NEW XENIA DITERPENOIDS FROM A SOFT CORAL *XENIA* SPECIES[1]

Tetsuo Iwagawa,* Yasuhisa Amano, Hiroaki Okamura, Munehiro Nakatani,* and Tsunao Hase*

Department of Chemistry, Faculty of Science, Kagoshima University, Korimoto, Kagoshima 890 Japan

Abstract - Six new xenia diterpenoids with an opened A-ring containing an aliphatic acid have been isolated from a soft coral *Xenia* sp. The structures were determined on the basis of the spectroscopy.

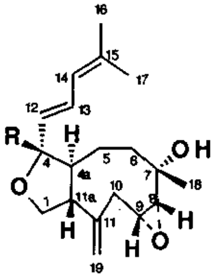
Bicyclic diterpenoids possessing a cyclononane skeleton which have been isolated from soft corals *Xenia* sp., *Nephtea* sp. and *Alcyonium* sp., as well as from gorgonians,[2] are called xenia diterpenoids.[3] The structures of the diterpenoids have been classified into three groups: xenicins, xeniolide, and xeniaphyllanes.[3]

As part of our studies on soft corals *Xenia* species we have recently undertaken an investigation of an unidentified *Xenia* sp., collected in the area of Bonotsu, Kagoshima prefecture.[1] Previous reports have described the structure elucidation of nine new xenia xeniolides and related compounds isolated from the methanol extract[4] and seven new xenia diterpenoids containing an opened A-ring, which were acylated with a series of C_{16}-C_{20} saturated fatty acids, from the acetone extract of the same organism.[5] Further investigation of chemical constituents of the acetone extract has led to the isolation of six new xenia diterpenoids, xeniaethers C (1), D (2), and E (3) and azamilides H (4), I (5), and J (6). In this report, we describe their isolation and structure elucidation.

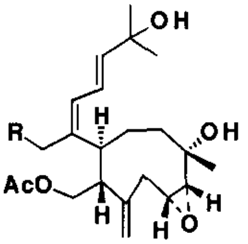
Xeniaether C (1), $C_{20}O_{30}O_4$, contained absorption bands corresponding to a hydroxyl group (3450 cm^{-1}) and a conjugated diene (1625 cm^{-1}) in the ir spectrum. The ^{1}H nmr spectrum was similar to that of xeniaether A (7),[4] except for resonances due to two methine protons on an epoxide (δ 2.79; 1H, d, J=4.0

Hz, H-8; δ 3.02; 1H, ddd, J=4.0, 5.5, and 11.0 Hz, H-9) in place of olefinic protons at C-8 and C-9 in 7. The gross structure was elucidated as follows. Resonances due to two olefinic methyl protons (δ 1.77 and 1.78, 3H each, br s, H-16 and H-17) and three olefinic protons (δ 5.62; 1H, d, J=15.2 Hz, H-12, δ 5.86; 1H, br d, J=11.0 Hz, H-14, and δ 6.67; 1H, dd, J=11.0 and 15.2 Hz, H-13) were observed, suggesting a 4-methyl-1*(E)*,3-pentadiene moiety. H-3 hydroxymethyl protons appeared at δ 3.57 (2H, d, J=6.2 Hz), which were coupled to a hydroxyl proton (δ 2.00; 1H, t, J=6.2 Hz, OH). H-1 oxymethylene protons (δ 3.40; 1H, dd, J=7.6 and 11.3 Hz, δ 3.82; 1H, t, J=7.6 Hz) were coupled to H-11a (δ 2.96; 1H, dt, J=7.6 and 11.3 Hz), the latter of which was further coupled to H-4a (δ 3.12; 1H, dd, J=7.7 and 11.3 Hz). The H-8 epoxy proton was coupled to the H-9 another epoxy proton, which in turn was coupled to H-10 (δ 2.71; 1H, br t, J=11.7 Hz, δ 2.72; 1H, overlapped). A broad singlet (δ 5.13; 2H) was due to *exo* methylene protons at C-19. The relative stereochemistry of all chiral centers was determined by nOe experiments in C_6D_6 (Figure 1). NOes from H-4a (δ 3.18; 1H, dd, J=8.1 and 11.4 Hz) to H-1α (δ 3.38; 1H, dd, J=8.0 and 11.9 Hz, 3.5%), as well as nOes from H-11a (δ 2.84; 1H, dt, J=8.0 and 11.9 Hz) to H-1β (δ 3.69; 1H, t, J=8.0 Hz, 5.4%), and to H-3 (δ 3.57; 1H, dd, J=6.6 and 11.9 Hz, δ 3.65; 1H, dd, J=5.9 and 11.4 Hz, 3.5%) were observed. These data suggested that in the major conformer H-4a and H-1α occurred on the same face of the ring system and H-11a, H-1β, and H-3 were on the opposite face to H-4a. The major conformer of the 9-membered ring was also elucidated by the observation of the nOes between H-4a and H-10α (δ 2.58; 1H, t, J=11.8 Hz, 11.5%) and H-6β (δ 1.41; 1H, br t, J=15.0 Hz, 2.7%), between H-6β and H-8 (δ 2.27; 1H, d, J=3.8 Hz, 3.1%) and H-9 (δ 2.72; 1H, dt, J=3.8 and 11.8 Hz, 1.1%), and between H-18 (δ 1.08; 3H, s) and H-5α (δ 1.24; 1H, br d, J=15.0 Hz, 1.2%) and H-6α (δ 1.80; 1H, dt, J=3.3 and 15.0 Hz, 1.4%). The stereochemistry of the epoxide and C-18 methyl group was therefore established to be α and β, respectively. Furthermore, the α-configuration of the epoxide was confirmed by the large coupling constant (J=11.8 Hz) between H-9 and one of methylene protons (H-10α), indicating a *trans*-diaxial relationship (Figure 2). Assuming a β-epoxide structure, the coupling constant between H-9 and H-10α would be predicted to be small by the torsion angle (*ca.*120°). The side chain moiety was deduced to be in the α-configuration from an nOe between H-4a and H-13 (4.3%). Therefore, the structure of 1 was deduced to be 8,9-α-epoxyxeniaether A.

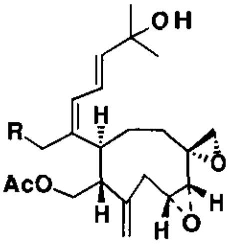
The ^1H nmr spectra of xeniaether D (2), $C_{40}H_{64}O_5$, and xeniaether E (3), $C_{38}H_{60}O_5$, were similar in many respects to those of 1, except that 2 and 3 displayed resonances due to an additional fatty acyl chain. The fatty acyl groups in 2 and 3 were determined to be stearoyl and palmitoyl respectively, as suggested by the fragment ions at *m/z* 283 and 255 in the negative ion FAB mass spectra. Location of the acyl groups was determined to be at C-3 by the downfield chemical shifts of H-3 methylene protons (δ 4.11) compared to those of **1** (δ 3.57). Thus, xeniaethers D (**2**) and E (**3**) are 3-stearylxeniaether C and 3-palmitylxeniaether C, respectively.



1 $R=\overset{3}{C}H_2OH$
2 $R=C_{17}H_{35}COOCH_2$
3 $R=C_{15}H_{31}COOCH_2$
7 $R=CH_2OH$, Δ^8



4 $R=C_{17}H_{35}COO$
5 $R=C_{15}H_{31}COO$
8 $R=C_{17}H_{35}COO$, Δ^8



6 $R=C_{17}H_{35}COO$

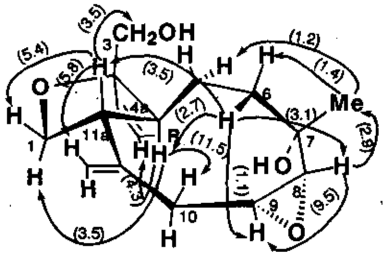


Figure 1. NOes (%) observed for **1**.

Figure 2. Conformations of α-and β-epoxides in **1**.

The ^1H nmr spectra of azamilide H (**4**), $C_{40}H_{68}O_7$, and azamilide I (**5**), $C_{38}H_{64}O_7$, were indistinguishable, and resembled those of azamilide A (**8**),[5] except for resonances due to additional epoxy protons at *ca*.. 2.67 (1H, m, H-9) and δ 2.75 (1H, d, *J*=4.0 Hz, H-8). In addition, the olefinic protons at δ 5.25 (1H, d, *J*=11.7 Hz, H-8) and 5.85 (1H, m, H-9), observed in **8**, were absent. The stereochemistry of the epoxide, which could not be unequivocally deduced by nOe experiments in **4** and **5**, was tentatively assumed to be α as in the case of related compounds (**2**) and (**3**) on comparison of the chemical shift data. The value of the coupling constant (*J*=11.9 Hz) between H-4a (δ 3.80; 1H, dd, *J*=8.6 and 11.9 Hz) and H-11a (δ 2.55; 1H, ddd, *J*=3.8, 8.5, and 11.9 Hz) proved that the ring junction was *trans*. The geometry of the olefinic bond at C-12 was concluded to be *E* on the basis of an nOe from H-13 (δ 6.96; 1H, dd, *J*=11.0 and 15.4 Hz) to H-4a (δ 3.80; 1H, dd, *J*=8.6 and 11.9 Hz, 15.3%). The presence of a stearoyl group in **4** and a palmitoyl group in **5** was confirmed by fragment ions at *m/z* 283 and 255 respectively in the negative ion FABmass spectra. Location of the acyl groups was determined to be at C-1 by the observation of nOes between the acetyl protons and H-4a (0.5 %) and H-10α (0.6 %). Thus, azamilides H (**4**) and I (**5**) are deduced to be 8,9-α-epoxyazamilide A and 8,9-α-epoxyazamilide B, respectively.

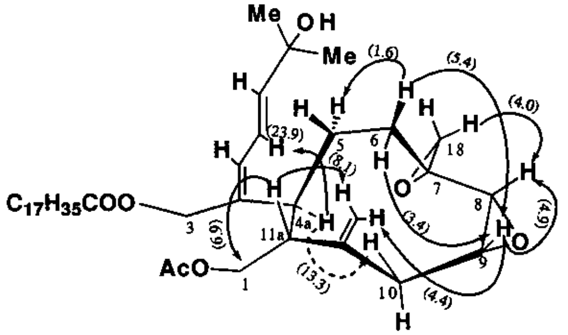


Figure 4. NOes (%) observed for **6**.

Azamilide J (**6**), $C_{40}H_{68}O_8$, has one more oxygen than **4**, and the molecular formula indicated an additional degree of unsaturation. The ^1H nmr spectrum was similar to that of **1**, except that resonances due to methyl protons at C-7 in **4** were absent and instead resonances due to an epoxy protons were observed at δ 2.48 and 2.76 (1H each, d, *J*=5.3 Hz). The relative stereochemistry was determined by nOe measurements. The observed nOes could be interpreted only when the conformation as depicted in Figure 4 was assumed. Thus, the nOe correlation between one of the H-18 methylene protons (δ 2.48) and H-8 (δ 3.15; 1H, d, J=3.9 Hz) (4.0%) suggested the α-orientation of the 7,18 epoxide. The presence of a stearoyl group was confirmed by a fragment ion at *m/z* 283 in the negative ion FAB mass spectrum. Comparison of the chemical shifts of C-1 (65.6) and C-3 (64.4) with those of **4** tentatively suggested the positions of the acetyl group at C-1 and the acyl group at C-3. Thus, azamilide J (**6**) is 7,18-α-epoxyazamilide H.

EXPERIMENTAL

Extraction and Isolation. The organisms (collection No. 114; dry weight: 750 g) collected at Bonotsu, Kagoshima prefecture[1] were chopped into small pieces and extracted twice with acetone (8 l x 2) for 3 days at r. t. The combined acetone solutions were concentrated to afford a dark reddish residue (22 g). The residue was suspended into H_2O (250 ml) and extracted with CH_2Cl_2 (200 ml x 3). The CH_2Cl_2 layer was dried over Na_2SO_4, filtered, and evaporated to dryness. A portion (7.5 g) of the CH_2Cl_2 extract (15 g) was absorbed on silica gel and subjected to column chromatography of silica gel packed in hexane, frs (200 ml) being collected as follows: A: CH_2Cl_2-hexane, 1:9, B: CH_2Cl_2, C: EtOH-CH_2Cl_2, 1:49, D: EtOH-CH_2Cl_2, 1:19, E: EtOH-CH_2Cl_2, 1:9, F: EtOH-CH_2Cl_2, 1:16, G: EtOH-CH_2Cl_2, 1:1, H: EtOH. Xeniaethers D (**2**) (0.7 mg), E (**3**) (4.2 mg), and J (**6**) (2.3 mg) were isolated from the fr B using

Sephadex LH-20 with MeOH-CH_2Cl_2 (1:1), prep. tlc with hexane-ether (1:1), and hplc on ods with H_2O-MeOH (3:2). Azamilides B (4.8 mg), C (1.3 mg), D (1.1 mg), H (4) (16.5 mg), I (5) (11.0 mg), and xeniaether C (1) (4.4 mg) were isolated from the fr D using Sephadex LH-20 with MeOH-CH_2Cl_2 (1:3 to 1:1), prep. tlc with hexane-ether (1:1) and ether-CH_2Cl_2 (1:3), and hplc on ods with H_2O-MeOH (12:13 to 1:9). The fr E was further subjected to silica gel chromatography with ether-CH_2Cl_2 mixtures of increasing polarity (1:4 to 1:1) and then EtOH-CH_2Cl_2 (1:19 to 3:22), to a column of Sephadex LH-20 with MeOH-CH_2Cl_2 (1:1), and to hplc on ods with H_2O-MeOH (19:1 to 3:17) to afford azamilides A (16 mg), G (1.4 mg), E (4.5 mg), and F (1.0 mg).

Xeniaether C (1). Oil, $[\alpha]_D$ -37.5° (*c* 0.07, MeOH); uv (MeOH) λmax 239 nm (ε 12000); ir (film) νmax 3450 and 1625 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$): δ 1.37 (3H, s, H-18), *ca.* 1.67 (2H, overlapped, H-5β and H-6α), 1.74 (1H, overlapped, H-5α), 1.77 and 1.78 (3H each, br s, H-16 and H-17), 1.94 (1H, dt, *J*=2.6 and 14.3 Hz, H-6β), 2.00 (1H, t, *J*=6.2 Hz, OH), 2.71 (1H, br t, *J*=11.7 Hz, H-10α), 2.72 (1H, overlapped, H-10β), 2.79 (1H, d, *J*=4.0 Hz, H-8), 2.96 (1H, dt, *J*=7.6 and 11.3 Hz, H-11a), 3.02 (1H, ddd, *J*=4.0, 5.5, and 11.0 Hz, H-9), 3.12 (1H, dd, *J*=7.7 and 11.3 Hz, H-4a), 3.40 (1H, dd, *J*=7.6 and 11.3 Hz, H-1α), 3.57 (2H, d, *J*=6.2 Hz, H-3), 3.82 (1H, t, *J*=7.6 Hz, H-1β), 5.13 (2H, br s, H-19), 5.62 (1H, d, *J*=15.2 Hz, H-12), 5.86 (1H, br d, *J*=11.0 Hz, H-14), and 6.67 (1H, dd, *J*=11.0 and 15.2 Hz, H-13); ^1H nmr (C_6D_6): δ 1.08 (3H, s, H-18), 1.24 (1H, br d, *J*=15.0 Hz, H-5α), 1.41 (1H, br t, *J*=15.0 Hz, H-6β), 1.62 and 1.67 (3H each, br s, H-16 and H-17), *ca.* 1.65 (1H, overlapped, H-5β), 1.80 (1H, dt, *J*=3.3 and 15.0 Hz, H-6α), 2.27 (1H, d, *J*=3.8 Hz, H-8), 2.41 (1H, dd, *J*=3.8 and 11.8 Hz, H-10β), 2.58 (1H, t, *J*=11.8 Hz, H-10α), 2.72 (1H, dt, *J*=3.8 and 11.8 Hz, H-9), 2.84 (1H, dt, *J*=8.0 and 11.9 Hz, H-11a), 3.18 (1H, dd, *J*=8.1 and 11.9 Hz, H-4a), 3.38 (1H, dd, *J*=8.0 and 11.9 Hz, H-1α), 3.57 (1H, dd, *J*=6.6 and 11.4 Hz, H-3), 3.65 (1H, dd, *J*=5.9 and 11.4 Hz, H-3), 3.69 (1H, t, *J*=8.0 Hz, H-1β), 4.82 and 4.89 (1H each, br s, H-19), 5.84 (1H, d, *J*=15.4 Hz, H-12), 5.95 (1H, br d, *J*=11.0 Hz, H-14), and 6.99 (1H, dd, *J*=11.0 and 15.4 Hz, H-13); ^{13}C nmr (100 MHz, $CDCl_3$): δ 18.5 (C-17), 21.7 (C-5), 26.0 (C-16), 30.0 (C-6), 32.4 (C-18), 35.0 (C-10), 44.4 (C-4a), 53.0 (C-11a), 61.1 (C-9), 62.1 (C-8), 65.8 (C-3), 70.6 (C-1), 72.0 (C-7), 86.0 (C-4), 119.2 (C-19), 124.9 (C-14), 126.2 (C-13), 132.5 (C-12), 136.0 (C-15), and 141.5 (C-11); (+) FABms *m/z* 357 (M^++Na); HREIms *m/z* 334.2115 (M^+, calcd for $C_{20}H_{30}O_4$, 334.2142).

Xeniaether D (2). Oil, $[\alpha]_D$ -30.0° (*c* 0.14, MeOH); uv (MeOH) λmax 240 nm (ε 14000); ir (film) νmax 3450, 1730 and 1620 cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.88 (3H, t, *J*=6.8 Hz, $C\underline{H}_3CH_2$-), 1.25 [s,

$-(CH_2)_n-]$, 1.37 (3H, s, H-18), *ca.* 1.65 (3H, overlapped, H-5α, H-5β, and H-6α), 1.77 (6H, br s, H-16 and H-17), *ca.* 1.95 (1H, overlapped, H-6β), 2.33 (3H, t, *J*=7.5 Hz, $-CH_2C\underline{H}_2COO-$), 2.70 (2H, overlapped H-10), 2.77 (1H, d, *J*=4.0 Hz, H-8), *ca.* 3.02 (2H, overlapped, H-9 and H-11a), 3.15 (1H, m, H-4a), 3.38 (1H, dd, *J*=7.9 and 11.0 Hz, H-1α), 3.83 (1H, t, *J*=7.9 Hz, H-1β), 4.09 and 4.13 (1H each, AB, *J*=11.9 Hz, H-3), 5.14 (2H, br s, H-19), 5.63 (1H, d, *J*=15.4 Hz, H-12), 5.85 (1H, br d, *J*=11.0 Hz, H-14), and 6.64 (1H, dd, *J*=11.0 and 15.4 Hz); ^{13}C nmr ($CDCl_3$): δ 14.1 ($\underline{C}H_3CH_2-$),18.5 (C-17), 22.0 (C-5), 22.7-34.5 [$-(\underline{C}H_2)_n-$], 26.0 (C-16), 29.7 (C-6), 32.4 (C-18), 35.1 (C-10), 44.9 (C-4a), 52.7 (C-11a), 61.1 (C-9), 62.0 (C-8), 66.8 (C-3), 70.7 (C-1), 72.0 (C-7), 84.3 (C-4), 119.3 (C-19), 124.9 (C-14), 126.0 (C-13), 131.9 (C-12), 136.0 (C-15), 141.6 (C-11), and 173.7 ($-CH_2\underline{C}OO-$); (+) FABms *m/z* 623 (M^++Na); (-) FABms *m/z* 599 (M^--H) and 283 ($C_{17}H_{35}COO^-$).

Xeniaether E (3). Oil, $[\alpha]_D$ -43.0° (*c* 0.03, MeOH); uv (MeOH) λmax 240 nm (ε 14000); ir (film) νmax 3450, 1735 and 1630 cm^{-1}. The ^{1}H and ^{13}C nmr spectra were indistinguishable with those of 2. (+) FABms *m/z* 595 (M^++Na); (-) FABms *m/z* 571 (M^--H) and 255 ($C_{15}H_{31}COO^-$).

Azamilide H (4). Oil, $[\alpha]_D$ -62.0° (*c* 0.10, MeOH); uv (MeOH) λmax 240 nm (ε 12000); ir (film) νmax 3450, 1730 and 1620 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 0.88 (3H, t, *J*=7.1 Hz, $C\underline{H}_3CH_2-$), 1.25 [s, $(CH_2)n$], 1.33 (3H, s, H-18), 1.34 (6H, s, H-16 and H-17), *ca.* 1.45 (2H, overlapped, H-5α and H-6α), *ca.* 1.80 (2H, overlapped, H-5β and H-6β), 1.98 (3H, s, AcO), 2.33 (2H, t, *J*=7.5 Hz, $-CH_2C\underline{H}_2COO$), 2.55 (1H, ddd, *J*=3.8, 8.5, and 11.9 Hz, H-11a), *ca.* 2.67 (1H, overlapped, H-9), *ca.* 2.74 (1H, overlapped, H-10β), 2.75 (1H, d, *J*=4.0 Hz, H-8), 3.18 (1H, dt, *J*=4.6 and 10.6 Hz, H-10α), 3.80 (1H, dd, *J*=8.6 and 11.9 Hz, H-4a), 3.85 (1H, dd, *J*=3.7 and 11.9 Hz, H-1α), 3.91 (1H, dd, *J*=8.4 and 11.9 Hz, H-1β), 4.63 (2H, br s, H-3), 5.13 (2H, br s, H-19), 5.89 (1H, d, *J*=15.4 Hz, H-14), 6.26 (1H, br d, *J*=11.0 Hz, H-12), and 6.96 (1H, dd, *J*=11.0 and 15.4 Hz, H-13); ^{13}C nmr ($CDCl_3$): δ 14.1 ($\underline{C}H_3CH_2-$), 21.0 ($\underline{C}H_3COO-$), 22.7-34.5 [$-(\underline{C}H_2)_n-$], 27.6 (C-10), 29.3 and 30.5 (C-5 and C-6), 33.2 (C-6), 34.2 (C-4a), 50.0 (C-11a), 60.5 (C-8 or C-9), 61.4 (C-9 or C-8), 64.4 (C-3), 65.3 (C-1), 71.2 (C-15), 72.5 (C-7), 118.8 (C-19), 122.9 (C-13), 131.6 (C-12), 135.7 (C-4), 142.9 (C-14), 144.2 (C-11), 170.8 ($\underline{C}H_3COO-$), and 173.6 ($-CH_2\underline{C}OO-$); (+) FABms *m/z* 683 (M^++Na); (-) FABms *m/z* 659 (M^- - H) and 283 ($C_{17}H_{35}COO^-$); HREIms *m/z* 642.4893 (M^+-H_2O, calcd for $C_{40}H_{66}O_6$, 642.4858).

Azamilide I (5). Oil, $[\alpha]_D$ -29.0° (*c* 0.07, MeOH); uv (MeOH) λmax 240 nm (ε 14000); ir (film) νmax 3450, 1735 and 1630 cm^{-1}. The ^{1}H and ^{13}C nmr spectra were indistinguishable with those of 4. (+) FABms *m/z* 655 (M^++Na); (-) FABms *m/z* 631 (M^--H) and 255 ($C_{15}H_{31}COO^-$).

Azamilide J (6). Oil, $[\alpha]_D$ -79.0° (*c* 0.08, MeOH); uv (MeOH) λmax 239 nm (ε 14000); ir (film) νmax 3450, 1735 and 1630 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 0.88 (3H, t, *J*=6.8 Hz, $\underline{H}_3$: C$\underline{H}_3$CH$_2$-), 1.25 [s, -(C$\underline{H}_2$)n-], 1.34 and 1.35 (3H each, s, H-16 and H-17), 1.63 (2H, overlapped, two protons of H-5α , H-5β, or H-6α), 1.91 (1H, dt, *J*=2.5 and 13.7 Hz, H-5α , H-5β, or H-6α), 1.99 (3H, s, OAc), 2.15 (1H, ddd, *J*=2.4, 4.2 and 12.8 Hz, H-6β), 2.33 (2H, t, *J*=7.7 Hz, -CH$_2$C$\underline{H}_2$COO-), 2.39 (1H, br t, *J*=12.3 Hz, H-10α), 2.48 (1H, d, *J*=5.3 Hz, H-18), 2.59 (1H, ddd, *J*=4.0, 7.4, and 12.0 Hz, H-11a), 2.76 (1H, d, *J*=5.3 Hz, H-15), 2.79 (1H, br dd, *J*=3.9 and 12.3 Hz, H-10β), 3.15 (1H, d, *J*=3.9 Hz, H-8), 3.22 (1H, dt, *J*=3.9 and 12.3 Hz, H-9), 3.45 (1H, dd, *J*=8.2 and 12.0 Hz, H-4a), 3.90 (1H, dd, *J*=7.4 and 12.0 Hz, H-1α), 3.94 (1H, dd, *J*=4.0 and 12.0 Hz, H-1β), 4.64 (2H, br s, H-3), 5.17 (2H, br s, H-19), 5.89 (1H, d, *J*=15.2 Hz, H-14), 6.23 (1H, br d, *J*=10.8 Hz, H-12), and 6.84 (1H, dd, *J*=10.8 and 15.2 Hz, H-13); ^{13}C nmr ($CDCl_3$): δ 14.1 ($\underline{C}H_3CH_2$-), 21.0 ($\underline{C}H_3COO$-), 22.7-34.4 [-($\underline{C}H_2$)n-], 27.3 (C-10), 29.2 (C-5), 29.5 and 29.8 (C-16 and C-17), 30.2 (C-6), 34.8 (C-4a), 46.3 (C-18), 49.7 (C-11a), 54.4 (C-9), 55.6 (C-7), 59.0 (C-8), 64.4 (C-3), 65.6 (C-1), 71.0 (C-15), 119.1 (C-19), 122.3 (C-13), 132.2 (C-12), 134.9 (C-4), 143.9 (C-14), 170.7 ($\underline{C}H_3COO$-), and 173.6 (-$CH_2\underline{C}OO$-); (+) FABms *m/z* 681 (M^++Na); (-) FABms *m/z* 657 (M^+-H) and 283 ($C_{17}H_{35}COO^-$).

ACKNOWLEDGMENTS

This work was partly supported by the Kagoshima Scholarship Foundation. We are grateful to Dr. Y. Minami (Taiho Yakugaku Co., Ltd.) for measuring the FABmass spectra, and to Drs. S. Moore (Massy University) and to Jeffrey L. C. Wright (NRC, Inst. Marine Bioscience, Canada) for valuable discussions.

REFERENCES

1. New xenia diterpenoids from *Xenia* sp. collected at Bonotsu, Kagoshima prefecture. 4. Part 3. ref. 5.
2. D. J. Faulkner, *Nat. Prod. Rep.*, 1995, **12**, 223. and references therein.
3. Y. Kashman and A. Groweiss, *J. Org. Chem.*, 1980, **45**, 3814.
4. T. Iwagawa, Y. Amano, T. Hase, and M. Shiro, *Tetrahedron*, 1995, **51**, 11111.
5. T. Iwagawa, Y. Amano, M. Nakatani, and T. Hase, *Bull. Chem. Soc. Jpn.*, 1996, **69** (in press).

Received, 11th March, 1996