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

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Abstract: The structures of nine new xenia diterpenoids, xeniatine A (**1**), xeniatine A epoxide (**2**), isoxeniatines A (**3**) and B (**4**), and xeniaethers A (**5**) and B (**6**), together with three methoxyacetals **7-9**, from a soft coral *Xenia* species have been elucidated.

The soft corals of the genus *Xenia* have proved to be a rich source of 9-membered macrocyclic diterpenoids named xenia diterpenoids, which have been structurally divided into three groups: xenicins, xeniolides, and xeniaphyllanes.[2] In the course of our investigations of the constituents of an unidentified *Xenia* species collected in the area of Bonotsu, Kagoshima prefecture, we have isolated four new xeniolides **1-4**, two xenia diterpenoids **5** and **6** containing a tetrahydrofuran fused to a 9-membered ring, and three xenia diterpenoids **7-9** possessing a methoxyacetal moiety. In a preliminary communication, we reported the structures of xeniatine A (**1**) and xeniaether A (**5**) established on the basis of spectroscopic and single crystal X-ray analyses.[3] In this paper, we describe the isolation and structure elucidation of xeniatine A epoxide **2**, isoxeniatines A (**3**) and B (**4**), xeniaether B (**6**), and methoxyacetals **7-9**.

The soft coral was thoroughly extracted with methanol. The methanol extract was partitioned between methylene chloride and water. Repeated column chromatography of the methylene chloride soluble portion gave a light brown residue containing a mixture of diterpenoids. Further purification of the residue by reversed phase HPLC yielded a series of xenia diterpenoids **1-9**. Their molecular formulas were determined by ^{1}H NMR, ^{13}C NMR, and MS spectroscopy.

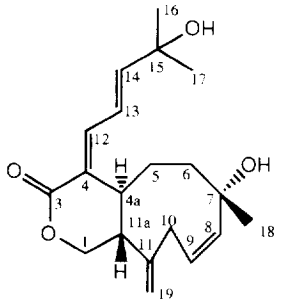
Xeniatine A epoxide **2** was isolated as an oil. The molecular formula $C_{20}H_{28}O_5$ had one more oxygen than that of **1** and indicated one degree of unsaturation more than **1**. Six olefinic carbons [δ 118.0 (t), 122.4 (d), 131.4 (s), 139.6 (d), 142.9 (s), and 149.8 (d)] and one lactone carbonyl [δ 169.9 (s)] in the ^{13}C NMR spectrum (Table 1) accounted for four double bond equivalents, suggesting that **2** was tricyclic. The gross structure was assigned by use of the NMR techniques including ^{1}H-^{1}H COSY experiments and by comparison of the NMR spectra of **2** with those of **1**. Thus, resonances due to following protons were readily assigned: H-1 (δ 3.94; 1H, t, *J*=10.6 Hz, δ 4.16; 1H, dd, *J*=3.6 and 10.6 Hz), H-4a (δ 3.75; 1H, m), H-10 (δ 2.84; 1H, dd, *J*=3.5 and 12.1 Hz, δ 2.97; 1H, t, *J*=12.1 Hz), H-11a (δ 2.70; 1H, dt, *J*=3.6 and 10.6 Hz), H-12 (δ 7.08; 1H, dd, *J*=1.7 and 11.5 Hz), H-13 (δ 6.99; 1H, dd, *J*=11.5 and 14.8 Hz), H-14 (δ 6.21; 1H, d, *J*=14.8 Hz), H-16 and H-17 (δ 1.38; 6H, s), H-18 (δ 1.42, 3H, s), and H-19 (δ 5.10; 1H, br s, δ 5.27; 1H, br s). The

major differences of the ^{1}H NMR spectral data between **2** and **1** were that resonances due to H-8 and H-9 in **2** suggested an epoxide (δ 2.84; 1H, d, *J*=3.5 Hz, H-8 and δ 3.04; 1H, dt, *J*=3.5 and 12.1 Hz, H-9), instead of the double bond in **1**. The chemical shifts of C-8 (δ 62.2; d) and C-9 (δ 59.7; d) in the ^{13}C NMR spectrum of **2** also supported the presence of an epoxide between C-8 and C-9. The relative stereochemistry of all chiral centers was determined by NOE experiments (Figure 1). NOEs from H-4a to H-1α (δ_H 3.94, 1.4%) and to H-13 (11.6%), as well as an NOE from H-11a to H-1β (δ_H 4.16, 3.8%) were observed. This suggested that H-4a and H-1α were on the same face of the ring and H-11a and H-1β were on the opposite face to H-4a, although an NOE between H-4a and H-11a (1.6%) was detected. The major conformer of the 9-membered ring was determined by the observation of NOEs between H-4a and H-10α (δ_H 2.97, 13%), between H-11a and H-5β (δ_H 1.74, 1.6%), H-6β (*ca* δ_H 1.9, 1.9%), and H-19 (δ_H 5.10, 2.0%), and between H-8 and H-18 (3.7%). The stereochemistry of the epoxide was established to be α from the value of the coupling constant between H-9 and H-10α (*J*=12.1 Hz). The large coupling constant suggested that H-9 was axial to H-10α, implying that the epoxide was in the α-configuration. If the epoxide is β and the torsion angel between H-9 and H-10β is below 120 degrees, the value of the coupling constant ($J_{9,10\beta}$) would be expected to be much smaller. Therefore, compound **2** is 8,9-α-epoxy xeniatine A. It is noteworthy that the major conformation of **2** was considerably different from that of **1** on the basis of NOE experiments as depicted in Figure 1. In particular, NOE enhancements of H-8 and H-9 but not H-10 was obtained when H-4a in **1** was irradiated.

Table 1. ^{13}C NMR spectral data of **1-9**.

C	1	2	3	4	5	6	7	8	9
1	68.8	70.6	68.9	68.9	69.9	69.9	64.0	64.0	64.0
3	170.5	169.9	168.4	168.4	64.7	65.5	96.2	96.4	96.3
4	131.5	142.9	130.9	128.6	87.3	87.8	148.5	148.6	148.5
4a	36.1	35.3	43.9	42.9	50.3	50.1	38.2	38.4	38.1
5	33.6	32.1	32.8	32.8	23.6	23.3	24.2	24.1	24.3
6	38.4	33.2	38.5	38.6	39.2	38.5	36.5	36.6	36.6
7	73.5	71.4	73.4	73.4	73.9	74.8	76.0	76.0	76.1
8	137.5	62.2	¶137.8	137.9	137.1	134.2	133.8	134.0	133.8
9	127.9	59.7	127.7	127.8	129.0	128.3	130.9	130.7	131.0
10	37.6	33.7	37.1	37.0	35.4	32.8	30.9	31.2	30.8
11	144.7	131.4	144.6	144.8	136.0	135.6	137.9	135.7	138.0
11a	42.7	44.9	42.8	43.9	49.4	50.1	51.8	51.5	51.8
12	137.7	139.6	¶138.3	139.7	124.6	124.4	120.8	121.5	*123.0
13	120.6	122.4	122.6	123.7	126.7	127.6	123.0	124.0	*123.5
14	150.1	149.8	148.3	149.8	132.1	130.0	142.8	143.5	140.3
15	71.2	71.3	70.9	31.5	146.3	146.3	70.9	*33.0	75.1
16	*29.3	*29.6	*29.3	22.0	26.0	25.8	*29.8	22.4	26.0
17	*30.0	*29.9	*29.6	22.0	18.4	18.2	*29.9	22.4	26.0
18	33.0	32.1	32.8	32.8	32.9	33.4	33.2	*31.5	33.2
19	111.8	118.0	111.9	111.8	112.4	113.6	115.2	114.9	115.2
3-Me							54.6	54.6	54.1
15-Me									50.6

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



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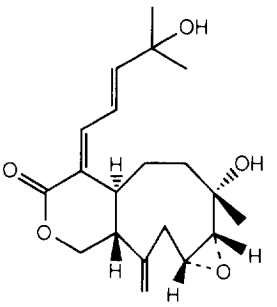

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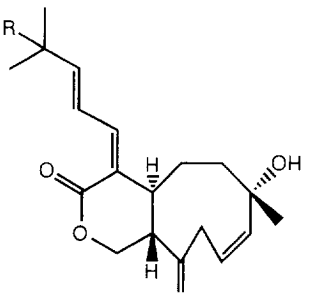
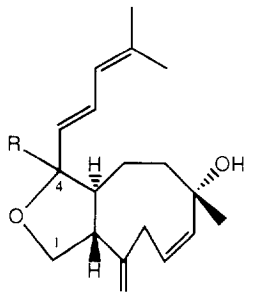
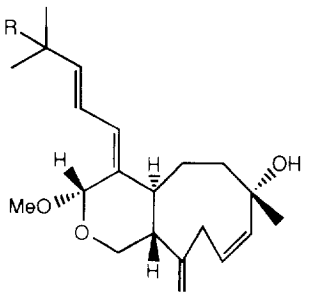


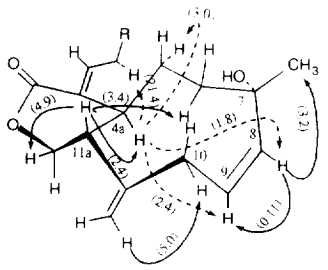
3 R=OH
4 R=H



5 R=β-CH_2OH
6 R=α-CH_2OH



7 R=OH
8 R=H
9 R=OMe



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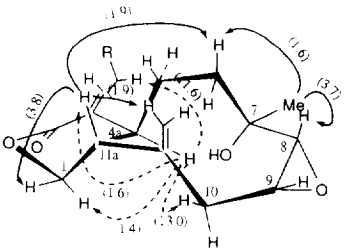

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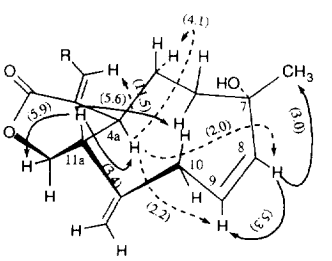

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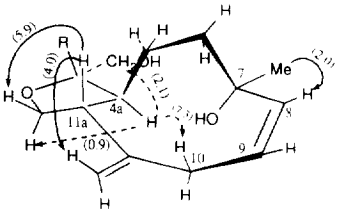

6

Figure 1. NOEs (%) observed for **1**, **2**, **3**, and **6**.
R=side chain.

Isoxeniatine A **3**, $C_{20}H_{28}O_4$, was an isomer of **1** with respect to the geometry of the 4,12 double bond. Comparison of the ^1H NMR spectrum of **3** with that of **1** showed the major difference for the resonance due to H-13 (δ 6.91; dd, *J*=11.0 and 14.4 Hz) being the most lowfield proton. This suggested that H-13 was close to the carbonyl function in the lactone group. The chemical shift of H-13 and an NOE between H-4a and H-12 (δ_H 6.32, d, *J*=11.0 Hz, 11.5%) suggested *Z*-configuration of the 4,12 double bond as opposed to the *E*-configuration for **1**.[3] The major conformer regarding the 9-membered ring was conclucded to be virtually the same as that of 1 on the basis of the results of the NOE experiments (Figure 1). Thus, the stereochemistry of the hydroxyl group at C-7 was determined to be α from an NOE of H-7 to H-18 (3.0%). Therefore, isoxeniatine A (**3**) was 4,12(*Z*)-xeniatine A.

Isoxeniatine B **4** was isolated as an oil with a molecular formula $C_{20}H_{28}O_3$, which had one less oxygen than that of **3**. The ^1H NMR spectrum was similar to that of **3**, except for resonances due to the side chain at C-4. Resonances due to methyl groups at C-16 and C-17 were observed as doublets (δ 1.02; 3H each, d, *J*=6.6 Hz). H-15 (δ 2.37-2.47; overlapped by H-6 signals) was coupled to H-14 (δ 5.91; 1H, dd, *J*=7.0 and 15.4 Hz), which in turn was coupled to H-13 (δ 6.76, 1H, ddd, *J*=1.3, 11.0, and 15.4 Hz). The latter proton was further coupled to H-12 (δ 6.30; 1H, d, *J*=11.0 Hz). The above results suggested that the C-15 hydroxyl group in **3** was replaced by hydrogen. *E*-stereochemistry of the 13,14-double bond was established by the value of the coupling constants between H-13 and H-14 (*J*=15.0 Hz). Thus, isoxeniatine B (**4**) was 15-dehydroxyisoxeniatine A.

Xeniaether B (**6**), $C_{20}H_{30}O_3$, was isomeric with **5**. The ^1H NMR spectrum was almost identical with that of **5**. However the resonance due to H-4a (δ 3.15; 1H, dt, *J*=5.9 and 9.3 Hz) shifted to downfield by 0.36 ppm compared to that of **5**, suggesting that **5** and **6** were stereoisomers at C-4. The stereochemistry of the hydroxymethyl at C-4 was determined by NOE experiments. Irradiation of H-4a resulted in enhancements of one of C-3 methylene protons (δ_H 3.53; 1H, d, *J*=12.1 Hz), as well as H-1α (δ_H 3.66; 1H, t, *J*=9.3 Hz, 2.1%) and H-10α (δ_H 3.42; 1H, dd, *J*=9.5 and 13.1 Hz, 7.3%), thus confirming that the hydroxymethyl group was α in configuration. As the major conformer inferred from the result of the NOE experiments was basically the same as that of **5**, an NOE between H-18 and H-8 (2.0%) suggested the β-configuration of the methyl group at C-7. Xeniaethers A (**4**) and B (**5**) are the first example of xenia diterpenoids containing a 9-membered monocarbocyclic skeleton fused to a tetrahydrofuran.

The ^{13}C NMR spectrum of compound **7**, oil, $C_{21}H_{32}O_4$, was similar to that of **3**, except for resonances due to an acetal carbon at δ 96.2 (d) instead of the lactone carbonyl at C-3 in **3**. In the ^1H NMR spectrum, additional resonances assigned to an acetal proton (δ 5.44; s) and methoxyl protons (δ 3.42; s) were observed. The stereochemistry of the acetal proton was deduced as 3β from the observation of a strong NOE of the acetal proton to H-13 (δ 6.51; 1H, dd, *J*=11.0 and 15.0 Hz, 22.1%). Therefore, the structure of **7** was as shown.

The molecular formula of **8**, $C_{21}H_{32}O_3$, had one less oxygen than **7**. The ^1H NMR spectrum was similar to that of **7**, except for resonances due to a side chain moiety. The signal patters of the resonances due to the side chain moiety were almost identical with those of **4**: δ 1.02 (6H, d, *J*=6.6 Hz, H-15 and H-16), 5.72 (1H, dd, *J*=7.5 and 14.7 Hz, H-14), 5.92 (1H, br d, *J*=9.2 Hz, H-12), and 6.25 (1H, dd, *J*=11.0 and 14.7 Hz, H-13). Thus, compound **8** was a 15-deoxy derivative of **7**.

The ^1H NMR spectrum of compound **9**, $C_{22}H_{34}O_4$, was similar to that of **7**, except for resonances due to additional methoxyl protons (δ 3.19; 3H, s). The location of the methoxyl group was determined to be 15 from

the downfield chemical shift of C-15 (δ 75.1) by 4.2 ppm in the ^{13}C NMR spectrum compared to that of **7**. Therefore compound **9** was a 15-methoxy derivative of **7**.

A series of the three compounds **7-9** possessing an acetal moiety with a methoxyl group would be artifacts which were formed by the extraction and/or isolation procedures.

The biosynthesis of xenicins and xeniolides has been explained as starting from an intermediate of dialdehyde **12** or a closely related form.[2, 4] The ocurrence of **5** and **6** suggested that a diol like **10** containing a 1,3 -dihydroxymethyl group might be a common precursor of xenicins **13**, xeniolactols **15**, and xeniolides **1-4**. Namely, the diol is oxidized to afford xeniolides **1-4** via hydroxy acids **14** or the lactols **15** that are derived from hydroxyaldehydes **11**. The lactols also gives methoxyacetals **7-9**. The possible biogenetic route from the diol **10** to compounds **1-9** and **11-15** is shown in Figure 2.

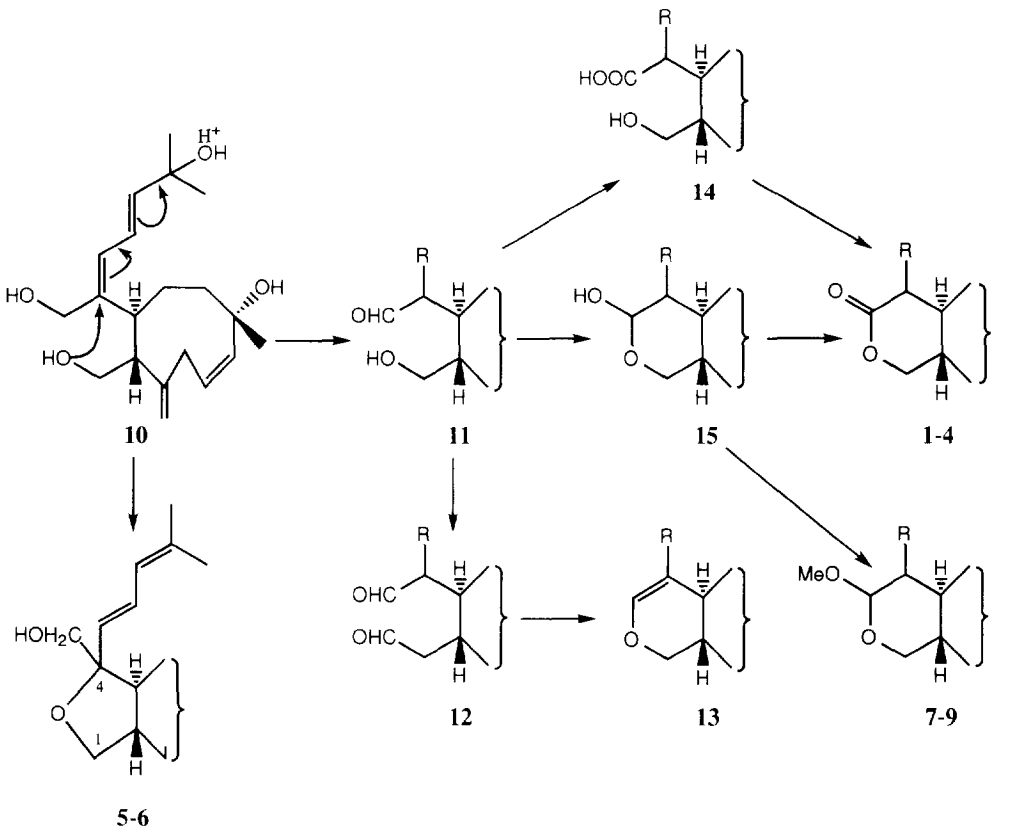

Figure 2. Possible biogenetic pathway of **1-15**.

EXPERIMENTAL

UV and IR spectra were recorded on Shimadzu IR-408 and UV-210, respectively. Optical rotations were measured on a JASCO J-20A spectropolarimeter. NMR spectra were recorded with a JEOL JNM-GX 400 spectrometer. Mass spectra were obtained with a JEOL JNM D300 spectrometer at 70 eV. A Rigaku AFC5R diffractometer was used in the X-ray work.

Extraction and Isolation. Specimens of *Xenia* sp. were collected at depth of -2 m at Bonotsu, Kagoshima prefecture. The reference sample (collection #68) was deposited in Wakayama Prefectural Museum of Natural History and identified by Dr. Y. Imahara. The organisms (wet weight: 4kg) were chopped into small pieces and extracted with CH_3OH immediately after collection. The CH_3OH was suspended in H_2O and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The CH_2Cl_2 extract (7g) was absorbed on silica gel and subjected to chromatography on silica gel packed in hexane, fractions (100 ml) being collected as follows: 1-2 (CH_2Cl_2-hexane, 1:1), 3-8 (CH_2Cl_2-hexane, 5:1), 9-11 (CH_2Cl_2), 12-21 (CH_3OH-CH_2Cl_2, 3:97), 23-26 (CH_3OH-CH_2Cl_2, 1:4), and 27-31 (CH_3OH). Fractions 12-21 were again chromatographed on silica gel using CH_2Cl_2 with CH_3OH increasing proportion of CH_3OH to elute the column. Elution with CH_3OH-CH_2Cl_2 (1:99 to 3:97) followed by reversed-phase C_{18} chromatography (ODS-HPLC) and elution with CH_3OH-H_2O (17:3 to 1:1) gave **2** (10 mg), **4** (21 mg), and **6** (11 mg). The fraction eluted with CH_3OH-CH_2Cl_2 (3:97 to 1:19) was purified by silica gel chromatography with hexane-ether (1:4) to afford a crude diterpenoid fraction. The crude diterpenoid fraction was further applied to silica gel chromatography with CH_3OH-CH_2Cl_2 (1:99 to 1:49) followed by reversed phase chromatography with CH_3OH-H_2O (17:3 to 1:1), giving **1** (18 mg), **3** (3.0 mg), **5** (59 mg), **6** (2.5 mg), **7** (20 mg), and **9** (3.0 mg). Spectral and physical data of xeniatine-A **1** and xeniaether-A **4** were recorded in ref. 3.

Xeniatine A epoxide (2). Oil, $[\alpha]_D^{27}$ -16.3° (*c* 0.07, CH_3OH); UV (CH_3OH) λmax 271 nm (ε 16400); IR (film) νmax 3450, 1710, 1635, 1590, 990, and 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (6H, s, H-16 and H-17), 1.42 (3H, s, H-18), *ca*1.66 (1H, m, H-6β), 1.74 (1H, tq, *J*=2.9 and 12.4 Hz, H-5β), *ca* 1.9 (1H, m, H-5α), 2.07 (1H, ddd, *J*=3.3, 12.1, and 15.4 Hz, H-6α), 2.70 (1H, dt, *J*=3.5 and 10.6 Hz, H-11a), 2.84 (1H, d, *J*=3.5 Hz, H-8), 2.84 (1H, dd, *J*=3.5 and 12.1 Hz, H-10β), 2.97 (1H, t, *J*=12.1 Hz, H-10α), 3.04 (1H, dt, *J*=3.5 and 12.1 Hz, H-9), 3.75 (1H, m, H-4a), 3.94 (1H, t, *J*=10.6 Hz, H-1α), 4.16 (1H, dd, *J*=3.6 and 10.6 Hz, H-1β), 5.10 and 5.27 (1H each, br s, H-11), 6.21 (1H, d, *J*=14.8 Hz, H-14), 6.99 (1H, dd, *J*=11.5 and 14.8 Hz, H-13), 7.08 (1H, dd, *J*=1.7 and 11.5 Hz, H-12); HREIms *m/z* 348.1937 (M^+, calcd for $C_{20}H_{28}O_5$, 348.1937).

Isoxeniatine A (3). Amorphor, $[\alpha]_D^{27}$ +300.0° (*c* 0.13, CH_3OH); UV (CH_3OH) λmax 253 nm (ε 7900); IR (film) νmax 3400, 1720, 1635, 1610, 985, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 and 1.36 (3H each, s, H-16 and H-17), 1.37 (3H, s, H-15), *ca* 1.45 (1H, m, H-5β), 1.80 (1H, br d, *J*=7.3 and 15.9 Hz, H-6β), 1.92-1.99 (1H, m, H-5α), 2.46 (1H, ddd, *J*=2.2, 12.1, and 15.9 Hz, H-6α), 2.65 (1H, dt, *J*=5.1 and 11.0 Hz, H-11a), 2.91 (1H, dd, *J*=7.7 and 12.1 Hz, H-10α), 3.07 (1H, br t, *J*=12.2 Hz, H-10β), 3.37 (1H, br d dt, *J*=5.5 and 11.0 Hz, H-4a), 4.40 (1H, t, *J*=11.0 Hz, H-1α), 4.24 (1H, dd, *J*=5.1 and 11.0 Hz, H-1β), 4.64 and 4.91 (1H each, s, H-19), 5.37 (1H, dt, *J*=7.7 and 12.2 Hz, H-9), 5.63 (1H, bt d, *J*=12.2 Hz, H-8), 6.05 (1H, d, *J*=14.4 Hz, H-14), 6.32 (1H, d, *J*=11.0 Hz, H-12), and 6.91 (1H, dd, *J*=11.0 and 14.4 Hz, H-13); HREIms *m/z* 332.1972(M^+, calcd for $C_{20}H_{28}O_4$, 332.1987).

Isoxeniatine B (4). Oil, $[\alpha]_D^{25}$ +433.0° (*c* 0.007, CH_3OH); UV (CH_3OH) λmax 264 nm (ε 20300); IR (film) νmax 3500, 1730, 1665, 1630, and 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (6H, d, *J*=6.6 Hz, H-16 and H-17), 1.37 (3H, s, H-18), *ca* 1.46 (1H, m, H-5β), 1.79 (1H, br dd, *J*=7.0 and 15.4 Hz, H-6β), 1.92-1.99 (1H, m, H-5α), 2.37-2.47 (2H, m, H-6β and H-15), 2.65 (1H, dt, *J*=5.6 and 11.4 Hz, H-11a), 2.93 (1H, dd, *J*=7.7 and 11.4 Hz, H-10α), 3.05 (1H, br t, *J*=11.4 Hz, H-10β), 3.34 (1H, dt, *J*=5.6 and 11.4 Hz, H-4a), 4.04 (1H, t, *J*=11.4 Hz, H-1α), 4.22 (1H, dd, *J*=5.3 and 11.4 Hz, H-1β), 4.64 and 4.91 (1H each, s, H-19), 5.38 (1H, dt, *J*=7.7 and 11.4 Hz, H-9), 5.63 (1H, br d, *J*=11.4 Hz, H-8), 5.91 (1H, dd, *J*=7.0 and 15.4 Hz, H-14), 6.30 (1H, d, *J*=11.0 Hz, H-12), and 6.76 (1H, ddd, *J*=1.3, 11.0, and 15.4 Hz, H-13); HREIms *m/z* 316.2029 (M^+, calcd for $C_{20}H_{28}O_3$, 316.2037).

Xeniaether B (6). Oil, $[\alpha]_D^{25}$ -75.0° (c 0.09, CH_3OH); UV (CH_3OH) λmax 241nm (ε 12300); IR (film) νmax 3450, 1660, 1640, and 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (3H, s, H-18), *ca* 1.51 (1H, m, H-5β), *ca* 1.6 (1H, m, H-5α), 1.79 (6H, s, H-16 and H-17), *ca* 1.8 (1H, m, H-6α)2.73 (1H, dd, *J*=8.4 and 13.1 Hz, H-10β), 2.79 (1H, t-like, *J*=9.3 Hz, H-11a), 3.15 (1H, dt, *J*=5.9 and 9.3 Hz, H-4a), 3.42 (1H, dd, *J*=9.5 and 13.1 Hz, H-10α), 3.50 and 3.53 (2H, AB, *J*=12.1 Hz, H-3), 3.66 (1H, t, *J*=9.3 Hz, H-1α), 3.94 (1H, t, *J*=9.3 Hz, H-1β), 4.92 and 4.94 (1H each, s, H-19), 5.31 (1H, d, *J*=12.1 Hz, H-8), 5.47 (1H, d, *J*=15.2 Hz, H-12), 5.51-5.53 (1H, obscured by H-12, H-9; δ 5.37, ddd, *J*=8.4, 9.5, and 12.1 Hz in C_6D_6), 5.86 (1H, br d, *J*=11.0 Hz, H-14), and 6.53 (1H, dd, *J*=11.0 and 15.2 Hz, H-13); HREIms *m/z* 300.2029 (M^+-H_2O, calcd for $C_{20}H_{28}O_2$, 300.20890).

Compound 7. Oil, $[\alpha]_D^{25}$ -93.0° (*c* 0.08, CH_3OH); UV (CH_3OH) λmax 238nm (ε 20000);; IR (film) νmax 3450, 1635 and 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (3H, s, H-18), 1.35 (6H, s, H-16 and H-17), 2.41 (1H, dt, *J*=4.8 and 11.6 Hz, H-11a), 2.53 (1H, dd, *J*=8.6 and 13.0 Hz, H-10α), 3.42 (3H, s, 1α-OMe), 3.46 (1H, overlapped, H-1α), *ca* 3.5 (2H, overlapped, H-1α and H-10β), 3.81 (1H, t, *J*=11.6 Hz, H-1β), 4.95 and 4.98 (1H each, s, H-19), 5.27 (1H, d, *J*=11.7 Hz, H-8), 5.44 (1H, s, H-3β), 5.67-5.74 (1H, m, H-9), 5.89 (1H, d, *J*=15.2 Hz, H-14), 5.95 (1H, br d, *J*=11.0 Hz, H-12), and 6.51 (1H, dd, *J*=11.0 and 15.2 Hz, H-13); EIms *m/z* 330 (M^+).

Compound 8. Oil, $[\alpha]_D^{25}$ -76.3° (*c* 0.07, CH_3OH); UV (CH_3OH) λmax 239nm (ε 12800); IR (film) νmax 3500 and 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (6H, d, *J*=6.6 Hz, H-16 and H-17), 1.33 (3H, s, H-18), 2.41 (2H, overlapped, H-4a and H-11a), 2.52 (1H, dd, *J*=8.6 and 13.0 Hz, H-10α), 3.39-3.50 (2H, m, H-1α and H-10β), 3.42 (3H, s, 1α-OMe), 3.82 (1H, t, *J*=11.4 Hz, H-1β), 4.94 and 4.97 (1H each, s, H-19), 5.28 (1H, d, *J*=12.1 Hz, H-8), 5.41 (1H, s, H-3β), 5.66-5.74 (1H, obscured by H-14, H-9), 5.72 (1H, dd, *J*=7.5 and 14.7 Hz, H-14), 5.92 (1H, br d, *J*=9.2 Hz, H-12), and 6.25 (1H, dd, *J*=11.0 and 14.7 Hz, H-13); HREIms *m/z* 300.2074 (M^+-CH_3OH, calcd for $C_{20}H_{28}O_2$, 300.2087)

Compound 9. Oil, $[\alpha]_D^{25}$ -82.8° (*c* 0.10, CH_3OH); UV (CH_3OH) λmax 240nm (ε 14200); IR (film) νmax 3500, 1640, and 990 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (6H, s, H-15 and H-16), 1.37 (3H, s, H-18), 2.45 (1H, dt, *J*=4.8 and 11.7 Hz, H-11a), 2.56 (1H, dd, *J*=8.8 and 12.8 Hz, H-10α), 3.19 (3H, s, 15-OMe), 3.46 (3H, s, 3α-OMe), 3.45-3.56 (2H, m, H-1α and H-10α), 3.85 (1H, t, *J*=11.4 Hz, H-1β), 4.99 and 5.01 (1H each, s, H-19), 5.31 (1H, d, *J*=12.1 Hz, H-8), 5.46 (1H, s, H-3β), 5.77 (1H, m, H-9), 5.77 (1H, d, *J*=14.3 Hz, H-14), 6.00 (1H, br d, *J*=10.6 Hz, H-12), 6.43 (1H, dd, *J*=10.6 and 15.4 Hz, H-13); HREIms *m/z* 344 (M^+-H_2O, 344.2375, calcd for $C_{22}H_{32}O_3$, 344.2352).

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