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Marine Natural Products. XV.[1] Chemical Constituents of an Okinawan Soft Coral of *Xenia* sp. (Xeniidae)

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Four new polyhydroxysterols, named xeniasterol-a (**4**), xeniasterol-b (**5**), xeniasterol-c (**6**), and xeniasterol-d (**7**), were isolated from an Okinawan soft coral of *Xenia* sp. (Xeniidae). On the basis of chemical and physicochemical evidence, the structures of xeniasterol-a, -b, -c, and -d have been elucidated respectively as 7-*O*-acetylergost-22*E*-ene-3β,5α,6β,7β-tetraol (**4**), 7-*O*-acetylergosta-3β,5α,6β,7β-tetraol (**5**), gorgosta-3β,5α,6β-triol (**6**), and 7-*O*-acetylgorgosta-3β,5α,6β,7β-tetraol (**7**). Germacrene-c (**1**) was also isolated from the same soft coral together with two guaiane-type compounds (**2**, **3**), and it has been shown that germacrene-c (**1**) is readily air-oxidized to yield these cyclization products (**2**, **3**).

Keywords——soft coral; *Xenia* sp.; Xeniidae; sterol polyhydroxylated; xeniasterol-a; xeniasterol-b; xeniasterol-c; xeniasterol-d; sesquiterpene; germacrene-c

In our continuing survey of bioactive marine natural products, we have been investigating the chemical constituents of marine organisms inhabiting in Okinawan coral reefs.[2] In this paper, we report the isolation of germacrene-c (**1**) in high content together with two of its guaiane-type cyclization products (**2**, **3**), and we also describe the structure elucidation of four new polyhydroxysterols named xeniasterol-a (**4**), xeniasterol-b (**5**), xeniasterol-c (**6**), and xeniasterol-d (**7**).[3]

The fresh whole animal of *Xenia* sp. (Xeniidae), collected in July at Zamami-jima in Okinawa Prefecture, was immersed in acetone, and the acetone solution was concentrated under reduced pressure at below 30 °C. The acetone extract was partitioned into an ethyl acetate–water mixture. Chromatographic separation of the ethyl acetate-soluble portion provided three sesquiterpenes, germacrene-c (**1**) and two guaiane-type compounds (**2**, **3**), in 21.0, 2.5, and 2.5% yields from the ethyl acetate-soluble portion. It also provided a mixture of polyhydroxysterols (**4**—**7**) which gave a single spot on an ordinary thin-layer chromatogram (TLC). High-performance liquid chromatography (HPLC) on a reversed-phase column of the sterol mixture furnished xeniasterol-a (**4**), -b (**5**), -c (**6**), and -d (**7**) in 0.4, 2.4, 0.2, and 0.5% yields from the ethyl acetate-soluble portion (Chart 1).

The major sesquiterpene (**1**) showed an ultraviolet (UV) absorption maximum at 254 nm due to a *transoid* conjugated diene moiety. Detailed analysis of the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra has shown that this sesquiterpene is identical with germacrene-c, which was previously isolated from dry fruits of a terrestrial plant *Kadsura japonica*.[4]

One of the minor sesquiterpenes (**2**) was shown by its ^{13}C-NMR spectrum to contain a terminal double bond [δc 106.4 (t), 153.7 (s)], a trisubstituted double bond [δc 121.6 (d), 149.1 (s)], and a tertiary hydroxyl group [δc 80.4 (s)]. Detailed examination of the ^{1}H- and ^{13}C-NMR spectra of this sesquiterpene alcohol has led us to conclude that it can be formulated as

2, a structure which was previously proposed for a guaiane-type alcohol isolated from an Australian soft coral *Nephthea chabrolii*.[5,6]

The ^{13}C-NMR spectrum of the other minor sesquiterpene (**3**) showed signals due to a trisubstituted double bond [δc 121.5 (d), 149.6 (s)] and two tertiary hydroxyl groups [δc 80.3 (s), 75.4 (s)] together with signals very similar to those observed in the ^{13}C-NMR spectrum of **2**. Thus, this sesquiterpene (**3**) was considered to be a hydrated derivative of **2**. Finally, detailed study of the ^{1}H- and ^{13}C-NMR data led us to conclude that the structure of this sesquiterpene is **3**, a structure which was previously assigned to a sesquiterpene diol isolated from an Australian soft coral *Lemnalia africana*.[5,6]

The two guaiane-type sesquiterpenes (**2**, **3**) isolated by us showed no significant optical activity. We found that germacrene-c (**1**) was fairly unstable in air and it was readily converted to **2** upon standing in the air and converted to **3** in an aqueous acetone solution, in high yields in both cases. These conversions also proceeded in the dark. Therefore, these guaiane-type sesquiterpenes (**2**, **3**) were considered to be secondary products formed during the isolation procedure.

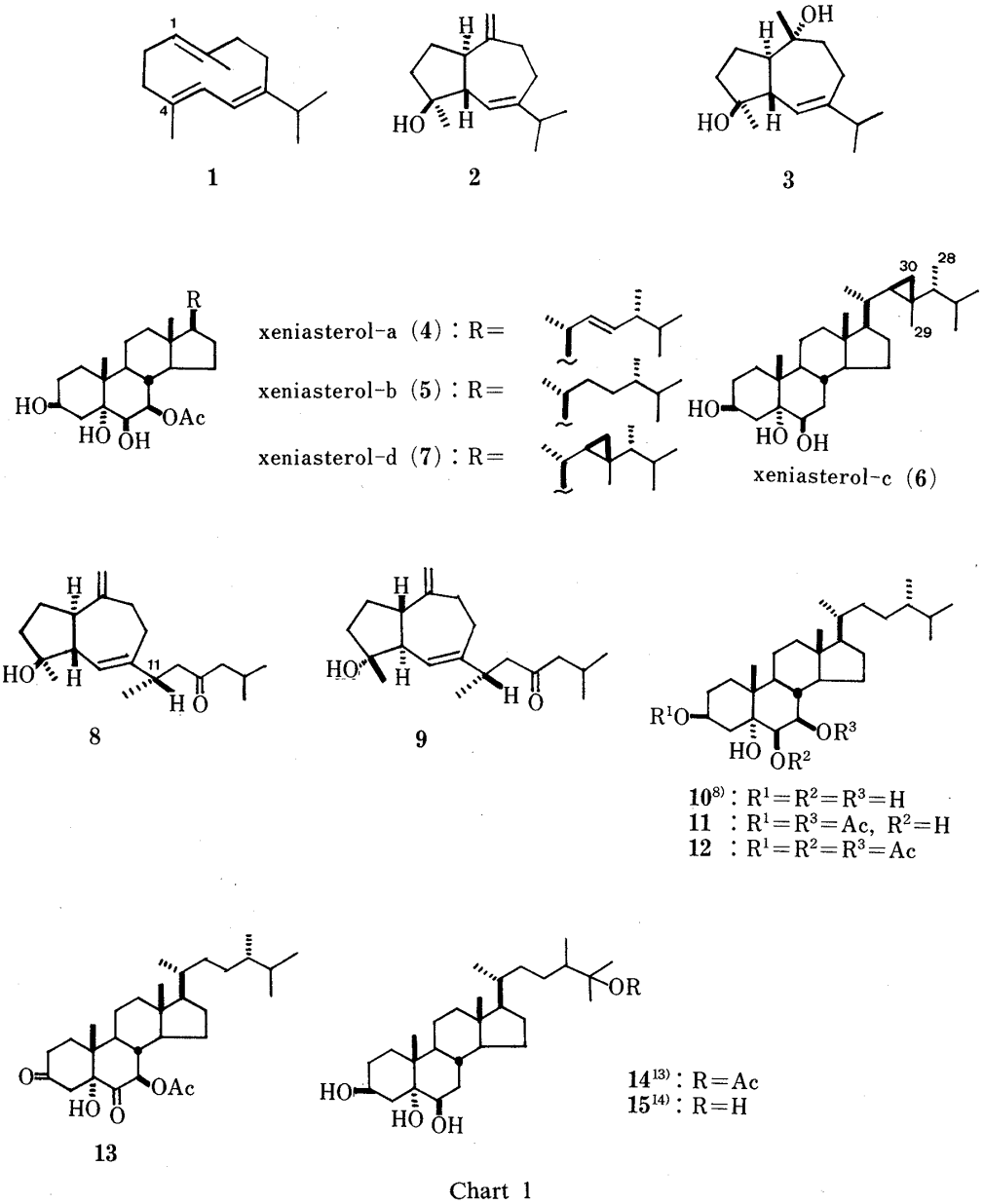

Chart 1

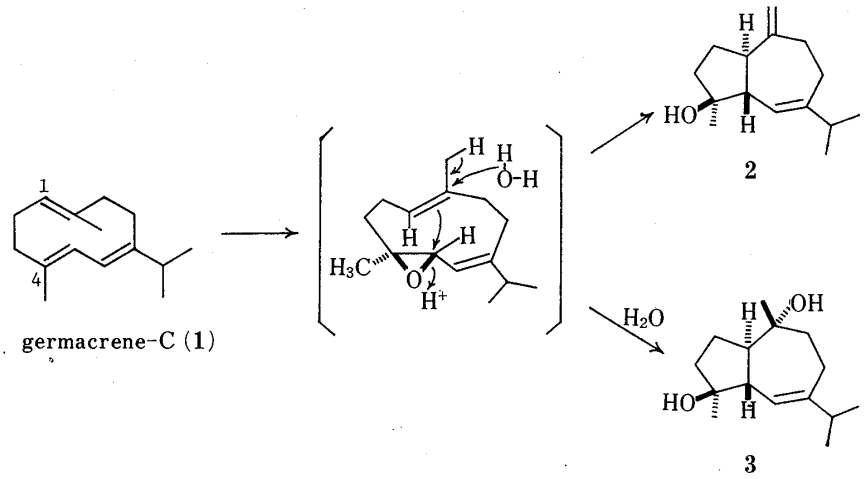

Chart 2

Taking into consideration these findings, we separated the two sesquiterpenes (**2**, **3**) as quickly as possible from the ethyl acetate-soluble portion. It was found that the fresh extract of the soft coral contained **2** and **3**, and that **2** obtained in this way showed an optical activity of $[\alpha]_D$ +2°. It is therefore likely that part of **2** and **3** may be biosynthesized in the soft coral. In regard to the chemical process leading to **2** and **3** from germacrene-c (**1**), the scheme shown in Chart 2 seems to be attractive: starting with epoxidation of **1** followed by epoxy-ring opening, cyclization, and finally deprotonation (giving **2**) or nucleophilic attack of water (giving **3**).

The hydroazulene skeleton of **2** is identical with or antipodal to hydroazulene moieties in xeniolone (**8**) and isoxeniolone (**9**), which were previously isolated by us from a soft coral of related *Xenia* sp. collected at Zamami-jima in Okinawa Prefecture.[7] As mentioned above, most of **2** was racemic and **2** could not be obtained in optically pure form. However, xeniolone (**8**) and isoxeniolone (**9**), which have an asymmetric carbon at position 11, may be readily separated into two diastereomers.

Xeniasterol-b (**5**) was obtained as the major constituent from the polyhydroxysterol fraction. The ^{1}H-NMR spectrum of **5** showed signals ascribable to two tertiary methyl residues, four secondary methyl residues, two protons (3α-H, 6α-H) geminal to a secondary hydroxyl group, and one proton (7α-H) geminal to a secondary acetoxyl group. The ^{13}C-NMR spectrum of **5** showed signals due to two carbons (C-3, C-6) bearing a secondary hydroxyl group [δc 77.5 (d), 76.3 (d)], one carbon (C-7) bearing a secondary acetoxyl group [δc 67.1 (d)], and one carbon (C-5) with a tertiary hydroxyl group [δc 76.6 (s)]. Methanolic potassium carbonate hydrolysis of **5** provided a tetrahydroxysterol, whose physical properties were found to be identical with those reported for **10** previously isolated from the soft coral *Anthelia glauca*.[8] Thus, xeniasterol-b (**5**) has been shown to be a monoacetyl derivative of **10**.

In order to determine the location of the acetyl function, xeniasterol-b (**5**) was first acetylated with acetic anhydride and pyridine to afford a diacetate (**11**) and a triacetate (**12**) in a 3 : 1 ratio. Thus, one of two secondary hydroxyl groups in **5** has been shown to be axial 6β-OH. Pyridinium chlorochromate (PCC) oxidation of **5** yielded a diketone (**13**). The ^{1}H-NMR spectrum of **13** showed a one-proton doublet (J=10.5 Hz) at δ 6.15 due to 7α-H. Therefore, the structure of xeniasterol-b has been established as 7-*O*-acetylergosta-3β,5α,6β,7β-tetraol (**5**).

Xeniasterol-a (**4**) is a dehydro derivative of xeniasterol-b (**5**) as judged from its elemental analysis. The ^{1}H-NMR spectrum of **4** was very similar to that of **5** except that the former showed signals due to two olefinic protons (δ 5.26, m). Catalytic hydrogenation of **4** over 10% palladium–carbon provided **5**. Detailed comparison of the ^{1}H- and ^{13}C-NMR data for **4** with

TABLE I. ^{13}C-NMR Data for **4**, **5**, **6**, and **7**[a]

Carbon	4	5	6	7	Carbon	4	5	6	7
1	32.3	32.3	32.5	32.2	17	55.4[b]	55.4[b]	56.5	57.5
2	33.3	33.4	33.3	33.4	18	12.6	12.4	12.5	12.4
3	67.0	67.1	67.4	67.1	19	17.7[c]	17.7[c]	17.2	17.8
4	42.4	42.6	42.8	42.5	20	40.3	36.3	35.6	35.5
5	76.6	76.6	75.9	76.6	21	21.3	19.3	22.4[b]	22.4[b]
6	77.4	77.5	76.3	77.5	22	131.8	34.0	32.2[c]	32.2[c]
7	76.2	76.3	35.7	76.2	23	136.3	30.8	26.0	26.0
8	35.8	35.9	31.3	36.0	24	43.0	39.4	50.9	50.9
9	45.1	45.2	46.0	45.3	25	33.3	31.8	32.5[c]	32.6[c]
10	38.5	38.6	39.2	38.5	26	17.8[c]	17.9[c]	14.4[b]	14.5[b]
11	22.0	21.8	21.8	22.0	27	19.8[d]	20.6	15.6[b]	15.6[b]
12	40.3	40.5	40.8	40.6	28	20.1[d]	15.7	21.6[b]	21.6[b]
13	43.7	43.9	43.6	44.4	29			21.5[b]	21.6[b]
14	55.3[b]	55.2[b]	58.5	55.2	30			21.5	21.6
15	26.5	26.6	24.9	26.8	OAc	170.6	170.6		170.6
16	29.2	28.9	28.7	29.2		21.7	21.8		21.8

a) All assignments were made by off-resonance decoupling, insensitive nuclei enhanced by polarization transfer (INEPT), hetero-decoupling without nuclear Overhauser effect (NOE), and weak-noise methods. *b*—*d*) Assignments may be interchangeable within the same column.

those for known sterols (^{1}H,[9] ^{13}C[10]) finally led us to formulate xeniasterol-a as 7-*O*-acetylergost-22*E*-ene-3β,5α,6β,7β-tetraol (**4**).

Xeniasterol-d (**7**) is a monoacetate of a tetrahydroxysterol. The ^{1}H-NMR spectrum of **7** showed signals assignable to 3α-H (δ 4.89, m), 6α-H (δ 4.44, d-like, J=*ca.* 3.0 Hz), and 7α-H (δ 5.85, dd, J=10.5, 3.0 Hz). It also showed signals characteristically ascribable to its cyclopropane-bearing gorgosterol-type side chain[11] [δ 0.48 (1H dd, J=9.0, 4.0 Hz), 0.26—0.18 (2H, m), −0.10 (1H, m)]. By comparing the ^{13}C-NMR data for xeniasterol-d (**7**) with those for xeniasterol-a (**4**) and -b (**5**) as given in Table I, the structure of xeniasterol-d was concluded to be 7-*O*-acetylgorgosta-3β,5α,6β,7β-tetraol (**7**).

Xeniasterol-c (**6**) is a trihydroxysterol. The ^{1}H-NMR spectrum of **6** again showed signals due to a gorgosterol-type side chain, as observed for **7** [δ 0.46 (1H dd, J=9.0, 4.0 Hz), 0.24—0.15 (2H, m), −0.11 (1H, m)]. The spectrum also showed signals assignable to two protons on carbons bearing a secondary hydroxyl group [δ 4.87 (1H, m), 4.17 (1H, br s)]. The ^{13}C-NMR spectrum of **6** showed signals due to three carbons each having a hydroxyl group [δc 76.3 (d), 75.9 (s), 67.4 (d)]. Detailed comparisons of the ^{1}H- and ^{13}C-NMR data for xeniasterol-c (**6**) with data reported for **14**[12] and **15**[13] (isolated from soft corals *Sarcophyton elegans*[12] and *Lobophytum pauciflorum*,[13] respectively) and data for **7**, finally led us to conclude that xeniasterol-c is gorgosta-3β,5α,6β-triol (**6**).

The polyhydroxysterol mixture containing the above four sterols (**4**—**7**) was shown to exhibit a weak growth-inhibitory activity against B-16 Melanoma cells (IC_{50} 5 μg/ml).[14]

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in our previous paper.[15]

Isolation of Germacrene-c (1)——The soft coral of *Xenia* sp. (Xen-83-ZM-1)[16] (500 g), collected at Zamami-jima, Okinawa Prefecture, in July 1983, was immersed in acetone for 12 h and the acetone solution was concentrated at below 30 °C under reduced pressure. The acetone extract was partitioned into an AcOEt–water mixture and removal of the solvent under reduced pressure from the AcOEt phase furnished the AcOEt extract (17.5 g). A part of the extract (2 g) was quickly purified by column chromatography (SiO_2 50 g, *n*-hexane) to afford germacrene-c (**1**)

(419 mg). **1**, colorless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1368, 987, 892, 861, 841. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 254 (11000). Mass spectrum (MS) *m/z* (%): 204 (40), 189 (16), 161 (44), 136 (52), 121 (100), 105 (42), 93 (88), 91 (44). ^{1}H-NMR (90 MHz, CCl_4) δ: 1.10 (6H, d, J=7 Hz), 1.14, 1.54 (both 3H, s), 4.85 (1H, m), 5.06, 6.07 (both 1H, ABq, J=10 Hz). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δc: 145.7 (s), 141.4 (s), 129.6 (d), 127.2 (s), 125.0 (d), 121.6 (d), 39.9 (2C, t), 36.6 (d), 31.8 (t), 27.6 (t), 22.3 (q), 22.1 (q), 20.5 (q), 16.5 (q).

Isolation of Guaiane-Type Sesquiterpenes (2, 3)——The fresh soft coral (finely cut, 50 g) was sonicated in acetone. The acetone solution was then concentrated at below 30 °C under reduced pressure to give the acetone extract, which was partitioned into an AcOEt–water mixture. Treatment of the AcOEt phase as described above furnished the AcOEt extract (2.36 g). A part of the extract (800 mg) was subjected quickly to column chromatography (SiO_2 40 g, hexane–AcOEt=4:1) to furnish **2** (22 mg) and a fraction containing **3**. Purification of the latter fraction by HPLC (Zorbax ODS, MeOH–$CHCl_3$–CH_3CN–H_2O=60:10:10:12) afforded **3** (21 mg). **2**, colorless oil, $[\alpha]_D^{18}$ +2° (c=1.5, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 3350, 3080, 1130, 950, 885. MS *m/z* (%): 220 (21), 205 (19), 202 (15), 177 (28), 119 (100). ^{1}H-NMR (90 MHz, CCl_4) δ: 0.99 (6H, d, J=7.0 Hz), 1.16 (3H, s), 2.48 (1H, br s), 4.63, 4.68 (both 1H, s), 5.51 (1H, br s). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δc: 153.7 (s), 149.1 (s), 121.6 (d), 106.4 (t), 80.4 (s), 54.8 (d), 47.1 (d), 40.0 (t), 37.4 (d), 37.0 (t), 29.9 (t), 24.8 (t), 24.0 (q), 21.4 (q), 21.2 (q). **3**, colorless needles (from AcOEt), mp 144—145 °C, $[\alpha]_D^{18}$ −0.3° (c=1.2, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 3310. High-resolution MS: Found 220.181. Calcd for $C_{15}H_{24}O$ ($M^+ - H_2O$)= 220.182. MS *m/z* (%): 220 (18), 205 (16), 202 (6), 187 (12), 162 (100). *Anal.* Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.36; H, 10.98. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.97, 0.98 (both 3H, d, J=6.5 Hz), 1.21, 1.26 (both 3H, s), 5.50 (1H, d, J=3.5 Hz). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δc: 149.6 (s), 121.5 (d), 80.3 (s), 75.4 (s), 50.8 (d), 50.4 (d), 42.7 (t), 40.5 (t), 37.3 (d), 25.1 (t), 22.7 (t), 22.7 (q), 21.6 (q), 21.5 (q), 21.2 (q).

Conversion of 1 Giving 2——Germacrene-c (**1**) (146 mg) was left standing at room temperature (25 °C) in the dark for 5 d. The product was purified by column chromatography (SiO_2 6 g, $CHCl_3$–MeOH=20:1) to furnish **2** (98 mg), together with recovered **1** (28 mg). **2** thus obtained was shown to be identical with an authentic sample by TLC (SiO_2 F_{254}, $CHCl_3$–MeOH=20:1, Rf=0.5) and ^{1}H-NMR comparisons.

Conversion of 1 Giving 3——A solution of **1** (139 mg) in 99% aq. acetone (1 ml) was left standing at room temperature in the dark for 5 d. Removal of the solvent under reduced pressure from the solution yielded a product, which was purified by column chromatography (SiO_2 6 g, $CHCl_3$–MeOH=10:1) to furnish **3** (79 mg) and **1** (recovered, 47 mg). **3** thus obtained was shown to be identical with an authentic sample by TLC (SiO_2 F_{254}, $CHCl_3$–MeOH=10:1, Rf=0.5) and ^{1}H-NMR comparisons.

Isolation of Xeniasterol-a (4), -b (5), -c (6), and -d (7)——Purification of the above AcOEt extract (10 g) by column chromatography (SiO_2 450 g, $CHCl_3$–MeOH=20:1) provided a polyhydroxysterol mixture (805 mg). The mixture was then subjected to HPLC separation (Zorbax ODS, MeOH–$CHCl_3$–CH_3CN–H_2O=70:10:10:12) to furnish xeniasterol-a (**4**) (42 mg), -b (**5**) (241 mg), -c (**6**) (16 mg), and -d (**7**) (51 mg). **4**, colorless needles (from EtOH), mp 208—209 °C, $[\alpha]_D^{20}$ +12° (c=0.6, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3482, 1714. High-resolution MS: Found 490.367, 430.346. Calcd for $C_{30}H_{50}O_5$ (M^+)=490.366, $C_{28}H_{46}O_3$ (M^+ − AcOH)=430.345. MS *m/z* (%): 490 (2), 430 (8), 412 (24), 69 (100). ^{1}H-NMR (90 MHz, d_5-pyridine) δ: 0.81 (6H, d, J=6.0 Hz), 0.92 (3H, s), 0.98, 1.08 (both 3H, d, J= 7.0 Hz), 1.63 (3H, s), 1.98 (3H, s), 2.90 (1H, dd, J=12.0, 12.0 Hz, 4β-H), 4.43 (1H, br s, 6α-H), 4.88 (1H, m, 3α-H), 5.26 (2H, m), 5.84 (1H, dd, J=10.0, 4.0 Hz, 7α-H). ^{13}C-NMR (22.5 MHz, d_5-pyridine) δc: Table I. **5**, colorless needles (from MeOH), mp 218—220 °C, $[\alpha]_D^{22}$ +50° (c=1.0, pyridine). *Anal.* Calcd for $C_{30}H_{52}O_5$: C, 73.13; H, 10.64. Found: C, 73.08; H, 10.69. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3460, 1716. High-resolution MS: Found 456.362, 438.349. Calcd for $C_{30}H_{48}O_3$ ($M^+ - 2H_2O$)=456.360, $C_{30}H_{46}O_2$ ($M^+ - 3H_2O$)=438.350. MS *m/z* (%): 456 (4), 438 (1), 432 (7), 414 (100). ^{1}H-NMR (500 MHz, d_5-pyridine) δ: 0.76 (3H, s), 0.84 (6H, d, J=6.5 Hz), 0.90 (3H, d, J=6.5 Hz), 1.00 (3H, d, J=7.0 Hz), 1.63 (3H, s, 19-CH_3), 2.00 (3H, s), 2.32 (1H, dd, J=13.0, 5.0 Hz, 4α-H), 2.42 (1H, ddd, J=10.5, 10.5, 10.5 Hz, 8β-H), 2.92 (1H, dd, J=13.0, 12.0 Hz, 4β-H), 4.44 (1H, dd, J=5.0, 4.0 Hz, 6α-H), 4.89 (1H, m, 3α-H), 5.84 (1H, dd, J=10.5, 4.0 Hz, 7α-H). ^{13}C-NMR (22.5 MHz, d_5-pyridine) δc: Table I. **6**, colorless needles (from $CHCl_3$), mp 255—256 °C, $[\alpha]_D^{22}$ −3° (c=0.9, $CHCl_3$–MeOH=1:1). IR ν_{max}^{KBr} cm^{-1}: 3424. High-resolution MS: Found 460.391.Calcd for $C_{30}H_{52}O_3$ (M^+)=460.391. MS *m/z* (%): 460 (12), 442 (14), 55 (100). ^{1}H-NMR (500 MHz, d_5-pyridine) δ: −0.11 (1H, m), 0.15—0.24 (2H, m), 0.46 (1H, dd, J=9.0, 4.0 Hz), 0.76 (3H, s), 0.85 (3H, d, J=6.5 Hz), 0.88 (3H, s), 0.96, 0.97, 1.10 (each 3H, d, J=6.0 Hz), 1.66 (3H, s), 2.96 (1H, dd, J=12.0, 12.0 Hz), 4.17 (1H, br s), 4.87 (1H, m). ^{13}C-NMR (22.5 MHz, d_5-pyridine) δc: Table I. **7**, colorless needles (from EtOH), mp 285—286 °C, $[\alpha]_D^{22}$ +32° (c=1.0, pyridine). *Anal.* Calcd for $C_{32}H_{54}O_5$: C, 74.08; H, 10.50. Found: C, 73.79; H, 10.52. IR ν_{max}^{KBr} cm^{-1}: 3432, 1712. High-resolution MS: Found 458.374. Calcd for $C_{30}H_{50}O_3$ (M^+ − AcOH)=458.376. MS *m/z*: (%): 458 (14), 55 (100). ^{1}H-NMR (500 MHz, d_5-pyridine) δ: −0.10 (1H, m), 0.18—0.26 (2H, m), 0.48 (1H, dd, J=9.0, 4.0 Hz), 0.79 (3H, s), 0.86 (3H, d, J=6.5 Hz), 0.91 (3H, s), 0.97 (3H, d, J=6.5 Hz), 1.00 (3H, d, J=7.0 Hz), 1.12 (3H, d, J= 6.5 Hz), 1.63, 1.96 (both 3H, s), 2.34 (1H, m, 4α-H), 2.42 (1H, ddd, J=10.5, 10.5, 10.5 Hz, 8β-H), 2.92 (1H, dd, J= 12.0, 12.0 Hz, 4β-H), 4.44 (1H, d-like, J=*ca.* 3 Hz, 6α-H), 4.89 (1H, m, 3α-H), 5.85 (1H, dd, J=10.5, 3.5 Hz, 7α-H). ^{13}C-NMR (22.5 MHz, d_5-pyridine) δc: Table I.

Alkaline Hydrolysis of Xeniasterol-b (5)——Xeniasterol-b (**5**) (35 mg), was treated with 0.1 M K_2CO_3–aq. 85% MeOH (11 ml) and the whole mixture was stirred at room temperature (25 °C) for 8 h. The reaction mixture was then partitioned into an AcOEt–water mixture. The organic phase was taken and washed with aq.

sat. NaCl and dired over $MgSO_4$. Removal of the solvent under reduced pressure from the filtrate gave a product (35 mg), which was purified by column chromatography (SiO_2 3 g, $CHCl_3$–MeOH = 10 : 1) to furnish **10** (32 mg). **10**, colorless needles (from MeOH), mp 238—239 °C, $[\alpha]_D^{22}$ +15° (c = 1.0, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3380. High-resolution MS: Found 450.371. Calcd for $C_{28}H_{50}O_4$ (M^+) = 450.371. MS m/z (%): 450 (2), 432 (18), 417 (13), 414 (100). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.71 (3H, s), 0.80 (6H, d, J = 6.5 Hz), 0.87 (3H, d, J = 6.5 Hz), 0.94 (3H, d, J = 6.0 Hz), 1.17 (3H, s), 3.50 (1H, m), 3.77 (1H, m), 4.09 (1H, m). ^{13}C-NMR (22.5 MHz, d_5-pyridine) δc: 32.3 (t, C-1), 33.2 (t, C-2), 67.0 (d, C-3), 42.8 (t, C-4), 76.6 (s, C-5), 79.2 (d, C-6), 72.8 (d, C-7), 39.3 (d, C-8), 44.5 (d, C-9), 38.4 (s, C-10), 21.8 (t, C-11), 40.7 (t, C-12), 43.8 (s, C-13), 56.3 (d, C-14), 27.7 (t, C-15), 29.1 (t, C-16), 55.8 (d, C-17), 12.5 (q, C-18), 17.4 (q, C-19), 36.5 (d, C-20), 19.2 (q, C-21), 34.0 (t, C-22), 30.9 (t, C-23), 39.3 (d, C-24), 31.7 (d, C-25), 17.7 (q, C-26), 20.6 (q, C-27), 15.6 (q, C-28).

Acetylation of Xeniasterol-b (5) Giving 11 and 12——A solution of **5** (35 mg) in pyridine (3 ml) was treated with Ac_2O (2 ml) and the whole mixture was stirred at room temperature (25 °C) for 4 h. The reaction mixture was poured into ice-water, and the whole was extracted with AcOEt. The AcOEt extract was washed with aq. sat. NaCl and dried over $MgSO_4$. Removal of the solvent under reduced pressure from the AcOEt extract gave a product, which was purified by column chromatography (SiO_2 20 g, hexane–AcOEt = 4 : 1) to provide the diacetate (**11**, 27 mg) and the triacetate (**12**, 9 mg). **11**, colorless needles (from MeOH), mp 218—220 °C. High-resolution MS: Found 534.389. Calcd for $C_{32}H_{54}O_6$ (M^+) = 534.392. MS m/z (%): 534 (0.1), 516 (0.2), 396 (100). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.69 (3H, s), 0.77 (6H, d, J = 6.5 Hz), 0.85 (6H, d, J = 6.5 Hz), 1.18 (3H, s), 2.02, 2.05 (both 3H, s), 3.67 (1H, d, J = 3.5 Hz), 5.06—5.22 (2H, m). ^{13}C-NMR (22.5 MHz, d_5-pyridine) δc: 32.2 (t, C-1), 26.8 (t, C-2), 71.4 (d, C-3), 37.3 (t, C-4), 76.3 (s, C-5), 76.7 (d, C-6), 75.7 (d, C-7), 36.2 (d, C-8), 44.2 (d, C-9), 37.9 (s, C-10), 21.3 (t, C-11), 39.9 (t, C-12), 43.7 (s, C-13), 55.3 (d, C-14), 26.1 (t, C-15), 28.6 (t, C-16), 54.5 (d, C-17), 12.2 (q, C-18), 17.1 (q, C-19), 35.2 (d, C-20), 19.1 (q, C-21), 33.8 (t, C-22), 30.7 (t, C-23), 39.2 (d, C-24), 31.6 (d, C-25), 17.8 (q, C-26), 20.5 (q, C-27), 15.6 (q, C-28), 171.1, 171.3 (both s), 21.5, 21.8 (both q) (2AcO). **12**, colorless amorphous solid. High-resolution MS: Found 576.400. Calcd for $C_{34}H_{56}O_7$ (M^+) = 576.402. MS m/z: (%): 576 (0.1), 558 (0.5), 396 (100). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.71 (3H, s), 0.78 (3H, d, J = 6.5 Hz), 0.85 (6H, d, J = 6.5 Hz), 0.91 (3H, d, J = 6.0 Hz), 1.17, 1.92, 2.03, 2.10 (each 3H, s), 4.98—5.24 (3H, m).

PCC Oxidation of Xeniasterol-b (5)——A solution of **5** (28 mg) in CH_2Cl_2 (8 ml) was treated with PCC (37 mg) and the whole mixture was stirred at room temperature (28 °C) under a nitrogen atmosphere for 18 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave a product, which was purified by column chromatography (SiO_2 15 g, hexane–AcOEt = 4 : 1) to furnish the diketone (**13**, 26 mg). **13**, colorless amorphous, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 1720. High-resolution MS: Found 488.350. Calcd for $C_{30}H_{48}O_5$ (M^+) = 488.350. MS m/z (%): 488 (2), 470 (3), 428 (100). ^{1}H-NMR (500 MHz, d_5-pyridine) δ: 0.71 (3H, s), 0.85, 0.86 (both 3H, d, J = 6.5 Hz), 0.92 (3H, d, J = 7.0 Hz), 1.01 (3H, d, J = 6.5 Hz), 1.07, 2.20 (both 3H, s), 2.81, 3.21 (both 1H, ABq, J = 15.0 Hz), 6.15 (1H, d, J = 10.5 Hz). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δc: 31.9 (t, C-1), 37.1 (t, C-2), 210.2, 204.5 (both s, C-3, 6), 44.2 (t, C-4), 82.7 (s, C-5), 78.1 (d, C-7), 42.3, 43.6 (both d, C-8, 9), 43.0 (s, C-10), 21.9 (t, C-11), 39.6 (t, C-12), 43.9 (s, C-13), 55.6 (d, C-14), 25.6 (t, C-15), 28.3 (t, C-16), 55.3 (d, C-17), 12.0 (q, C-18), 13.9 (q, C-19), 36.1 (d, C-20), 19.0 (q, C-21), 33.7 (t, C-22), 30.7 (t, C-23), 39.2 (d, C-24), 31.5 (d, C-25), 17.7 (q, C-26), 20.5 (q, C-27), 15.6 (q, C-28), 171.3 (s), 21.0 (q), (AcO).

Catalytic Hydrogenation of Xeniasterol-a (4) Giving Xeniasterol-b (5)——A suspension of 10% Pd–C (26 mg) in AcOEt (1 ml) was stirred under a hydrogen atmosphere for 15 min. The suspension was then treated with a solution of **4** (12 mg) in AcOEt (1 ml) and the reaction mixture was stirred for further 20 h, then filtered. Removal of the solvent from the filtrate under reduced pressure gave a product. HPLC purification (Zorbax ODS, MeOH–$CHCl_3$–CH_3CN–H_2O = 70 : 10 : 10 : 12) of the product furnished **5** (4 mg) and **4** (recovered, 1.5 mg). **5** thus obtained was shown to be identical with an authentic sample of xeniasterol-b by mixed melting point determination and HPLC comparison.

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16) Since the soft coral investigated in this work has not yet been identified precisely, the specimen reported in this paper is designated as Xen-83-ZM-l, which indicates that it is a sample of *Xenia* sp. collected at Zamami-jima in July, 1983.