New Xenicane Diterpenes Isolated from the Acetone Extract of the Soft Coral *Xenia florida*[1]

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Six new xenicane diterpenes have been isolated from the acetone extract of the soft coral *Xenia florida*. Two of them are diterpenes containing a bicyclic [4.3.1] ring system. Three of them seem to be precursors for diterpenes possessing the bicyclic [4.3.1] ring system. One is a common monocarbocyclic diterpene with a cyclononane skeleton.

Soft corals belonging to the genus *Xenia* are rich sources of xenicane-type monocarbocyclic diterpenes, containing a cyclononane skeleton.[2] The methanol extract of *X. florida* has yielded 13 new tricarbocyclic and dicarbocyclic diterpenes, possessing a bicyclic [4.3.1] ring system, and three monocarbocyclic diterpenes, containing a cyclononane skeleton.[1,3−4] In this study acetone was used for extraction of the same corals, inasmuch as the methanol extract gave several artifacts due to methanolyis.[5]

The acetone extract of *X. florida* was partitioned between dichloromethane and water. The organic extract was subjected to Si gel chromatography, and reversed-phase HPLC afforded four new xenicane diterpenes (**1**−**6**) together with floridicin (**7**), florlides D (**8**) and E (**9**), and 2-*O*-methylfloridicin (**10**).[1,3−4]

Results and Discussion

Compound **1** was isolated as an oil, and its molecular formula was established as $C_{21}H_{32}O_5$ by HREIMS and NMR spectral data. The ^{1}H NMR spectrum of **1** was similar to that of florlide A (**11**),[1] except for an additional methoxy group (δ 3.20, 3H, s)(Table 1). Comparison of the ^{13}C NMR data (Table 2) for **1** and **11** indicated that the C-11 resonance was shifted lower field (Δ +3.1 ppm), whereas the C-10, C-11a, and C-19 signals were shifted higher field [Δ −7.2, −4.5, and −5.7 (or −5.2) ppm], respectively. These shifts were consistent with the location of the methoxy group at C-11; hence compound **1** was identified as 11-*O*-methylflorlide A. The configuration of the methoxy group was determined to be β from the observation of an NOE between the methoxy group and H-11a.

The UV (224 nm) and IR data (1686 and 1618 cm^{-1}) of compound **2**, $C_{20}H_{28}O_4$, suggested a conjugated carbonyl system. The ^{1}H NMR spectrum indicated the presence of a tertiary methyl group (δ 0.64, 3H, s, H-15), two olefinic methyl groups (δ 1.73, 6H, br s, H-19 and H-20), and an α,β-unsaturated aldehyde (δ 5.92, 1H, t-like, J = 2.4 Hz, H-11, δ 9.23, 1H, br s, H-16). The spectral data were similar to those of floridicin (**7**), except for those of H-3 and H-4: H-3 (δ 2.50, 1H, d, J = 6.0 Hz) was coupled to a methylene proton (δ 1.93, 1H, ddd, J = 6.0, 8.2, and 17.2 Hz, H-4), which in turn was coupled geminally to another methylene proton (δ 1.59, 1H, d, J = 17.2 Hz, H-4) and vicinally to a proton on a carbon bearing a hydroxyl group (δ 3.00, 1H, br d, J = 8.2 Hz, H-5); H-4, at δ 1.59, was not coupled to H-3 or H-5, implying that it was situated perpendicular to these hydrogens. The chemical shift of H-3 (δ 2.50) in the ^{1}H NMR spectrum and the chemical shifts of C-2 (δ 62.5) and C-3 (δ 52.2) in the ^{13}C NMR spectrum indicated that an epoxide was located between C-2 and C-3. The relative stereochemisty of all chiral centers was elucidated from the proton−proton coupling constants and NOE experiments on **2** (Figure 1). NOEs from H-1 (δ 1.90, 1H, t, J = 10.3 Hz) to H-12 (δ 3.29, 1H, m) and H-14 (δ 1.39, 1H, dd, J = 1.5 and 13.4 Hz) showed H-1 and H-12 occur on the same face of the ring system (β). α-Configurations of H-9 (δ 1.78, 1H, m) and H-13 (δ 3.09, 1H, dd, J = 8.4, 10.3 Hz) were determined from the large coupling constants (J = 10.3 Hz) between H-1 and H-9 and (J = 10.3 Hz) between H-1 and H-13. This was confirmed by the observation of an NOE between H-9 and H-13. NOEs from H-7 (δ 0.69, 1H, dd, J = 11.7, 15.0 Hz) to H-4 (δ 1.93), H-5, and H-9 indicated these protons were α-oriented. β-Orientation of the epoxide was deduced from the coupling of H-3 with H-4α (δ 1.93) but not with H-4β (δ 1.59) and from the observation of an NOE between H-3 and H-13. Therefore, the structure of **2** was established as 2β-epoxyfloridicin.

The molecular formula $C_{20}H_{28}O_3$ of **3** indicated seven degrees of unsaturation. The ^{13}C NMR spectrum indicated an epoxide (δ 59.9, 63.7), three olefinic bonds (δ 120.2, 123.2, 137.4, 145.8, 146.4, 150.7), and an aldehyde carbon (δ 193.6), suggesting that **3** was tricyclic. In the ^{1}H NMR spectrum, resonances corresponding to the A ring with a 2-methylbutenyl group in **2** were observed: H-1 (ca δ 2.23, 1H, overlapped), H-9 (δ 2.81, br d-like, J = 8.8 Hz), H-11 (δ 6.33, 1H, br s), H-12 and H-13 (ca δ 3.25, 2H, overlapped), H-16 (δ 9.38, 1H, br s), H-17 (δ 5.04, 1H, br d, J = 6.2 Hz), and H-19 and H-20 (δ 1.75, 3H, br s and δ 1.81, 3H, br s). The presence of a methyl carbon (δ 19.0), four methylene carbons (δ 26.1, 27.5, 32.6, and 38.3), epoxide carbons, and terminal olefinic carbons (δ 120.2 and 145.8) in the ^{13}C NMR spectrum suggested that **3** possessed a cyclononane skeleton containing an epoxide like florlide D (**8**).[1] On the basis of the results, the gross structure was concluded to be the same as that of xeniafaraunol B,[6] although the stereochemisty of the epoxide had not been determined yet. The stereochemistry was deduced from the observation of the NOE experiments (Figure 2). NOEs between H-1 and H-14 (δ 5.20, 1H, br s), between H-5 and H-9, and between H-14 and H-15 indicated that the stereochemisty of the epoxide was 5β,6α-oriented. Therefore, xeniafaraunol B was elucidated as the structure **3**.

The ^{1}H NMR spectrum of florlide F (**4**), $C_{23}H_{28}O_4$, indicated signal patterns similar to those of a side chain in azamilide G (**12**), isolated from *Xenia* sp.[7] in the area of

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Table 1. ^{1}H NMR Spectral Data for **1** and **3**−**5** in $CDCl_3$ and **2** in C_6D_6[a]

no.	1	2	3	4	5	6
1		1.90 t (10.3)	ca. 2.23[d]			
2						
3	4.36 d (12.1)	2.50 d (6.0)	ca. 2.00[d]	4.59 d (12.5)	3.58 br dd (9.7, 12.8)	4.41 d (11.9)
	4.94 br d (12.1)		2.47 br d (13.9)	4.80 d (12.5)	3.75 br dd (2.6, 12.8)	4.70 br d (11.9)
4		1.93 ddd (6.0, 8.2, 17.2)	ca. 1.50[d]			
		1.59 d (17.2)	ca. 2.20[d]			
4a	ca. 2.83 (m)			2.72 br d-like (11.7)	3.08 br dd (7.0, 7.0, 13.0)	3.12 m
5		3.00 br d (8.2)	3.06 dd (2.8, 11.4)	1.56[d]	ca. 1.50[d]	2.34 br dd (7.3, 12.5)
				1.69 m	ca. 1.89[d]	2.84 ddd (5.9, 12.5, 12.5)
6				ca. 1.15[d]	ca. 1.13[d]	5.21 br dd (5.9, 12.5)
				1.69 m	2.14 ddd (3.3, 3.3, 13.2)	
7		0.69 dd (11.7, 15.0)				
		1.21 dd *(8.4, 15.0)				
8	3.43 (br s)	0.87 dd (11.7, 14.3)	ca. 1.40[d]	2.99 dd (2.2, 11.4)	2.95 dd (2.9, 11.7)	4.75 m
		2.96 br dd (8.4, 14.3)	ca. 1.90[d]			
9		1.78 m	2.81 br d-like (8.8)	ca. 1.36 m	1.36 ddd (3.7, 3.7, 11.7)	ca. 2.02 2H m
				2.11 m	2.24 m	
10				2.31 m 2H	ca. 1.85 m	2.09 m
					2.67 m	2.66 ddd (6.3, 6.3, 14.7)
11		5.92 t-like (2.4)	6.33 br s			
11a	2.72 d (12.5)			3.28 d (11.7)	3.21 d (13.0)	3.22 d (11.7)
12	6.01 br d (11.2)	3.29 m	ca. 3.25[d]	5.99 br d (10.8)	5.51 br d (15.2)	6.08 br d (11.4)
13	6.18 dd (11.2, 15.0)	3.09 dd	ca. 3.25[d]	6.42 dd (10.8, 15.2)	6.58 dd (10.8, 15.2)	6.15 dd (11.4, 13.2)
14	5.91 d (15.0)	1.39 dd (1.5, 13.4)	5.20 br s	5.82 br d (15.2)	5.84 br d (10.8)	5.80 dd (6.4, 13.7)
		1.81 d (13.4)	5.26 br s			
15		0.64 s	1.21 s			2.40 hept (6.4)
16	1.35 (s)	9.23 br s	9.38 br s	1.30 s	1.78[b] br s	1.05 d (6.4)
17	1.36 (s)	4.97 br d (9.2)	5.04 br d (6.2)	1.30 s	1.80[b] br s	1.05 d (6.4)
18	1.07 (s)			1.21 s	1.13 s	1.80 br s
19	1.89 d (14.3)	1.73 br s	1.75[b] br s	5.07 br s	5.20 br s	5.15 br s
				5.30 br s	5.24 br s	5.47 br s
20		1.73 br s	1.81[b] br s			
MeO	3.20 (s)					
AcO				2.03 s		
*Me*OCO				3.52 s		

[a] Chemical shift values are in ppm from TMS, and *J* values (in Hz) are presented in parentheses. [b,c] These values may be interchangeable in any vertical column. [d] Overlapped signals.

Bonotsu in Kagoshima Prefecture: δ 1.30 (6H, s, H-16 and H-17), 4.59 and 4.80 (1H each, AB, J = 12.5 Hz, H-3), 5. 82 (1H, br d, J = 15.2 Hz, H-14), 5.99 (1H, br d, J = 10.8 Hz, H-12), and 6.42 (1H, dd, J = 10.8, 15.2 Hz, H-13). In the case of **4**, the acyl group in **12** was replaced by an acetyl group (δ 2.03, 3H, s). Furthermore, signal patterns corresponding to those of the B ring in **3** were also observed in the ^{1}H NMR spectrum: δ 1.21 (3H, s, H-18), 2.72 (1H, br d-like, 11.7 Hz, H-4a), 2.99 (1H, dd, J = 2.2, 11.4 Hz, H-8), 3.28 (1H, br d, J = 11.7 Hz, H-11a), and 5.07 and 5.30 (1H each, br s, H-19). The remaining carbomethoxy group (δ_H 3.52, 3H, s; δ_C 51.7, q; δ_C 170.9, s) to be assigned was deduced to be located at C-11a. The relative stereochemistry was determined by the values of the coupling constants and NOE experiments. The large coupling constant ($J_{4a,11a}$ = 11.7 Hz) of H-4a to H-11a suggested that they have a configuration opposite of each other. The *E* geometry of the olefinic bond $\Delta^{4(12)}$ was assigned on the basis of NOEs from H-12 to H-4a and H-11a. The orientation of the epoxide was deduced to be 7α,8β from the presence of a NOE between H-4a and H-8α and the absence of a NOE between H-8 and H-18.

The IR spectrum of compound **5**, named florlide G, $C_{20}H_{28}O_4$, showed absorptions indicative of a hydroxyl group (3426 cm^{-1}), a γ-lactone carbonyl (1765 cm^{-1}), and an olefinic bond (1644 cm^{-1}). In the ^{1}H NMR spectrum, resonances due to a cyclononane containing an epoxide between C-7 and C-8 as seen in **3** appeared: δ 1.13 (3H, s, H-18), 2.95 (1H, dd, J = 2.9, 11.7 Hz, H-8), 3.08 (1H, br ddd, J = 7.0, 7.0, 13.0 Hz, H-4a), 3.21 (1H, d, J = 13.0 Hz, H-11a), and 5.20 and 5.24 (1H each, br s, H-19). The presence of a 4-methyl-1(*E*),3-pentadiene moiety was evident from proton resonances: δ 1.78 and 1.80 (3H each, br s, H-16, H-17), 5.51 (1H, br d, J = 15.2 Hz, H-12), 5.84 (1H, br d, J = 10.8 Hz, H-14), and 6.58 (1H, dd, J = 10.8, 15.2 Hz, H-13). Two broad double doublets at δ 3.58 (1H, J = 9.7, 12.8 Hz, H-3) and 3.75 (1H, J = 2.6, 12.8, H-3) were due to hydroxymethylene protons. Two broad doublets at δ 5.20 and 5.24 (1H each, br s) were typical of exocyclic methylene protons at C-19. On the basis of the results, it was deduced that the γ-lactone was fused to the cyclooctanone, in which the oxygen atom was attached to C-4 (δ 88.4, s). Confirmation of the relative stereochemistry was aided by proton signal patterns and NOE experiments. A NOE between H-4a and H-8 indicated that these hydrogens were α-oriented. The large coupling constant (J = 13.0 Hz) between H-4a and H-11a indicated that the ring junction was *trans*, and therefore H-11a was in a β-orientation. Unfortunately, the stereochemistry at C-4 was not able to be assigned by the NOE data. This is the first isolation of xenicane diterpene containing a γ-lactone as the A ring.

The ^{13}C NMR spectrum of florlide H (**6**), $C_{20}H_{28}O_4$, showed resonances due to a lactone carbonyl (δ 174.0) and eight olefinic carbons (δ 117.3, 120.4, 121.6, 129.5, 132.0,

Table 2. ^{13}C NMR Spectral Data for **1** and **3**−**5** in $CDCl_3$ and **2** in C_6D_6

no.	1	2	3	4	5	6
1	171.3 (s)[c]	51.7 (d)	60.4 (d)	172.6 (s)	175.3 (s)	174.0 (s)
2		62.5 (s)	145.8 (s)			
3	70.9 (t)	52.2 (d)	26.1 (t)[a]	69.8 (t)	63.8 (t)	73.0 (t)
4	137.1 (s)	31.3 (t)	27.5 (t)[a]	139.3 (s)	88.4 (s)	132.0 (s)
4a	37.0 (d)			53.4 (d)	41.3 (d)	38.3 (d)
5	34.1 (t)	72.1 (d)	63.7 (d)	30.8 (t)	25.5 (t)	30.6 (t)
6	38.5 (t)[a]	36.1 (s)	59.9 (s)	38.3 (t)	38.4 (t)	120.4 (d)
7	38.0 (s)	37.3 (t)	38.3 (t)	59.5 (s)	59.1 (s)	144.0 (s)
8	73.9 (d)	22.4 (t)	32.6 (t)	63.4 (d)	64.2 (d)	67.4 (d)
9	27.9 (t)	43.1 (d)	35.3 (d)	26.1 (t)[a]	27.5 (t)	34.3 (t)[a]
10	21.2 (t)	142.0 (s)	146.4 (s)	27.2 (t)[a]	28.9 (t)	34.9 (t)[a]
11	75.7 (s)	153.5 (d)	150.7 (d)	143.1 (s)	142.5 (s)	142.3 (s)
11a	54.1 (d)			62.2 (d)	58.5 (d)	48.1 (d)
12	127.8 (d)	45.7 (d)	44.0 (d)	129.6 (d)	122.6 (d)[a]	129.5 (d)
13	120.6 (d)	71.8 (d)	71.7 (d)	121.5 (d)	123.8 (d)[a]	121.6 (d)
14	145.0 (d)	38.1 (t)	120.2 (s)	143.4 (d)	130.3 (d)	146.2 (d)
15	73.6 (d)	24.7 (q)	19.0 (q)	70.9 (s)	139.1 (s)	31.6 (d)
16	29.8 (q)	192.6 (d)	193.6 (d)	29.8 (q)	26.1 (q)	22.2 (q)
17	29.9 (q)	124.1 (d)	123.2 (d)	29.8 (q)	18.3 (q)[b]	22.2 (q)
18	30.5 (q)	135.4 (s)	137.4 (s)	18.7 (q)	18.6 (q)[b]	17.2 (q)
19	38.0 (t)[a]	18.4 (q)	121.0 (t)	122.2 (t)	117.3 (t)	
20		25.8 (q)	26.0 (q)			
MeO	48.5 (q)					
*Me*COO				21.0 (q)		
Me*C*OO				170.9 (s)		
*Me*OCO				51.7 (q)		

[a,b] These values may be interchangeable in any vertical column. [c] Multiplicity was deduced by DEPT.

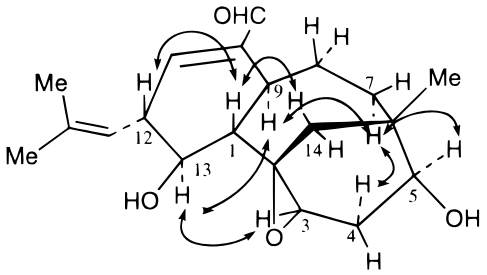


Figure 1. NOE correlations of **2**.

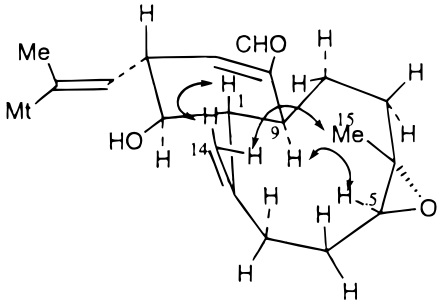


Figure 2. NOE correlations of **3**.

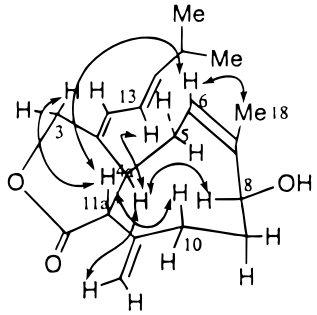
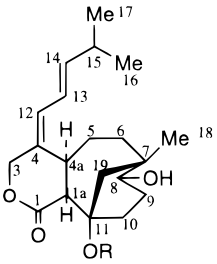


Figure 3. NOE correlations of **6**.

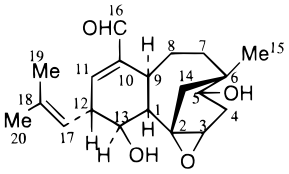
142.3, 144.0, 146.2), suggesting that **6** was bicyclic. In the ^1H NMR spectrum, resonances corresponding to the A ring with a side chain in florlide D (**8**)[1] were observed: δ 1.05 (6H, br d, J = 6.4 Hz, H-16 and H-17), 2.40 (1H, hept, J = 6.4 Hz, H-15), 3.12 (1H, m, H-4a), 4.41 (1H, d, J = 11.9 Hz, H-3α), 4.70 (1H, br d, J = 11.9 Hz, H-3β), 5.80 (1H, dd, J = 6.4, 13.7 Hz, H-14), 6.08 (1H, br d, J = 11.4 Hz, H-12), and 6.15 (1H, dd, J = 11.4, 13.2 Hz, H-13). The structure of a cyclononane skeleton as the B ring was also assumed from the ^1H NMR spectral data. Two broad singlets at δ 5.15 and 5.47 (1H each) were typical of resonances due to exocyclic methylene protons at C-19. An olefinic proton (δ 5.21, 1H, br dd, J = 5.9, 12.5 Hz) was determined to be located at C-6, because the proton was coupled to H-5 (δ 2.34, 1H, br dd, J = 7.3, 12.5 Hz, δ 2.84, 1H, ddd, J = 5.9, 12.5.5, 12.5 Hz), which was coupled to H-4a. The lowfield chemical shift (δ 4.75, 1H, m) of a proton on a carbon bearing a hydroxyl group suggested that the hydroxyl group was located either at C-8 or at C-10. Placement of the hydroxyl group at C-8 was assumed on the basis of the fact that many compounds possessing a hydroxyl group at C-8 have been isolated from this soft coral.[1,3−5] To establish the relative stereochemistry of chiral centers, NOE experiments (Figure 3) were performed. NOEs from H-11a to H-3 (δ 4.70), H-6, and H-10 (δ 2.09, m) indicated that these hydrogens occur on the same face of the ring (β). α-Configurations of H-4a and H-8 were elucidated from the observation of an NOE between H-4a and H-8. An NOE between H-4a and H-19 (δ 5.15) suggested that the exocyclic methylene group was directed downward. The *E*-geometries of the olefinic bonds between H-4a and H-12 and between C-6 and C-7 were confirmed by NOEs between H-4a and H-13 and between H-6 and H-18, respectively.

Compounds **3**−**5**, as well as **8** and **9**, possessing an epoxide and an exocyclic methylene group, would be precursors for xenicane diterpenes with bicyclic [4.3.1] ring systems as **1**, **2**, **7**, and **10**−**11** (Chart 1). Thus, compound **3** could be a precursor for floridicin (**7**), which seems to be further transformed into **2** via dehydration and oxidation processes. Although several cleaved methyl esters derived

Chart 1



1 R=Me
11 R=H



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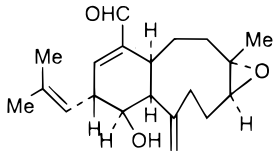

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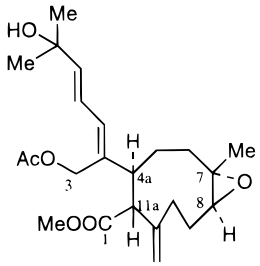

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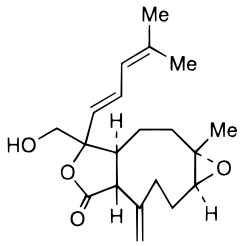

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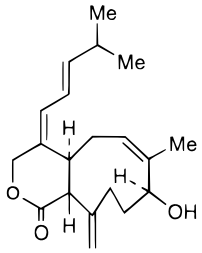

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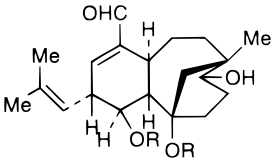
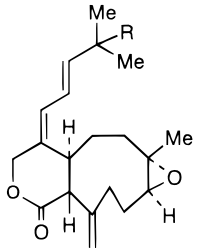
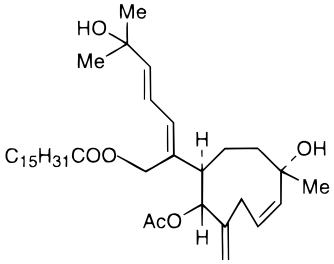


7 R=H
10 R=Me



8 R=H
9 R=OOH



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from δ-lactones were isolated from the methanol extract of the coral, such compounds have not been found in the acetone extract.

Experimental Section

General Experimental Procedures. UV and IR spectra were recorded on a UV-210 and a JASCO FT/IR 5300 spectrometers. NMR spectra were recorded with a JEOL JNM-GX 400 or a JEOL JNM-ECP 500 NMR spectrometer using TMS as internal standard and $CDCl_3$ or C_6D_6 as a solvent. MS spectra were obtained with JEOL JMS DX-300 instrument.

Animal Material. Specimens of *X. florida* (Lesson, 1826) were collected at depth of −2 m at Bonotsu, Kagoshima Prefecture in June 1990. A voucher specimen (no. 89) is deposited at the Chemistry Department of Kagoshima University.

Extraction and Isolation. The organisms (dry wt, 480 g) were immersed in acetone (50 L × 3). The acetone extract was partitioned between CH_2Cl_2 and H_2O. The CH_2Cl_2-soluble portion (6.64 g) was subjected to column chromatography of Si gel (Merck 60H, 60 g) packed in hexane, fractions (100 mL) being collected as follows: 1−3 (CH_2Cl_2−hexane, 4:1), 4 (CH_2Cl_2), 5−6 (MeOH−CH_2Cl_2, 1:99), 7−8 (MeOH−CH_2Cl_2, 1:49), 8−9 (MeOH−CH_2Cl_2, 1:24), 10−11 (MeOH−CH_2Cl_2, 3:47), 12−15 (MeOH−CH_2Cl_2, 1:9), 16−17 (1:4), and 18−19 (MeOH). Fractions 9−12 (2.1 g) were again chromatographed on Si gel using MeOH−CH_2Cl_2 with increasing proportions of MeOH to elute the column. The fractions eluted with MeOH−CH_2Cl_2 (1:49) were further subjected to Si gel column chromatography using ether and MeOH−CH_2Cl_2 (1:24 to 3:49). The faster fraction (333 mg) from the ether elution was again chromatographed on Si gel using ether−hexane (4:1) and applied to HPLC (ODS) with MeOH−H_2O (7:3) to afford florlides D (**8**) (12.1 mg) and E (**9**) (0.9 mg), 2-*O*-methylfloridicin (**10**) (1.0 mg), and **3** (1.2 mg). From the slower fractions (327 mg), 2β-epoxyfloridicin (**2**) (1.5 mg) and florlides G (**5**) (0.4 mg), F (**4**) (1.2 mg), and H (**6**) (1.2 mg) were isolated after Si gel chromatography using ether, preparative TLC with MeOH−CH_2Cl_2 (1:19), and HPLC with MeOH−H_2O (7:3). One (49.6 mg) of the fractions (3.4 g) eluted with MeOH−CH_2Cl_2 (3:49) was applied to HPLC with MeOH−H_2O (1:1) to yield 2-*O*-methylflorlide A (**1**) (0.6 mg). Floridicin (**7**) (10.2 mg) was obtained from fraction 13 (553 mg) by column chromatography on Si gel with MeOH−CH_2Cl_2 (1:19) and HPLC with MeOH−H_2O (7:3). All known compounds were identified by comparing the spectroscopic data with those of authentic samples.

11-*O*-Methylflorlide A (**1**): oil, $[\alpha]_D$ +29° (*c* 0.08, MeOH); UV (MeOH) λ_{max} (log ϵ) 239 (4.13) nm; IR (film) ν_{max} 3432, 1742, 1663 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HREIMS *m/z* 346.2141 $[M - H_2O]^+$ (calcd for $C_{21}H_{30}O_4$, 346.2143).

2β-Epoxyfloridicin (**2**): needles, mp 203−205 °C, $[\alpha]_D$ −36° (*c* 0.09, MeOH); UV (MeOH) λ_{max} (log ϵ) 224 (4.18) nm; IR (film) ν_{max} 3459, 1686, 1618 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HREIMS *m/z* 332.1971 $[M]^+$ (calcd for $C_{20}H_{28}O_4$, 332.1987).

Xeniafaraunol B (**3**): oil, $[\alpha]_D$ −73° (*c* 0.04, MeOH); UV (MeOH) λ_{max} (log ϵ) 245 (4.20) nm; IR (film) ν_{max} 3461, 1686, 1640 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; LREIMS *m*/*z* 316 $[M]^+$.

Florlide F (**4**): oil, $[\alpha]_D$ −117° (*c* 0.05, MeOH); UV (MeOH) λ_{max} (log ϵ) 242 (4.23) nm; IR (film) ν_{max} 3426, 1765, 1644 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HREIMS *m*/*z* 332.1996 $[M]^+$ (calcd for $C_{23}H_{32}O_5$, 332.1987).

Florlide G (**5**): oil, $[\alpha]_D$ −123° (*c* 0.08, MeOH); UV (MeOH) λ_{max} (log ϵ) 245 (4.15) nm; IR (film) ν_{max} 3428, 1732, 1640 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HREIMS *m*/*z* 388.2207 $[M]^+$ (calcd for $C_{20}H_{28}O_4$, 388.2249).

Florlide H (**6**): oil, $[\alpha]_D$ +305° (*c* 0.06, MeOH); UV (MeOH) λ_{max} (log ϵ) 246 (4.16) nm; IR (film) ν_{max} 3439, 1742, 1653 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; HREIMS *m*/*z* 316.2058 $[M]^+$ (calcd for $C_{20}H_{28}O_3$, 316.2039).

References and Notes

(1) For the previous report of diterpenoids from *Xenia florida*, see Iwagawa, T.; Kawasaki, J.; Hase, T. *J. Nat. Prod*. **1998**, *61*, 1513−1515.
(2) Faulkner, D. J. *Nat. Prod. Rep*. **1999**, *16*, 155−198, and references therein.
(3) Iwagawa, T.; Kawasaki, J.; Hase, T.; Yu, C.-M.; Walter, J. A.; Wright, J. L. C. *J. Chem. Commun*. **1994**, 2073−2074.
(4) Iwagawa, T.; Kawasaki, J.; Hase, T.; Wright, J. L. C. *Tetrahedron* **1997**, *53*, 6809−6818.
(5) Several methyl esters, which could be due to methanolysis of δ lactones, have been obtained (unpublished results).
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(7) Iwagawa, T.; Amano, Y.; Nakatani, M.; Hase, T. *Bull. Chem. Soc. Jpn*. **1996**, *69*, 1309−1312.

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