, H-1α), 4.16 (1H, t J = 7.7 Hz, H-1β), 5.56 (1H, d, J = 15.2 Hz, H-12), 5.84 (1H, br d, J = 11.0 Hz, H-14), 6.55 (1H, dd, J = 11.0, 15.2 Hz, H-13); LREIMS m/z 336 [M]$^+$; HREIMS m/z 336.2934 ([M]$^+$, calcd for $C_{20}H_{32}O_4$, 336.2899).

Florether B (4): amorphous white solid; $[\alpha]_D$ +79.4° (*c* 0.08, MeOH); UV (MeOH) λ_{max} (log ϵ) 241 nm (4.24); IR (KBr) ν_{max} 3400, 1655, 1000, 970, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (3H, s, H-18), 1.63 (1H, br d, J = 13.7 Hz, H-19), 1.80 (1H, d, J = 13.7 Hz, H-19), 1.78 (3H × 2, s, H-16 and H-17), 1.95 (1H, m, H-4a), 2.10 (1H, m, H-9), ca. 2.16 (1H, overlapped, H-11a), 3.37 (1H, br s, H-8), 3.86 (1H, dd, J = 7.7, 10.6, H-1α), 4.12 (1H, t, J = 7.7 Hz, H-1β), 5.32 (1H, d, J = 15.0 Hz, H-12), 5.83 (1H, br d, J = 11.4 Hz, H-14), 6.51 (1H, dd, J = 11.4, 15.0 Hz, H-13); HREIMS m/z 336.2275 ([M]$^+$, calcd for $C_{20}H_{32}O_4$, 336.2300).

Florlide D (5): needles, mp 178 °C; $[\alpha]_D$ +178° (*c* 0.09, MeOH); UV (MeOH) λ_{max} (log ϵ) 246 nm (4.11); IR (KBr) ν_{max} 1745, 1655, 980, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (3H × 2, d, J = 6.6 Hz, H-16 and H-17), 1.21 (3H, s, H-18), 1.39 (1H, m, H-6α), 1.48 (1H, dt, J = 4.3, 11.9 Hz, H-9α), 1.77 (1H, m, H-5β), 1.94 (1H, m, H-5α), ca. 2.11 (1H, m, H-10β), 2.16 (1H, overlapped, H-6β), ca. 2.22 (1H, overlapped, H-9β), 2.38 (1H, hept, J = 6.6 Hz, H-15), 2.82 (1H, br d, J = 14.7 Hz, H-10α), 3.03 (1H, dd, J = 2.7, 11.4 Hz, H-8), 3.07 (1H, m, H-4a), 3.22 (1H, d, J = 9.9 Hz, H-11a), 4.42 (1H, d, J = 12.1 Hz, H-3α), 4.90 (1H, br d, J = 12.1 Hz, H-4β), 5.15 and 5.19 (1H each, br s, H-19), 5.83 (1H, dd, J = 6.6, 14.7 Hz, H-14), 5.97 (1H, dd, J = 11.0, 14.7 Hz, H-13), 6.04 (1H, d, J = 11.0 Hz, H-12); LREIMS m/z 316 [M]$^+$; HREIMS m/z 316.2019 ([M]$^+$, calcd for $C_{20}H_{28}O_3$, 316.2037).

Florlide C (6): amorphous white solid; $[\alpha]_D$ +173° (*c* 0.09, MeOH); UV (MeOH) λ_{max} (log ϵ) 245 nm (4.24); IR (KBr) ν_{max} 3450, 1735, 1650, 980, 915 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.20 (3H, s, H-18), 1.29 and 1.30 (3H each, s, H-16 and H-17), 1.44−1.54 (2H, overlapped, H-6α and H-9α), 1.88−1.93 (2H, m, H-5), 2.07−2.17 (3H, overlapped, H-6β, H-9β, and H-10α), 2.73 (1H, m, H-10β), 3.17 (1H, dd, J = 2.9, 11.4 Hz, H-8), 3.17 (1H, overlapped, H-4a), 3.54 (1H, d, J = 10.3 Hz, H-11a), 4.45 (1H, d, J = 12.1 Hz, H-3α), 5.04 (1H, br d, J = 12.1 Hz, H-3β), 5.16 and 5.27 (1H each, br s, H-19), 5.98 (1H, d, J = 15.0 Hz, H-14), 6.15 (1H, br d, J = 11.4 Hz, H-12), 6.36 (1H, dd, J = 11.4, 15.0 Hz, H-13); LREIMS m/z 332 [M]$^+$; HREIMS m/z 314.1926 ([M − H_2O]$^+$, calcd for $C_{20}H_{26}O_3$, 314.1883).

Florlide D (7): amorphous white solid; $[\alpha]_D$ +157° (*c* 0.07, MeOH); UV (MeOH) λ_{max} (log ϵ) 251 nm (3.94); IR (KBr) ν_{max} 3350, 1735, 1645, 970, 915 cm^{-1}; ^{1}H NMR (CD_3OD) δ 1.20 (3H, s, H-18), 1.31 and 1.33 (3H each, s, H-16 and H-17), 1.40−1.53 (2H, overlapped, H-6α and H-9α), 1.88−1.92 (2H, m, H-5 × 2), 2.06−2.18 (3H, overlapped, H-6β, H-9β, H-10α), 2.72 (1H, m, H-10β), 3.17 (1H, dd, J = 2.4, 8.9 Hz, H-8), ca. 3.17 (1H, overlapped, H-4a), 3.55 (1H, d, J = 10.6 Hz, H-11a), 4.46 (1H, d, J = 11.9 Hz, H-3α), 5.04 (1H, br d, J = 11.9 Hz, H-3β), 5.16 and 5.28 (1H each, br s, H-19), 5.96 (1H, d, J = 15.6 Hz, H-14), 6.16 (1H, br d, J = 11.0 Hz, H-12), 6.33 (1H, dd, J = 11.0, 15.6 Hz, H-13); LREIMS m/z 330 [M − H_2O]$^+$; HREIMS m/z 330.1837 ([M − H_2O]$^+$, calcd for $C_{20}H_{26}O_4$, 330.1832).

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References and Notes

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