

## New Cytotoxic Xenia Diterpenoids from the Formosan Soft Coral *Xenia umbellata*

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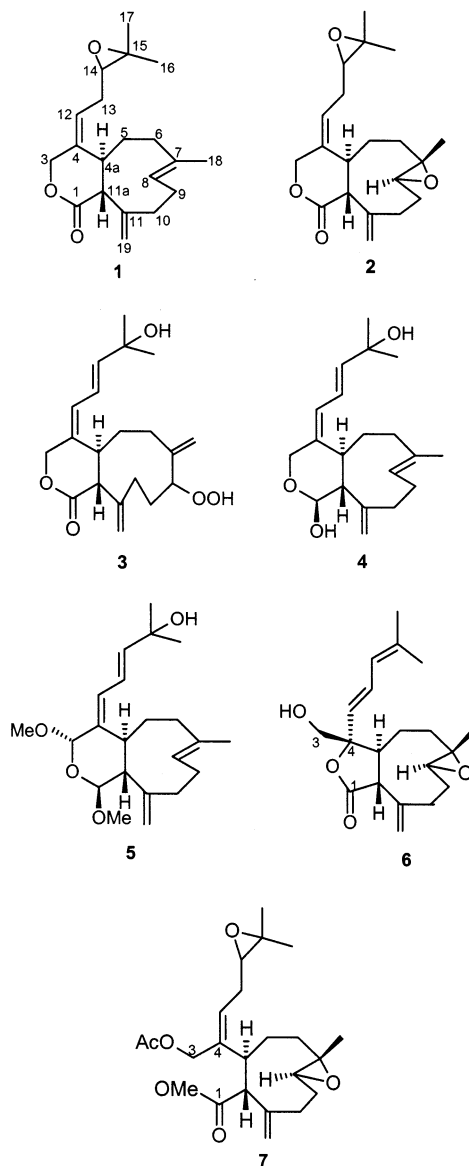
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Seven new cytotoxic xenicane-type diterpenoids, 9-deoxyxeniloide-E (**1**), 9-deoxy-7,8-epoxyxeniloide-E (**2**), xenilide-G (**3**), 9-deoxyxenialactol-C (**4**), xenibecin (**5**), xenilide-H (**6**), and xenitacin (**7**), were isolated from the methylene chloride solubles of the Formosan soft coral *Xenia umbellata*. The structures were elucidated by 1D and 2D NMR spectral analysis, and their cytotoxicity against selected cancer cells was measured in vitro.

Soft corals belonging to the genus *Xenia* (order Alcyonacea, family Xenidiidae) have proved to be a rich sources of terpenoids and have afforded several types of bioactive diterpenoids.<sup>1</sup> As part of our search for bioactive substances from marine organisms, the Formosan soft coral *Xenia umbellata* Lamarck was studied because the CH<sub>2</sub>Cl<sub>2</sub> extracts showed significant cytotoxicity to A549 (human lung adenocarcinoma), HT-29 (human colon adenocarcinoma), and P-388 (mouse lymphocytic leukemia) cell cultures as determined by standard procedures.<sup>2,3</sup> Bioassay-guided fractionations resulted in the isolation of seven new cytotoxic xenicane-type diterpenoids, 9-deoxyxeniloide-E (**1**), 9-deoxy-7,8-epoxyxeniloide-E (**2**), xenilide-G (**3**), 9-deoxyxenialactol-C (**4**), xenibecin (**5**), xenilide-H (**6**), and xenitacin (**7**), from *X. umbellata*.

### Results and Discussion

The molecular formula of **1** was established as C<sub>20</sub>H<sub>28</sub>O<sub>3</sub> by HREIMS. This formula, indicating seven degree of unsaturation, was fully supported by <sup>13</sup>C NMR and DEPT spectral data. Subsequent analysis of 2D NMR correlation data, focusing in particular on the interpretation of COSY, HMQC, and HMBC experiments, allowed the structure of **1** to be defined as 9-deoxyxenilide-E. The <sup>13</sup>C NMR spectrum of **1** showed a carbonyl carbon at  $\delta$  173.3 and six additional olefinic carbons (three quaternary, two tertiary, one secondary), which accounted for 4 degrees of unsaturation. Hence, **1** was clearly a tricyclic diterpene. The <sup>1</sup>H NMR spectrum showed one methyl bearing a trisubstituted double bond [ $\delta$  1.64 (3H, br s); 5.39 (1H, dd,  $J$  = 12.0, 4.5 Hz)], one exomethylene [ $\delta$  4.91 (1H, s); 5.03 (1H, s)], two methyl groups on an oxygenated carbon [ $\delta$  1.35 (3H, s); 1.36 (3H, s)], two geminal lactone methylene protons [ $\delta$  4.44 (1H, d,  $J$  = 11.7 Hz); 4.84 (1H, d,  $J$  = 11.7 Hz)], a single allylic methine proton [ $\delta$  2.92 (1H, m)], an epoxymethine [ $\delta$  2.80 (1H, t,  $J$  = 6.3 Hz)], and a tertiary olefinic methine [ $\delta$  5.60 (1H, t,  $J$  = 7.5 Hz)]. Using proton-detected hetero-correlation NMR methods (HMQC and HMBC (Figure 1)), all protons were correlated with their respective carbons and the structural features of **1** were clearly assigned. The relative stereochemistry of 9-deoxyxenilide-E was established by a NOESY experiment (Figure 2) and by compari-



sons of the relevant vicinal coupling constants with several xenilides possessing identical partial structures.<sup>4–14</sup> The *E* configuration of the carbon–carbon double bond (C-4, 12) was determined by a NOESY correlation between H-3 and H-12. The *trans*-ring junction was assigned according to

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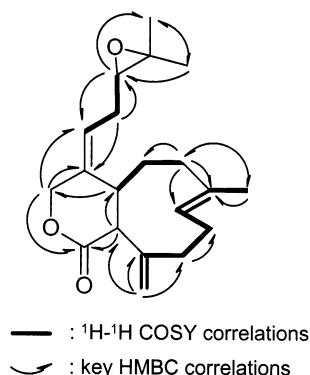


Figure 1.  $^1\text{H}$ - $^1\text{H}$  COSY and key HMBC correlations of **1**.

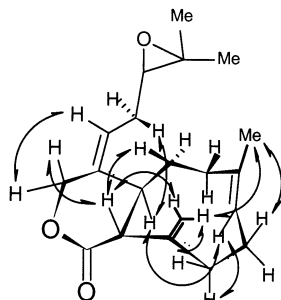


Figure 2. Selected NOESY correlations of **1**.

NOESY correlations between H-4a and H-8, between Me-18 and H-19, and between H-11a and H-19 and H-11a and H-3<sub>ax</sub>. NOESY correlation between H-4a and H-11a was not observed.

Compound **2** was analyzed for  $\text{C}_{20}\text{H}_{28}\text{O}_4$  by HREIMS and NMR spectral data. The NMR features of compound **2** were analogous to those of compound **1** with the exception that the resonances for the methyl-bearing *E*-trisubstituted olefin were replaced by those of a methyl-bearing *E*-trisubstituted epoxide ( $\delta_{\text{H}}$  1.21 s, 2.96 dd;  $\delta_{\text{C}}$  18.5 q, 58.6 s, 64.1 d). Cross-peaks in the  $^1\text{H}$ - $^1\text{H}$  COSY spectrum showed couplings between the epoxide methine proton at  $\delta$  2.96 (dd, H-8) and the methylene proton at  $\delta$  1.47 (dd, H-9 $\beta$ ) and 2.17 (m, H-9 $\alpha$ ). HMBC correlations between H-8 and C-6, C-7, C-9, C-10 and between Me-18 and C-6, C-7, C-8 positioned the methyl-bearing trisubstituted *E*epoxide at C-7, C-8, and C-18. The relative stereochemistry of **2** was established by a NOESY experiment (Supporting Information). NOESY correlations from H-11a to H-3 $\beta$  ( $\delta$  4.87), H-19 ( $\delta$  5.19), and H-5 ( $\delta$  1.80) and from H-19 to Me-18 showed that these protons occurred on the same face of the ring system ( $\beta$ ). The coupling constant ( $J = 9.9$  Hz) between H-4a and H-11a suggested a *trans* ring junction, which implied that H-4a was  $\alpha$ -oriented.<sup>5</sup> NOESY correlations from H-4a to H-8 showed that these protons occurred on the same face of the ring system ( $\alpha$ ).

Compound **3** has the molecular formula  $\text{C}_{20}\text{H}_{28}\text{O}_5$ , as determined by HREIMS and NMR spectral data. The NMR spectra resembled those of **1**. However, a secondary hydroperoxy ( $\delta_{\text{H}}$  4.48 dd;  $\delta_{\text{C}}$  88.7 d)  $\alpha$  to an exocyclic methylene ( $\delta_{\text{H}}$  5.29 s, 5.37 s;  $\delta_{\text{C}}$  116.5 t, 149.4 s) in **3** replaced the *E*-trisubstituted double bond bearing a methyl group in **1**, and a side chain of xeniolide-B replaced the 14,15-epoxy terminus side chain in **1**.<sup>6</sup> COSY cross-peaks between H-8 and H-9 as well as HMBC correlations between H-8 and C-9, C-18; Me-18 and C-7, C-8; and H-9 and C-7, C-8, C-10 positioned the *exo*-methylene and secondary hydroperoxyl at C-7 and C-8, respectively. The coupling constant ( $J = 9.9$  Hz) between H-4a and H-11a

suggested a *trans* ring junction. The relative stereochemistry of the secondary hydroperoxyl at C-9 was not determined due to the flexibility of the nine-membered ring.

The molecular formula  $\text{C}_{20}\text{H}_{30}\text{O}_3$  of compound **4** was revealed by HREIMS and NMR spectral data. The NMR features of compound **4** were analogous to those of xeniolactol-C with the exception that the resonance for the 9-hydroxyl methine was replaced by a methylene ( $\delta_{\text{H}}$   $\delta$  2.15, 2.49;  $\delta_{\text{C}}$  24.9).<sup>4</sup> HMBC correlations between H-18 and C-6, C-7, C-8; H-6 and C-5, C-7, C-18; and H-9 and C-7, C-8, C-11 confirmed the absence of a hydroxyl at C-9. In the NOESY experiment, NOEs between H-19 and H-1, H-4a, and between H-4a and H-8 allowed H-1, H-19, H-4a, and H-8 to be assigned to the  $\alpha$ -face of the molecule. Further, NOEs between H-18 and H-9 $\beta$  and between H-11a and H-3 $\beta$ /5 $\beta$  allowed H-18, H-9 $\beta$ , H-11a, H-3 $\beta$ , and H-5 $\beta$  to be assigned to the  $\beta$ -face of the molecule. Additional NOESY correlations between H-4a and H-13 and H-3 $\alpha$  and H-12 confirmed the *E* configuration of the carbon-carbon double bond at C-4, 12 (Figure 3).

The molecular formula of **5** was established as  $\text{C}_{22}\text{H}_{34}\text{O}_3$  by HREIMS and NMR spectral data. The NMR features of compound **5** were analogous to those of **4** with the exception that two methoxyl groups replaced the hydroxyl group at C-1 and the  $\alpha$ -methylene proton at C-3. HMBC correlations between H-1 and C-3, C-11, C-11a; H-3 and C-1, C-4, C-12, C-4a; OMe-1 and C-1; and OMe-3 and C-3 positioned the methoxyl groups at C-1 and C-3. The relative stereochemistry of **5** was established by a NOESY experiment. NOESY correlations from H-4a to H-19/H-8 and from H-19 to H-1/9 $\alpha$  showed that these protons occurred on the same face on the ring system ( $\alpha$ ). NOESY correlations from H-11a to H-3/5 $\beta$  and from Me-18 to H-9 $\beta$  showed that these protons occurred on the same face of the ring system ( $\beta$ ).

Compound **6** has the molecular formula  $\text{C}_{20}\text{H}_{28}\text{O}_4$ , as determined by HREIMS and NMR spectral data. The  $^1\text{H}$  NMR data of compound **6** were very close to those of florlide G isolated from the Japanese soft coral *Xenia florida* except chemical shifts for H-4a (2.56 for **6**; 3.08 for florlide G) and H-3 (3.77 and 3.93 for **6**; 3.58 and 3.75 for florlide G).<sup>7</sup> HMBC correlations between H-3 and C-4/C-4a/C-5 confirmed these assignments. The relative stereochemistry of **6** was established by a NOESY experiment (Figure 4). Correlations from H-4a to H-12/H-10 $\alpha$ /H-6 $\alpha$  and from H-8 to H-6 $\alpha$ /H-10 $\alpha$  showed that these protons occurred on the same face of the ring system ( $\alpha$ ). Similarly, NOESY correlations from H-19 to H-11a/Me-18 and from H-11a to H-3 showed that these protons occurred on the same face of the ring system ( $\beta$ ).

The molecular formula  $\text{C}_{23}\text{H}_{34}\text{O}_6$  of compound **7** was revealed by HREIMS and NMR spectral data. The NMR data of compound **7** were analogous to those of florlide F isolated from the Japanese soft coral *Xenia florida* except that compound **7** had a C-14,15-epoxy terminous side chain.<sup>7</sup> HMBC correlations between H-14 and C-12, C-13, C-15, C-17 confirmed the position of the epoxy group.

The cytotoxicity of compounds **1**–**7** is shown in Table 3. Compound **7** exhibited cytotoxicity against P-388, HT-29, and A549 cells. Compound **3** showed potent cytotoxicity against P-388 cells maybe due to the hydroperoxide functionality.<sup>15</sup> Compounds **1** and **2** and **4**–**6** exhibited moderate cytotoxicity against P-388 cells.

## Experimental Section

**General Experimental Procedures.** Melting points were determined using a Yanagimoto micromelting point apparatus and are reported uncorrected. Optical rotations were determined on a JASCO DIP-181 polarimeter. UV spectra were

**Table 1.**  $^1\text{H}$  NMR Spectral Data<sup>a</sup> of **1–7** in  $\text{CDCl}_3$ 

	1	2	3	4	5	6	7
1				4.61 d (8.4)	4.31 d (9.0)		
3 $\alpha$	4.44 d (11.7)	4.45 d (12.0)	4.44 d (12.0)	4.69 d (13.6)	5.25 s	3.77 d (12.6)	3.52 d (4.2)
3 $\beta$	4.84 d (11.7)	4.87 d (12.0)	4.88 d (12.0)	4.30 d (13.6)		3.93 d (12.6)	
4a	2.92 m	2.85 m	3.20 m	2.86 d (10.5)	2.87 d (10.4)	2.56 m	3.44 m
5 $\alpha$	1.69 m	1.92 m	2.13 m	1.53 m	1.40 m	2.06 m	1.73 m
5 $\beta$	1.71 m	1.80 m	2.56 m	1.98 m	1.88 m	1.90 m	1.55 m
6 $\alpha$	2.16 m	1.36 m	2.87 m	2.34 m	2.36 m	1.05 m	1.17 m
6 $\beta$		2.16 m	2.20 m	2.37 m	2.34 m	2.08 m	1.99 m
8	5.39 dd (12.0, 4.5)	2.96 dd (11.4, 2.7)	4.48 dd (5.6, 3.2)	5.43 t (10.2)	5.41 t (10.1)	2.87 dd (12.0, 3.6)	3.01 dd (11.4, 1.8)
9 $\alpha$	2.12 m	2.17 m	2.26 m	2.15 m	2.15 m	2.19 m	2.13 m
9 $\beta$	2.46 m	1.47 m	1.97 m	2.09 m	2.46 m	1.38 m	1.43 m
10 $\alpha$	2.59 m	1.85 m	2.58 m	2.22 m	2.30 m	1.88 m	2.13 m
10 $\beta$	2.17 m	2.14 m	2.33 m	2.26 m	2.34 m	2.58 m	2.34 m
11a	2.92 m	3.22 d (9.9)	3.32 d (9.9)	1.80 m	1.69 m	3.77 d (12.6)	3.44 m
12	5.60 t (7.5)	5.76 t (7.5)	6.08 d (11.4)	5.84 d (10.5)	6.25 d (9.6)	5.51 d (15.3)	5.52 dd (13.8, 7.2)
13	2.35 m	2.32 m	6.40 dd (15.3, 11.4)	6.45 dd (14.7, 10.5)	6.49 dd (15.3, 9.6)	6.50 dd (15.3, 12.0)	2.48 m
		2.12 m					2.32 m
14	2.80 t (6.3)	2.80 dd (7.5, 4.8)	5.95 d (15.3)	5.84 d (14.7)	5.95 d (15.3)	5.79 d (12.0)	2.75 dd (7.5, 6.0)
16	1.36 s	1.34 s	1.38 s	1.36 s	1.34 s	1.78 br s	1.31 s
17	1.35 s	1.29 s	1.37 s	1.36 s	1.34 s	1.80 br s	1.31 s
18	1.64 br s	1.21 s	5.29 s	1.77 br s	1.73 br s	1.19 s	1.14 s
			5.37 s				
19	4.91 s	5.16 s	5.10 s	4.72 s	4.66 s	5.22 s	5.08 s
	5.03 s	5.19 s	5.29 s	4.84 s	4.78 s	5.25 s	5.29 s
OMe-1					3.38 s		3.56 s
OMe-3					3.55 s		
OAc							2.04 s
OOH-8			8.20 br s				

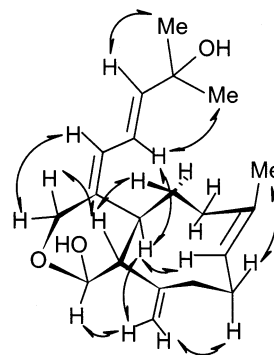
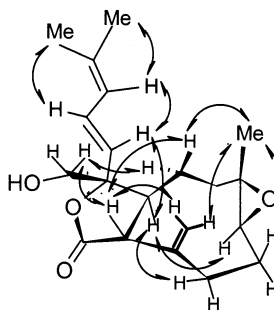
<sup>a</sup> Recorded in  $\text{CDCl}_3$  at 300 MHz.**Table 2.**  $^{13}\text{C}$  NMR Spectral Data<sup>a</sup> ( $\delta$ ) of **1–7** in  $\text{CDCl}_3$ 

	1	2	3	4	5	6	7
1	173.3	172.6	173.0	100.0	104.5	176.6	172.5
3	71.7	71.4	71.6	69.8	99.4	65.6	65.2
4	138.6	138.8	135.1	140.1	139.5	88.2	138.2
4a	38.2	36.3	37.1	44.6	44.5	47.9	38.3
5	36.7	35.4	30.7	35.6	35.9	25.6	28.7
6	39.7	38.8	31.8	35.9	40.5	38.8	38.3
7	134.9	58.6	149.4	135.6	135.4	59.2	59.7
8	124.2	64.1	88.7	124.3	124.3	64.4	63.6
9	29.7	27.2	35.8	24.9	24.8	28.8	27.3
10	34.4	28.7	30.3	40.4	35.8	27.7	26.1
11	148.1	143.8	145.0	155.1	154.7	143.9	143.0
11a	57.0	57.4	50.9	57.6	56.2	59.2	60.6
12	125.9	126.0	128.4	121.9	124.5	126.3	126.6
13	28.4	28.9	120.8	121.1	121.0	127.7	28.1
14	62.8	62.6	145.2	142.0	144.0	123.9	63.2
15	58.6	59.4	71.1	71.0	71.0	138.8	58.8
16	24.8	24.7	29.9	29.9	29.9	26.1	24.8
17	18.9	18.9	30.0	30.0	29.9	18.6	18.9
18	17.8	18.5	116.5	16.7	16.7	18.2	18.8
19	116.9	119.8	118.2	110.7	110.3	121.6	121.2
OMe-1					57.0		51.7
OMe-3					55.3		
OAc							170.8
							21.1

<sup>a</sup> Recorded in  $\text{CDCl}_3$  at 75 MHz.

obtained on a Shimadzu UV-160A spectrophotometer, and IR spectra were recorded on a Hitachi 26-30 spectrophotometer. The NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer at 300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$ , respectively, in  $\text{CDCl}_3$  using TMS as internal standard. EIMS spectra were obtained with a JEOL JMS-SX/SX 102A mass spectrometer at 70 eV. Si gel 60 (Merck, 230–400 mesh) was used for column chromatography; precoated Si gel plates (Merck, Kieselgel 60  $\text{F}_{254}$ , 0.25 mm) were used for TLC analysis.

**Animal Material.** The soft coral *Xenia umbellata* was collected at Green Island, off Taiwan, in April 2001, at a depth of 2–3 m and was stored for 1 month in a freezer until extraction. A voucher specimen, NSUGN-045, was deposited in the Department of Marine Resources, National Sun Yat-sen University, Taiwan.

**Figure 3.** Selected NOESY correlations of **4**.**Figure 4.** Selected NOESY correlations of **6**.

**Extraction and Isolation.** The bodies of the soft coral *X. umbellata* were freeze-dried to give 0.45 kg of a solid, which was extracted with  $\text{CH}_2\text{Cl}_2$  (3.0 L  $\times$  3). After removal of solvent in vacuo, the residue (30 g) was chromatographed over Si gel 60 using *n*-hexane and *n*-hexane–EtOAc mixtures of increasing polarity. Elution by *n*-hexane–EtOAc (6:1) afforded fractions containing compound **7**. Elution by *n*-hexane–EtOAc (4:1) afforded fractions containing compounds **1** and **5**. Elution by *n*-hexane–EtOAc (3:1) afforded fractions containing compounds **2** and **6**. Elution by *n*-hexane–EtOAc (2:1) afforded fractions containing compound **4**. Elution by EtOAc afforded fractions containing compound **3**. Compounds **1** and **5** were further purified by Si gel column chromatography, by eluting with *n*-hexane–acetone (9:1). Compounds **2** and **6** were further

**Table 3.** Cytotoxicity<sup>a</sup> of **1–7**

compound	cell line ED <sub>50</sub> (μg/mL)		
	A549	HT-29	P-388
<b>1</b>	11.2	21.1	2.87
<b>2</b>	11.6	7.77	3.35
<b>3</b>	4.77	8.31	0.04
<b>4</b>	4.85	12.9	3.45
<b>5</b>	13.4	12.5	3.96
<b>6</b>	18.8	5.33	3.66
<b>7</b>	3.26	1.12	1.09

<sup>a</sup> For significant activity of pure compounds, an ED<sub>50</sub> of 4.0 μg/mL is required.

purified by Si gel column chromatography by eluting with *n*-hexane–EtOAc (6:4).

**9-Deoxyxeniloid-E (1):** oil (23 mg); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +16.8° (*c* 0.46, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  nm (log  $\epsilon$ ) 206 (3.98); IR (KBr)  $\nu_{\max}$  1736, 1608, 1236 cm<sup>-1</sup>; <sup>1</sup>H NMR, see Table 1; <sup>13</sup>C NMR, see Table 2; EIMS *m/z* 316 [M]<sup>+</sup> (1), 300 (1), 272 (4), 43 (100); HREIMS *m/z* 316.2038 (calcd for C<sub>20</sub>H<sub>28</sub>O<sub>3</sub>, 316.2031).

**9-Deoxy-7,8-epoxyxeniloid-E (2):** oil (7 mg); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +20.6° (*c* 0.23, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  nm (log  $\epsilon$ ) 204 (3.76); IR (KBr)  $\nu_{\max}$  1734, 1610, 1240 cm<sup>-1</sup>; <sup>1</sup>H NMR, see Table 1; <sup>13</sup>C NMR, see Table 2; EIMS *m/z* 332 [M]<sup>+</sup> (1), 316 (1), 300 (1), 272 (3), 55 (100); HREIMS *m/z* 332.1975 (calcd for C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>, 332.1980).

**Xeniloid-G (3):** oil (12 mg); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +27.5° (*c* 0.40, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  nm (log  $\epsilon$ ) 222 (3.88); IR (KBr)  $\nu_{\max}$  3360, 1732, 1621, 1230 cm<sup>-1</sup>; <sup>1</sup>H NMR, see Table 1; <sup>13</sup>C NMR, see Table 2; EIMS *m/z* 348 [M]<sup>+</sup> (1), 332 (3), 292 (5), 91 (100); HREIMS *m/z* 348.1922 (calcd for C<sub>20</sub>H<sub>28</sub>O<sub>5</sub>, 348.1929).

**9-Deoxyxenialactol-C (4):** amorphous solid (26 mg); [ $\alpha$ ]<sub>D</sub><sup>25</sup> -18.8° (*c* 0.52, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  nm (log  $\epsilon$ ) 221 (3.79); IR (KBr)  $\nu_{\max}$  3305, 1616 cm<sup>-1</sup>; <sup>1</sup>H NMR, see Table 1; <sup>13</sup>C NMR, see Table 2; EIMS *m/z* 318 [M]<sup>+</sup> (1), 300 (2), 287 (2), 43 (100); HREIMS *m/z* 318.2195 (calcd for C<sub>20</sub>H<sub>30</sub>O<sub>3</sub>, 318.2187).

**Xenibecin (5):** oil (47 mg); [ $\alpha$ ]<sub>D</sub><sup>25</sup> -18.2° (*c* 0.24, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  nm (log  $\epsilon$ ) 218 (3.96); IR (KBr)  $\nu_{\max}$  3420, 1610 cm<sup>-1</sup>; <sup>1</sup>H NMR, see Table 1; <sup>13</sup>C NMR, see Table 2; EIMS *m/z* 362 [M]<sup>+</sup> (1), 344 (1), 314 (3), 284 (4), 43 (100); HREIMS *m/z* 362.2443 (calcd for C<sub>22</sub>H<sub>34</sub>O<sub>4</sub>, 362.2448).

**Xeniloid-H (6):** oil (18 mg); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +16.3° (*c* 0.46, CHCl<sub>3</sub>); IR (KBr)  $\nu_{\max}$  3500, 1742, 1608 cm<sup>-1</sup>; <sup>1</sup>H NMR, see Table 1; <sup>13</sup>C NMR, see Table 2; EIMS *m/z* 332 [M]<sup>+</sup> (1), 314 (2), 298 (3), 55 (100); HREIMS *m/z* 332.1988 (calcd for C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>, 332.1980).

**Xenitacin (7):** oil (2 mg); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +12.3° (*c* 0.12, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  nm (log  $\epsilon$ ) 211 (4.02); IR (KBr)  $\nu_{\max}$  1740, 1730, 1600, 1240 cm<sup>-1</sup>; <sup>1</sup>H NMR, see Table 1; <sup>13</sup>C NMR, see Table 2; EIMS *m/z* 406 [M]<sup>+</sup> (2), 388 (3), 374 (8), 346 (5), 71 (100); HREIMS *m/z* 406.2337 (calcd for C<sub>23</sub>H<sub>34</sub>O<sub>6</sub>, 406.2346).

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**Supporting Information Available:** Tables of HMBC correlations and NOESY correlations of **1–7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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