Pergamon

Tetrahedron, Vol. 53, No. 20, pp. 6809-6816, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00316-5

NEW DI- AND TRICARBOCYCLIC DITERPENES POSSESSING A BICYCLIC [4.3.1] RING SYSTEM ISOLATED FROM THE SOFT CORAL, *XENIA FLORIDA*[1]

Tetsuo Iwagawa,*,[a] Jun-ichi Kawasaki,[a] Tsunao Hase,*,[a] and Jeffrey L. C. Wright*,[b]

[a]Faculty of Science, Department of Chemistry, Kagoshima University
Korimoto, Kagoshima 890, Japan

[b]The National Research Council, Institute for Marine Biosciences, 1411 Oxford St.
Halifax, Nova Scotia B3H 3Z1, Canada

Abstract: Four new tricarbocyclic diterpenes **2-5** containing the bicyclic [4.3.1] ring system found in floridicin (**1**), and an additional four dicarbocylic terpenes **6-9** containing the same bicyclic moiety, have been isolated from the soft coral, *Xenia florida*. Their structures were elucidated by spectroscopic means.

The prenyl derivative geranylgeranyl pyrophosphate is the key biosynthetic substrate for a series of prenyl carbocyclases that ultimately yield a plethora of carbocyclic diterpenoid structures found in nature.[2,3] Despite a remarkable variety of diterpenes that have been found and characterized, inspection shows that most of these compounds arise from a few basic cyclisation products that undergo further manipulation and transformation. In this context then, it is interesting that a remarkable number of unusual and often unique terpenes have been reported from the Octocorallia (Phylum Coelenterata).[2] In particular, at least nine structural types of carbocyclic diterpenoids have been isolated from soft corals belonging to the family Xeniidae (Order Alcyonacea). A frequently encountered class of these diterpenes are the xenicins which have also been found in other families of the Alcyonacea including Neptheidae,[4] and Alcyoniidae.[5] A structural characteristic of the xenicins is a C_9 monocarbocyclic ring system, though recently we reported the isolation and structure of floridicin **1**, an unprecedented tricarbocyclic diterpene from *Xenia florida* in which the C_9 ring forms a [4.3.1] bicyclic system.[1] This discovery has prompted further chemical investigation of the organism in order to determine if the bicyclic structure occurs in other diterpene structures, and this has led to the isolation of several new structural analogs, including the tricarbocyclic derivatives **2-5** and the bicyclic derivatives of the xenicins **6-9**.

RESULTS AND DISCUSSION

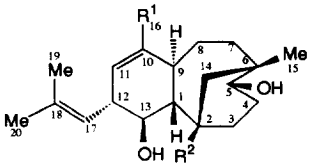
The MeOH extract of fresh *X. florida* was partitioned between CH_2Cl_2 and H_2O and the organic extract subjected to flash Si gel chromatography. Fractions eluting with 1% MeOH-CH_2Cl_2 were purified by further Si gel chromatography and finally by C_{18} reversed phase HPLC to yield **1** as the major component (300 mg)

together with smaller amounts of the later-eluting **2** (13 mg). The UV (230 nm) and IR data (1690, 1640, and 940 cm^{-1}) for **2** suggested the presence of a conjugated carbonyl system, and the HREIMS and ^{13}C NMR data for **2** (Table 1) indicated a molecular formula of $C_{21}H_{32}O_4$. The ^1H NMR spectrum of **2** was very similar to that of **1**, and contained resonances characteristic of the bicyclic [4.3.1] system[1] as well as the typical aldehyde resonance (δ_H 9.30, 1H, s). In addition, the spectrum also contained a characteristic singlet resonance (δ 3.30, 3H, s) which was assigned to a methoxy group. Comparison of the ^{13}C NMR data for **1** and **2** revealed that the C-2 resonance was shifted to lower field (Δ +6.7 ppm) in **2**, whereas the C-1, C-3, and C-14 signals were shifted to higher field (Δ -4.7, -3.4 and -5.4 ppm, respectively). These shifts were consistent with location of a methoxy group at C-2, hence compound **2** is identified as 2-*O*-methylfloridicin. The configuration of the methoxy group was determined to be β from the observation of NOEs between the methoxy protons to H-1 (1.8%) and H-14 (δ_H 1.72, 0.8%; δ_H 1.86, 1.0%) whereas no correlation was observed between H-15 and H-5.

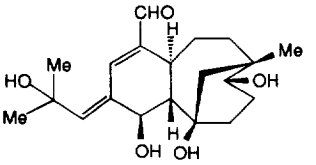
Other fractions eluted from the initial flash chromatography step were repeatedly subjected to further Si gel chromatography and final clean-up by C_{18} reversed phase HPLC to yield three compounds, floridicin A (**3**) (2.0 mg), floridicin B (**4**) (10.7 mg), and floridicin C (**5**) (1.4 mg). The molecular formula for compound **3**, ($C_{20}H_{32}O_4$) established by MS and ^{13}C NMR data was isomeric with **2**. The UV spectrum showed end absorption only (209 nm), while the IR spectrum was unexceptional and showed absorption bands corresponding to hydroxyl (3250 cm^{-1}) and a double bond (1650 cm^{-1}), though significantly there was no absorption corresponding to an aldehyde group. Although the ^1H NMR spectrum of **3** was similar to that of **1**, the resonance corresponding to the aldehyde proton was indeed absent, whereas new resonances ascribed to a hydroxymethyl group (δ_H 3.89 and 4.18, AB, J=12.8 Hz) were present and the H-11 resonance (δ_H 5.29, 1H, s) was shifted upfield by 1.1 ppm. Thus **3** was characterized as the dihydro derivative of **1** and this was confirmed by the smooth conversion of **1** to **3** with sodium borohydride. The MS and NMR spectral data of the reduction product were identical with those of **3**.

The UV spectrum of **4** exhibited an absorption maximum at 282 nm, suggesting an α, β, γ, δ-diunsaturated carbonyl system. The molecular formula $C_{20}H_{30}O_5$, established by MS and ^{13}C NMR data, indicated an additional oxygen compared with the compounds **1**-**3**. The ^1H and ^{13}C NMR spectra of **4** all displayed resonances that could be assigned to the bicyclic [4.3.1] system, but there were differences in other portions of the molecule compared with **1** (e.g. differences in the resonances due to C-10 to C-13 and C-17 to C-20) (Table 1). In the ^1H NMR spectrum, the broad, low field, singlet resonance (δ_H 8.08, 1H) was assigned to H-11, which is deshielded by both the C-16 aldehyde and C-12 double bond. The COSY spectrum showed that H-11 was weakly coupled to the aldehydic proton H-16 (δ_H 9.38, 1H, s), and H-17 (δ_H 6.17, 1H, s). The latter proton was also weakly coupled to H-13 (δ_H 4.19, 1H, d, J=11.0 Hz), which in turn was coupled to H-1 δ_H *ca* 1.7, 1H, overlapped). Another notable feature of the ^1H spectrum of **4** was that the resonances assigned to the olefinic methyl groups in **1** were replaced by two resonances (δ_H 1.41 and 1.42, 3H each, s,) assigned to two methyl groups (H_3-19 and H_3-20 respectively) attached to a carbon bearing oxygen. On the basis of the above results, the double bond at Δ^{17} in **1** was assumed to be shifted to $\Delta^{12(17)}$ in **4**. The *E* geometry of this double bond was established by NOE experiments: irradiation of the H-11 signal caused a 3.1% enhancement of the H-19 and H-20 methyl protons. A strong NOE between H-9 and H-13 (4.4%) indicated both protons were on the same α face.

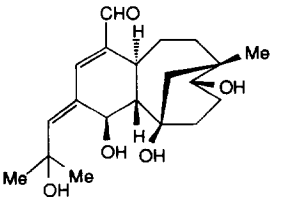
The molecular formula ($C_{20}H_{30}O_5$) for **5** revealed that it was an isomer of **4**. Indeed, the ^{13}C NMR spectrum of **5** was similar to that of **4**, except that resonances assigned to C-10, C-11, and C-17 were shifted downfield (Table 1). In the ^1H NMR spectrum, the resonance at δ_H 6.86 (1H, br s) assigned to H-11, showed weak coupling with H-9 (δ_H 2.57, 1H, m), H-16 (δ_H 9.34, 1H, s) and H-17 (δ_H 6.03, 1H, br s). Thus **5** was identified as the $\Delta^{12(17)}$ *Z* geometrical isomer of **4**, and a substantial NOE (14.4%) of H-17 upon irradiation of H-11 confirmed this assignment. As in **4**, both H-9 and H-13 were determined to be α by the observation of a strong NOE (7.4%) between them. Compound **5** could be an artifact of handling or the purification process since a peak due to **5** was detected by HPLC analysis during HPLC purification of **4**.



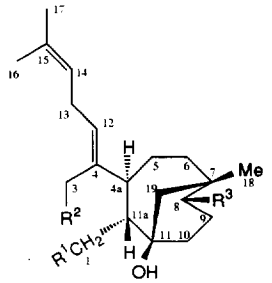
1 R^1=CHO R^2=OH
2 R^1=CHO R^2=OMe
3 R^1=CH_2OH R^2=OH



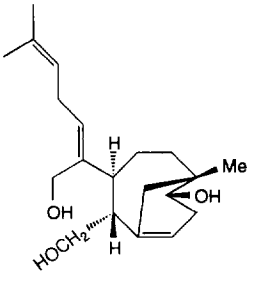
4



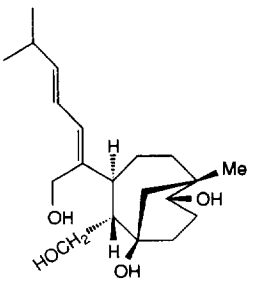
5



6 R^1=OAc R^2=OH R^3=OH
7 R^1=OH R^2=OH R^3=OH
10 R^1=OAc R^2=OAc R^3=OAc



8



9

Compounds **6-9** were present in the same primary flash chromatography fraction as compounds **1-3**, and were separated during the secondary Si gel fractionation step and finally purified using C_{18} reversed phase HPLC. Compound **6** was obtained as an oil and preliminary inspection of the spectral data highlighted some important differences compared with the corresponding spectra of compounds **1-5**. For example, the UV data (207 nm) indicated no conjugation, and the ^1H resonances associated with the conjugated aldehyde system were missing. The IR data was compatible with the presence of hydroxyl (3350 cm^{-1}), an ester (1720 cm^{-1}) and double bond (1650-1665 cm^{-1}) functions.

The molecular formula ($C_{22}H_{36}O_5$) obtained by MS and ^{13}C NMR data indicated five degrees of unsaturation, two of which are accounted for as double bonds (four olefinic carbons δ_C 122.3 (d), 129.0 (d), 132.5 (s), and 142.2 (s)), and a third as an ester (δ_C 170.7). Thus **6** was concluded to contain two rings and the gross structure was assigned as follows: The ^1H NMR data for the diunsaturated side chain were similar to those reported for the side chain in deoxyxeniolide B[6] and the COSY data showed that the allylic methylene group H_2-13 was coupled to both H-12 and H-14, while the latter proton was also weakly coupled to the olefinic methyl groups H_3-16 and H_3-17. A strong NOE of H-12 (11.8%) upon irradiation of H-4a established a *Z*-configuration for the $\Delta^{4(12)}$ double bond. Two sets of resonances (δ_H 4.20, 1H, dd, *J*=4.5, 11.4 Hz; δ_H

4.29, 1H, dd, 3.7, 11.4 Hz, H_2-1) and (δ_H 4.12, 1H, dd, *J*=5.9, 12.1 Hz; δ_H 4.17, 1H, dd, *J*=4.2, 12.1 Hz, H_2-3) were ascribed to two oxymethylene groups. The former group was assigned to C-1 since the COSY data showed that it was coupled to H-11a which in turn was coupled to H-4a. The second oxymethyl group, which showed a NOE (3.3%) upon irradiation of H-13, was concluded to be located at C-3. The characteristic resonance at δ_H 2.02 (3H, s) was assigned to the methyl of an acetate, which was placed at C-1 as suggested by the low field chemical shift of the oxymethyl protons. Finally, the large $^3J_{HH}$ (*J*=11.4 Hz) between H-4a and H-11a indicated a *trans* relationship for these protons. The remaining unassigned carbons in **6** appeared to comprise the same bicyclic [4.3.1] ring system observed in floridicin (**1**).[1] For example, the ^{13}C chemical shifts for C-5 through C-11a in **6** were very similar to the shifts observed for the corresponding positions in **1** (Table 1). In addition, the ^1H NMR data for H-8 (δ 3.38, 1H, br s), H-9 (δ *ca* 1.66, 1H, overlapped), H-18 (δ 1.00, 3H, s) and H-19 (δ 1.56, 1H, d, *J*=13.9 Hz; δ 1.80, 1H, br d, *J*=13.9 Hz) in **6** was a match with the corresponding data for **1**.[1] A weak, but consistent NOE between H-18 and H-19 (1.3%) supplied further proof of the structure revealed that both groups were on the same face, presumably β, of the bicyclic system. Thus the combined data indicated that the structure to be as shown in **6**.

Table 1. 13C NMR Spectral Data of Compounds **1-10**.

C	1	2	3	4	5	C	6	7	8	9	10
1	56.7	52.0	58.0	58.1	57.4	1	65.7	63.4	63.2	63.8*	65.2
2	76.4	83.1	76.6	76.4	76.8	3	58.8	58.1	61.5	64.1*	60.5
3	28.9	25.5	28.8*	28.5	28.3*	4	142.2	142.4	142.4	141.9	142.8
4	29.3	29.3	28.9*	29.2	28.5*	4a	51.9	50.6	50.2 ¶	41.1	51.9
5	74.9	74.5	75.0	74.8	74.8	5	31.1	31.5	31.6	29.9	30.6
6	38.0	37.8	37.8	38.0	37.9	6	37.0	38.6	38.8*	38.7	38.1
7	39.8	39.6	40.2	39.8	39.7	7	38.3	36.9	40.0	36.9	36.1
8	29.5	29.0	27.6	29.6	29.0	8	74.0	74.2	74.4	74.1	75.7
9	40.4	39.9	43.5	40.5	40.2	9	27.4	27.5	38.8*	27.6¶	24.8
10	146.5	146.3	141.5	144.2	146.8	10	29.0	28.1	117.0	27.9¶	29.5
11	153.8	153.9	127.9¶	146.7	152.0	11	74.0	75.3	141.7	75.7	73.8
12	48.1	47.7	47.3	138.0	139.8	11a	51.9	54.2	48.6 ¶	53.3	53.4
13	75.3	75.4	76.3	72.5	72.5	12	129.0	128.6	127.6	127.5	131.7
14	45.0	39.6	44.6	45.1	45.2	13	26.8	26.7	28.8	121.7	26.9
15	31.3	31.3	31.0	31.2	31.2	14	122.3	122.6	122.1	144.0	121.6
16	195.4	195.4	65.6	195.6	194.8	15	132.5	132.3	132.3	29.3	132.8
17	124.8	125.2	127.6¶	138.7	144.1	16	17.8	17.8	17.9	22.4	17.7
18	137.7	137.0	135.5	72.9	71.5	17	25.7	25.7	25.7	22.5	25.7
19	18.7	18.7	18.5	31.5	31.0	18	30.9	29.6	22.6	31.6	29.3
20	26.2	26.1	26.2	32.0	31.1	19	44.1	44.0	34.0§	44.1	44.9
MeO		48.2				MeCOO	21.1				21.0 x 2, 21.2
						MeCOO	170.7				170.6, 170.7, 171.0

Compounds **1-5** and **6-10** were measured in CD_3OD and $CDCl_3$, respectively.

*, ¶ These values may be interchangeable in any vertical column.

Compound **7**, which eluted after **6** in the HPLC step, was identified as the deacetyl derivative of **6**. The molecular formula ($C_{20}H_{34}O_4$) supported this proposal and the IR data for **7** showed no acetate carbonyl stretch, and no acetate resonances were observed in the ^{13}C NMR spectrum. While the ^1H NMR spectrum also

contained no evidence of an acetate group, the C-1 hydroxymethyl proton resonances were shifted upfield (Δ 0.48 ppm) compared with those in **6**, consistent with loss of acetate from this position. The remainder of the resonances were characteristic of the same C_8 side chain and bicyclo[4.3.1]decane ring system found in **6** (Tables 1). Acetylation of **7** gave a triacetate **10** ($C_{26}H_{40}O_{7}$), possessing an ^{1}H NMR spectrum, in which the resonances assigned to H_2-1, H_2-3 and H-8 were characteristically shifted down field, and the resonance for H-4a, which overlapped other signals in the ^{1}H NMR spectrum of **7**, was now observed as a broad triplet (δ_H 2.19, J=11.0 Hz).

The molecular formula ($C_{20}H_{32}O_3$) for **8** indicated loss of water and an additional degree of unsaturation compared with **7**. The ^{13}C NMR spectrum of **8** supported the molecular formula and contained two new olefinic resonances [δ_C 117.0 (d) and 141.7 (s)] concordant with a trisubstituted double bond which was found to form an unusual bridgehead olefin structure. The ^{1}H NMR spectrum of **8** showed a new resonance (δ_H 5.52, 1H, m) which was assigned to the olefinic proton H-10. The COSY data showed H-10 was coupled to the methylene protons H-9, which in turn were coupled to H-8, and thus located the additional double bond at Δ^{10}. The remainder of the ^{1}H NMR spectrum was essentially similar to that of **7**, and the resonances associated with the unsaturated side chain were readily distinguishable. This observation, and the fact that the ^{13}C NMR chemical shifts of C-4, C-4a, and C-12 to C-17 in the spectrum of **8** were comparable with those of **7** (Table 1), implied the same double bond geometry.

The final product **9** was isomeric ($C_{20}H_{34}O_4$) with **7** and the ^{13}C NMR spectrum of **9** displayed resonances that could be readily matched with those of the bicyclic [4.3.1] ring system in **7** (Table 1). Nevertheless the UV data (238 nm) indicated a conjugated double bond system, and inspection of the ^{1}H NMR data revealed obvious differences in the side chain. The COSY data was used to identify the 2-methyl-3,5-heptadienol side chain of **9** and the *E* geometry of the conjugated system was determined from the *J* value (14.1 Hz) between H-13 and H-14, and an NOE between H-4a and H-12. The magnitude of the coupling constant between H-4a and H-11a (J=11.0 Hz) was in the same range as the related compounds in this series and hence the stereochemistry of the ring junction was determined to be *trans* .

The remarkable variety of diterpenes from corals possessing different carbocyclic structures indicates the presence of a number of varied and unique prenyl carbocyclases in the Alcyonaria. The range includes representatives of mono-, di- and the much rarer tricarbocyclic diterpenes. Part of this variety likely results from the initial formation of large-ringed compounds (e.g. C_9, C_{13}, and C_{14}) with sufficient conformational flexibility to allow other internal cyclisations to occur. This, coupled with further rearrangements and modification of various groups or moieties leads to the great diversity of diterpenoid structures that have been observed from corals. The xenicins, which are found in several families of the Order Alcyonacea, also occur in more distant families of different Orders such as the Gorgonacea[7] and Coenothecalia.[8] Interestingly, xenicin derivatives are also found in several species of brown seaweeds (family Dictyotacea),[9] indicating that a similar coral prenyl carbocyclase occurs in these algae. Usually xenicin diterpenes are all monocarbocyclic, and this work is the first report of dicarbocyclic derivatives containing a bicyclic [4.3.1] moiety extends the range of such compounds derived from the xenicin as well as the efflatournia skeletons.[10] To date, we have only been able to isolate such bicyclic diterpenes from a single species of *Xenia florida* collected from the Kagoshima prefecture, and it is not possible to predict if this is the result of two unique carbocyclases or the presence of an additional tailoring enzyme that acts upon the initial cyclisation product. The latter seems most plausible since the bicyclic [4.3.1] moiety is found in both types of cyclisation product (i.e. xenicins and efflatournia types)

found in *X. florida*. Further studies are aimed at exploring the frequency of these bicyclic derivatives in other coral species.

EXPERIMENTAL

UV and IR spectra were recorded on Shimadzu UV-210 and IR-408 , respectively. Optical rotations were measured on a JASCO J-20A spectropolarimeter. NMR spectra were recorded with a JEOL JNM-GX 400 spectrometer. The chemical shifts are reported in δ (ppm) and the coupling constants are in Hz. Mass spectra were obtained with a JEOL JNM D300 spectrometer at 70 eV.

Extraction and Isolation. Specimens of *Xenia florida* (Lesson, 1826) were collected at depth of -2 m at Bonotsu, Kagoshima prefecture. The reference sample was deposited in Kushikino Marine Park and identified by Dr. F. Iwase. The organisms (wet weight: 12 kg) were immersed in MeOH. The MeOH extract was partitioned between CH_2Cl_2 and H_2O. The CH_2Cl_2 soluble portion (12.2 g) was subjected to a column chromatography of silica gel (Merck 60H, 60 g) packed in hexane, fractions (100 ml) being 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 silica gel using MeOH-CH_2Cl_2 (1:99) and applied to HPLC (ODS) with MeOH-H_2O (7:3) to afford **1** (300 mg) and **2** (13 mg). Elution with MeOH-CH_2Cl_2 (3:47) gave a residue, from which **6** (2.6 mg), **8** (1.8 mg), **9** (3.4 mg), and **7** (34.2 mg) were separated by use of HPLC with MeOH-H_2O (3:2). Fractions 37-41 (2 g) were repeatedly subjected to silica gel column chromatography with MeOH-CH_2Cl_2 (1:9) and HPLC with MeOH-H_2O (3:7 to 1:1) to give **3** (2.0 mg), **4** (10.7 mg), and **5** (1.4 mg).

2-*O*-Methyfloridicin (2). Oil, $[\alpha]_D$ -89.2° (*c* 0.25, MeOH); UV (MeOH) λmax 230 nm (ε 9800); IR (film) νmax 3400, 2720, 1690, 1640, and 940 cm^{-1}; ^1H NMR (CD_3OD) δ 1.02 (3H, s. H-15), 1.36-1.44 (2H, m, H-8*endo* and H-7*endo*), 1.58 (1H, dd, *J*=4.8 and 12.5 Hz, H-7*exo*), 1.72 (1H, d, *J*=13.7 Hz, H-14), 1.75, (3H , br s, H-19), 1.77 (3H , br s, H-20), 1.84 (1H, br d, *J*=13.7 Hz, H-14), 1.89-1.94 (2H, m, H-3), 2.04 (1H, t, *J*=10.3 Hz, H-1), *ca* 2.1 (1H, m, H-4*endo*), 2.13 (1H, dd, *J*=5.1 and 11.0 Hz,. H-8*exo*), 2.55 (1H, m, H-9), 3.30 (3H, s, OMe), 3.34 (1H, br s, H-5), 3.37 (1H, m, H-12), 3.55 (1H, dd *J*=8.8 and 10.3 Hz, H-13), 4.98 (1H, dq, *J*=1.5 and 9.6 Hz, H-17), 6.38 (1H, t, *J*=2.0 Hz, H-11), 9.30 (1H, s, H-16); ^{13}C NMR, see Table 1. HREIMS *m/z* 330.2201 [$(M-H_2O)^+$, calcd for $C_{21}H_{30}O_3$, 330.2195)].

Floridicin A (3). Oil, $[\alpha]_D$ -101.4° (*c* 0.12, MeOH); UV (MeOH); λmax 209 nm (ε 9800); IR (film) νmax 3250, 1650, and 940 cm^{-1}; ^1H NMR (CD_3OD) δ 0.99 (3H, s, H-15), 1.45 (1H, br dd, *J*=13.7 and 26.6 Hz, H-8*endo*), 1.62 (1H, d, *J*=13.6 Hz, H-14), 1.67, (3H , d, *J*=1.5 Hz, H-19), *ca* 1.70 (1H, m, H-1), 1.74 (3H, d, *J*=1.1 Hz, H-20), 1.76 (1H, br d, *J*=13.6 Hz, H-14), *ca* 1.80 (1H, m, H-3), 2.00-2.08 (3H, m, H-3, H-4, and H-8*exo*), 2.35 (1H, br t, *J*=10.3 Hz, H-9), 3.05 (1H, br t, *J*=9.3 Hz, H-12), 3.63 (1H, dd, *J*=9.3 and 10.3 Hz, H-13), 3.89 and 4.18 (1H each, AB, *J*=12.8 Hz), 4.92 (1H, qd, *J*=1.5 and 9.3 Hz, H-17), 5.29 (1H, s, H-11); ^{13}C NMR, see Table 1. EIMS: *m/z* 336 (M^+).

Floridicin B (4). Oil, $[\alpha]_D$ +382.5° (*c* 0.12, MeOH); UV (MeOH) λmax 282 nm (ε 14500); IR (film) νmax 3350, 1670, 1640, and 950 cm^{-1}; ^1H NMR (CD_3OD) δ 0.99 (3H, s, H-15), 1.41 and 1.42 (3H each, s, H-19 and H-20), *ca* 1.4 (2H, m, H-7*endo* and H-8*endo*), 1.58 (1H, m, H-7*exo*), 1.66 (1H, d, *J*=14.3 Hz, H-14), 1.72 (1H, br d, *J*=14.3 Hz, H-14), *ca* 1.75 (1H, m, H-4*exo*), 1.86 (1H, dd, *J*=5.5 and 14.1 Hz, H-3),

2.07-2.18 (3H, m, H-3, H-4, and H-8*exo*), 2.65 (1H, br t, *J*=9.0 Hz, H-9), 4.19 (1H, d, *J*=11.0 Hz, H-13), 6.17 (1H, s, H-17), 8.06 (1H, s, H-11), and 9.38 (1H, s, H-16); ^{13}C NMR, see Table 1. EIMS: *m/z* 350 (M^+); HREIMS *m/z* 350.2113 (M^+, calcd for $C_{20}H_{30}O_5$, 350.2133).

Floridicin C (5). Oil, $[\alpha]_D$ +121.2° (*c* 0.01, MeOH); UV (MeOH) λmax 280 nm (ε 18000); IR (film) νmax 3300, 1660, 1620 and 950 cm^{-1}; ^1H NMR (CD_3OD) δ 0.99, *ca* 1.37 (2H, m, H-7*endo* and H-8*endo*), 1.42 and 1.45 (3H each, s, H-19 and H-20), 1.59 (1H, dd, *J*=4.8 and 12.5 Hz, H-7*exo*), 1.66 (1H, d, *J*=14.6 Hz, H-14), *ca* 1.74 (2H, m, H-1 and H-4), 1.78 (1H, br d, *J*=14.6 Hz, H-14), *ca* 1.85 (1H, m, H-3), 2.02-2.11 (2H, m, H-3 and H-4), 2.40 (1H, dd, *J*=5.7 and 11.5 Hz, H-8*exo*), 2.57 (1H, m, H-9), 3.34 (1H, br s, H-5), 4.63 (1H, dd, *J*=2.2 and 11.0 Hz, H-13), 6.03 (1H, br s, H-17), 6.86 (1H, br s, H-11), and 9.34 (1H, s, H-16); ^{13}C NMR, see Table 1. EIMS: *m/z* 332 (M^+-H_2O).

Compound 6 Oil, $[\alpha]_D$ -11.5° (*c* 0.087, MeOH); UV (MeOH) λmax 207 nm (ε 5700); IR (film) νmax 3350, 1720, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$): δ *ca* 1.21 (1H, m, H-6), *ca* 1.53 (2H, overlapped, H-5 and H-6), *ca* 1.66 (2H, overlapped, H-9 and H-10), 1.66 (1H, d, *J*=13.9 Hz, H-19), 1.69 (3H x 2, br s, H-16 and H-17), 1.80 (1H, br d, *J*=13.9 Hz, H-19), *ca* 1.82 (2H, overlapped, H-5 and H-10), *ca* 1.85 (1H, overlapped, H-11a), 2.02 (3H, s, OAc), *ca* 2.04 (1H, overlapped, H-9), 2.19 (1H, br t, *J*=11.4 Hz, H-4a), 2.79 (2H, t, *J*=7.1 Hz, H-13), 3.38 (1H, br s, H-8), 4.12 (1H, dd, *J*=5.9 and 12.1 Hz, H-3), 4.17 (1H, dd, *J*=3.7 and 12.1 Hz, H-3), 4.20 (1H, dd, *J*=4.5 and 11.4 Hz, H-1), 4.29 (1H, dd, *J*=3.7 and 11.4, H-1), 5.04 (1H, br t, *J*=7.1 Hz, H-14), and 5.33 (1H, t, *J*=7.1 Hz, H-12); ^{13}C NMR, see Table 1. EIMS *m/z* 362 (M^+-H_2O) and 347 (M^+-H_2O-Me); HREIMS *m/z* 347.2227 (M^+-H_2O-Me, calcd for $C_{21}H_{31}O_4$, 347.2222).

Compound 7 Oil, $[\alpha]_D$ -16.2° (*c* 1.14, MeOH); IR (film) νmax 3350 and 1660 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.98 (3H, s, H-18), 1.16 (1H, br t, *J*=13.6 Hz, H-6), 1.43 (1H, br d, *J*=13.6 Hz, H-5), 1.51 (1H, br d, *J*=13.6 Hz, H-6), *ca* 1.65 (3H, overlapped, H-9, H-10, and H-19), 1.69 (6H, br s, H-16 and H-17), *ca* 1.78 (2H, overlapped, H-5 and H-11a), 1.78 (1H, d, *J*=13.6 Hz), 1.96 (3H, overlapped, H-4a, H-9 and H-10), 2.80 [(2H, m); 2.80 (1H, t, *J*=7.1 Hz) at 60° C, H-13], 3.33 (2H, m, H-8), 3.77 (1H, br s, H-1), 4.12 [(2H, m), 4.09 and 4.20 (1H each, AB, *J*=11.7 Hz) at 60° C, H-3], 5.06 (1H, br t, *J*=7.0 Hz, H-14), and 5.30 (1H, t, *J*=7.3 Hz); ^{13}C NMR, see Table 1. EIMS: *m/z* 322 (M^+-H_2O); HREIMS *m/z* 320.2414 (M^+-H_2O, calcd for $C_{20}H_{32}O_3$, 320.2315).

Compound 8 Oil, $[\alpha]_D$ +116.7° (*c* 0.06, MeOH); IR (film) νmax 3350 and 1665 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.02 (3H, s, H-18), 1.63 and 1.70 (3H each, br s, H-16 and H-17), 1.75 (1H, d, *J*=12.8 Hz, H-19), 1.85 (1H, t, *J*=12.0 Hz, H-4a), 1.95 (1H, br d, *J*=16.5 Hz, H-9), 2.09 (1H, br d, H-19), *ca* 2.70 (3H, overlapped, H-11a and H-13), 2.86 (1H, dt, 7.6 and 16.5 Hz, H-9), 3.45 (1H, m, H-8), *ca* 3.63 (1H, m, H-1), 3.71 (1H, t, *J*=10.1 Hz, H-1), 4.12 (2H, br s, H-3), 5.05 (1H, t, *J*=7.1 Hz, H-14), 5.46 (1H, m, H-12), and 5.52 (1H, m, H-10); ^{13}C NMR, see Table 1. EIMS: *m/z* 320 (M^+).

Compound 9 Oil, $[\alpha]_D$ -32.8° (*c* 0.11, MeOH); IR (film) νmax 3350 and 1665 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.00 (3H, s, H-18), 1.02 (6H, d, *J*=6.8 Hz, H-16 and H-17), 1.21 (1H, m, H-6), 1.41 (1H, m, H-5), 1.57 (1H, dd, *J*=3.7 and 15.0 Hz, H-6), 1.63 (1H, d, *J*=13.9 Hz, H-19), 1.69 (1H, overlapped, H-10), *ca* 1.73 (1H, overlapped, H-9), 1.81 (1H, br d, *J*=13.9 Hz, H-19), *ca* 1.92 (1H, overlapped, H-5, *ca* 1.97 (1H, overlapped, H-10), *ca* 2.00 (1H, overlapped, H-11a), *ca* 2.07 (1H, overlapped, H-9), 2.37 (1H, m, H-15), 2.54 (1H, br t, *J*=11.0 Hz, H-4a), 3.41 (1H, br s, H-8), 3.67 (1H, br d, *J*=8.1 Hz, H-1), 3.75 (1H, dd, *J*=8.1 and H-11.4 Hz, H-1), 4.10 and 4.25 (1H each, br d, *J*=13.2 Hz, H-3), 5.71 (1H, dd, *J*=7.1 and 14.1

Hz, H-14), and 6.04-6.14 (2H, overlapped, H-12 and H-13); ^{13}C NMR, see Table 1. EIMS *m/z* 338 (M^+); HREIMS *m/z* 338.2470 (M^+, calcd for $C_{20}H_{34}O_4$, 338.2475),

Reduction of 1. Treatment of a solution of **1** (4.5 mg) in MeOH (1.5 mL) with $NaBH_4$ (7.5 mg) gave an oil (3.5 mg); EIMS *m/z* 336 (M^+). The MS and NMR spectral data were identical with those of **3**.

Acetylation of 7. Compound **7** (2.1 mg) was acetylated with Ac_2O in pyridine to give a triacetate **10** (2 mg), oil, IR (film) vmax 3450, 1730, 1235 and 965 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.92 (3H, s, H-18), 1.28 (1H, br t, *J*=13.2 Hz, H-6), *ca* 1.50 (3H, overlapped, H-5, H-6, and H-10), 1.66 (1H, d, *J*=13.9 Hz, H-19), 1.69 (6H, br s, H-16 and H-17), *ca* 1.74 (1H, overlapped, H-9), *ca* 1.80 (2H, overlapped, H-5 and H-11a), 1.85 (1H, 1H, br d, *J*=13.9 Hz, H-19), *ca* 1.99 (2H, overlapped, H-9 and H-10), 2.02, 2.07, and 2.08 (3H each, s, OCOMe), 2.19 (1H, br t, *J*=11.0 Hz, H-4a), 2.75 (1H, br t, *J*=7.3 Hz, H-13), 4.16 (1H, dd, *J*=5.1 and 11.7 Hz, H-1), 4.26 (1H, dd, *J*=3.3 and 11.7 Hz, H-1), 4.59 (2H, s, H-3), 4.60 (1H, overlapped, H-8), 5.02 (1H, qt, *J*=1.5 and 7.3 Hz, H-14), and 5.44 (1H, t, *J*=7.3 Hz, H-12); ^{13}C NMR ($CDCl_3$): d 17.7 (H-16), 21.0 x 2, and 21.2 (OCOMe), 24.8 (C-9), 25.7 (C-17), 26.9 (C-13), 29.3 (C-18), 29.5 (C-10), 30.6 (C-5), 36.1 (C-7), 38.1 (C-6), 44.9 (C-19), 51.9 (C-4a), 53.4 (C-11a), 60.5 (C-3), 65.2 (C-1), 73.8 (C-11), 75.7 (C-8), 121.6 (C-14), 131.7 (C-15), 132.8 (C-15), 142.8 (C-4), 170.6, 170.7, and 171.0 (OCOMe). EIMS *m/z* 464 (M^+) and 446 (M^+-H_2O); HREIMS *m/z* 446.2678 (M^+-H_2O, calcd for $C_{26}H_{38}O_6$, 446.2668).

Acknowledgments: We are grateful to Dr. F. Iwase (Yaeyama Marine Park) for identifying the coral and Dr. S. Moore for suggestions during preparation of the manuscript.

REFERENCES

1. For the previous report on diterpenoids from *Xenia florida*, see: Iwagawa, T.; Kawasaki, J.; Hase, T.; Yu, C.-M.; Walter, J. A.; Wright, J. L. C. *J. Chem. Soc., Chem. Commun.*, **1994**, 2073. The configuration of the hydroxyl group at C-2 in floridicin, should have been depicted as β based on the published NOE results and X-ray data.
2. For a recent review of coral terpenes, see: Coll, J. C. *Chem Rev.* **1992**, *92*, 613. For annual updates see: Faulkner, D. J. *Nat. Prod. Rep.* **1996**, *13*, 75, and references cited therein.
3. Coolbear, T.; Threlfall, D. R. in *Microbial Lipids*; Ratledge, C.; Wilkinson, S.G.; Eds.; Academic Press: London, UK, 1989; pp 115-254.
4. Hooper, G. J.; Davies-Coleman, M. T. *Tetrahedron*, **1995**, *51*, 9973.
5. Rudi, A.; Ketzinel, S.; Goldberg, I.; Stein, Y.; Kashman, Y.; Benayahu, Y.; Schleyer, M. *J. Nat. Prod.* **1993**, *58*, 1581, and references cited therein.
6. Miyamoto, T.; Takenaka, Y.; Yamada, K.; Higuchi, R. *J. Nat. Prod.* **1995**, *58*, 924.
7. (a) Schwartz, R. E.; Scheuer, P. J.; Zabel, V.; Watson, W. H. *Tetrahedron*, **1981**, *37*, 2725.
   (b) Fusetani, N.; Asano, M.; Matsunaga, S.; Hashimoto, K. *Tetrahedron* ,**1989**, *45*, 1647.
8. (a) Ochi, M.; Kataoka, K.; Tatsukawa, A.; Kotsuki, H.; Shibata, K. *Heterocycles*, **1994**, *38*, 151.
   (b) Tanaka, J.; Ogawa, N.; Liang, T.; Higa, T.; de Nys, R.; Bowden, B. F.; Carroll, A. R.; Coll, J. C.; Bernardinelli, G.; Jefford, C. W. *Tetrahedron*, **1994**, *50*, 9989.
9. (a) Finer, J.; Clardy, J.; Fenical, W.; Minale, L.; Riccio, R.; Battaile, J.; Kirkup, M.; Moore, R. E. *J. Org. Chem.* **1979**, *44*, 2044.
   (b) Ishitsuka, M. O.; Kusumi, T.; Kakisawa, H. *J. Org. Chem.* **1988**, *53*, 5010
   (c) Norte, M.; Gonzalez, A. G.; Zarraga, M.; Perez, C.; Rodriguez, M. L; Ruiz-Perez, C.; Dorta, L. *Tetrahedron*, **1990**, *46*, 6125.
   (d) König, G. M.; Wright, A. D.; Sticher, O. *Tetrahedron*, **1991**, *47*, 1399.
10. Burns, K. P.; Englert, G.; Kazlauskas, R.; Murphy, P. T.; Schönholzer, P.; Wells, R. J. *Aust. J. Chem.* **1983**, *36*, 171.

(*Received in Japan* 3 *February* 1997; *accepted* 21 *March* 1997)