Ichthyotoxic Cembranoids from the Soft Coral, *Sarcophyton* sp.[1)]

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Ten new ichthyotoxic cembranoids: sartol A (**1**), 4-*O*-methylsartol A (**2**), sartones A (**3**), B (**4**), C (**5**), D (**6**), 4-*O*-methylsartone B (**7**), epoxysartone A (**8**), 6β-hydroxysarcotol acetate (**9**), and 4-*O*-methylsarcotol (**10**) have been isolated from the soft coral, *Sarcophyton* sp. The ichthyotoxicity tests were performed for **1**, **3**—**7**, and **10**, including the reduction product and the acetate of **1**.

It has been suggested that soft corals can avoid predators, although they do not have any physical method of defense, by producing chemical defense compounds such as cembranoids in their tissue.[2)] A number of cembranoids possessing ichthyotoxicity have been isolated so far,[3)] and in a previous paper,[4)] we reported the isolation of three ichthyotoxic cembranoids containing a 13-membered carbocyclic ring, sarcotol (**11**), sarcotol acetate (**12**), and sarcotal acetate (**13**) from the soft coral, *Sarcophyton* sp. Further investigation of the same species has led to the isolation of ten new ichthyotoxic cembranoids: sartol A (**1**), 4-*O*-methylsartol A (**2**), sartones A (**3**), B (**4**), C (**5**), D (**6**), 4-*O*-methylsartone B (**7**), epoxysartone A (**8**), 6β-hydroxysarcotol acetate (**9**), and 4-*O*-methylsarcotol (**10**). In this paper, we describe the isolation and structural elucidation of **1**—**10** (Chart 1).

Results and Discussion

The molecular formula $C_{20}H_{34}O_2$ for sartol A (**1**) resulted in four degrees of unsaturation, and the IR spectrum indicated a hydroxy group (3385 cm^{-1}) and a double bond (1667 cm^{-1}). The ^{13}C NMR spectrum showed the presence of three olefinic bonds [δ = 128.4 (d), 129.5 (d), 129.6 (s), 131.2 (d), 137.2 (d), and 139.0 (s)] (Table 1), suggesting that **1** is monocyclic. The gross structure was determined by comparing the ^1H NMR spectral data with those of sarcotol (**11**) and by analysis of the ^1H–^1H, ^{13}C–^1H COSY, and COLOC spectra of **1**. Resonances due to methyl protons on a carbon bearing a hydroxy group (δ = 1.36; 3H, s, Me-18) and isopropyl protons (δ = 0.82 and 0.85; 3H each, d, J = 6.4 Hz, Me-16 and Me-17 and ca. 1.51; 1H, overlapped, H-15) were observed. Resonances due to *trans*-olefinic protons appeared at δ = 5.24 (1H, dd, J = 9.2 and 15.8 Hz, H-2) and 5.60 (1H, d, J = 15.8 Hz, H-3), and the H-2 was further coupled with H-1 (δ = ca. 1.51; 1H, overlapped). H-7 (δ = ca. 5.20; 1H, overlapped) was coupled to H-6 (δ = ca. 2.10; 1H, overlapped and δ = ca. 2.44; 1H, overlapped) and also weakly to Me-19 (δ = 1.64; 3H, br s). The H-6 at δ = ca. 2.10 was further coupled to one of H-5 (δ = ca. 1.97; 1H, overlapped). The Me-19 resonances showed cross peaks C-7 (δ = 131.2, d), C-8 (δ = 129.6, s), and C-9 (δ = 48.3, t) in the COLOC experiments (Fig. 1), establishing the connectivity of C-7 to C-9. The H-9 methylene protons (δ = 2.15; 1H, dd, J = 8.2 and 12.6 Hz; δ = 2.44; 1H, overlapped) were coupled to H-10 (δ = 4.53; 1H, dt, J = 4.8 and 8.2 Hz) on a carbon carrying a hydroxy group. The H-10 was further coupled to H-11 (δ = 5.20; 1H, br d, J = 8.2 Hz); the latter in turn weakly coupled to the olefinic methyl protons (δ = 1.67; 3H, br s, Me-20). The connectivity of C-11 to C-13 was confirmed by the observation of cross peaks between Me-20 and C-11 (δ = 128.4, d), C-12 (δ = 139.0, s), and C-13 (δ = 36.5, t) in the COLOC spectrum. Both geometries of the olefinic bonds at C-7 and C-11 were determined to be *E* by the chemical shifts of the methyl groups at C-19 (δ = 16.3) and at C-20 (δ = 14.8) in the ^{13}C NMR spectrum.[5)] On the basis of these results, the gross structure was determined (Fig. 1). The relative stereochemistry was indicated by a series of NOE experiments of the monoacetate **14** in C_6D_6 (Fig. 2) obtained by the treatment of **1** with acetic anhydride in pyridine. It was concluded that H-1, H-6β, H-7, H-9β, H-10, and H-11 were β-oriented. Thus, the irradiation of H-3 (δ = 5.71; 1H, d, J = 15.5 Hz) resulted in a 5.0, 5.1, and 1.7% enhancement

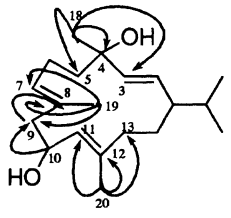


Fig. 1. COLOC correlation for **1**.

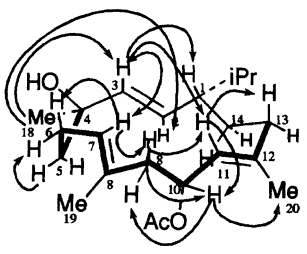
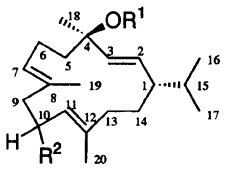
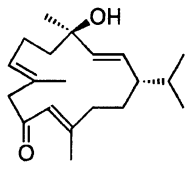


Fig. 2. NOEs observed for **14**.



1=16 R^1=H R^2=α-OH
2 R^1=Me R^2=α-OH
8 R^1=H 11α,(12β)-epoxy
14 R^1=H R^2=α-OAc
15 R^1=H R^2=α-*p*-BrBzO
17 R^1=H R^2=β-OH



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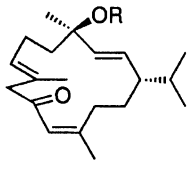
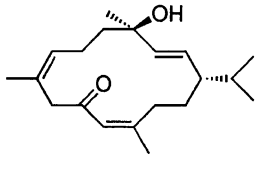


4 R=H
7 R=Me



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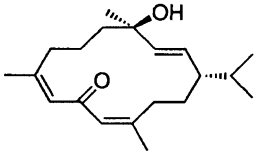

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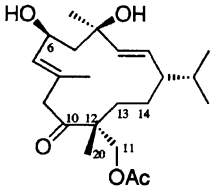

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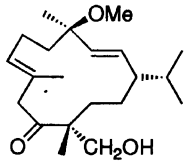

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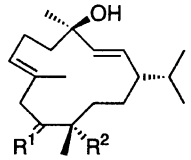

11 R^1=O R^2=CH_2OH
12 R^1=O R^2=CH_2OAc
13 R^1=β-OAc R^2=CHO

Chart 1.

Table 1. ^{13}C NMR Spectral Data of **1**—**10** ($CDCl_3$)

C	1	2	3	4	5	6	7	8	9	10
1	46.3	46.5	46.3	47.6	47.7	48.4	48.5	47.2	49.1	49.8
2	129.5	132.6	130.0	129.7	130.2	131.3	133.1	130.8	130.0	133.6
3	137.2	134.5	137.4	137.8	137.8	138.0	135.8	137.9	137.0	136.1
4	72.5	76.7	72.4	72.8	73.0	73.8	77.1	73.3	72.3	77.5
5	42.5	42.5	42.4	42.2	42.1	41.6	41.9	42.8	45.4	42.3
6	22.0	21.3	22.3	22.9	24.3	33.2	22.3	23.0	79.6	23.1
7	131.2	131.5	133.4	128.9	125.9	25.1	129.5	133.3	127.8	131.7
8	129.6	129.3	128.8	129.7	128.0	152.9[a]	127.9	128.0	130.0	128.4
9	48.3	48.8	57.1	52.1	47.2	124.5[b]	52.1	54.8	48.3	49.3
10	65.5	65.6	199.9	200.9	199.3	194.0	200.8	204.5	210.6	214.5
11	128.4	128.3	122.1	128.3	128.6	128.3[b]	128.1	62.0	66.3	65.9
12	139.0	138.8	157.8	155.4	154.0	155.8[a]	155.6	64.8	51.6	53.7
13	36.3	36.5	38.6	31.1	29.7[a]	30.0[c]	31.0	33.2	34.9	34.9
14	27.2	27.4	27.6	29.0	29.8[a]	30.5[c]	29.8	27.4	25.4	26.5
15	33.0	33.5	32.8	33.1	32.5	32.3	33.2	31.1	32.7	32.5
16,17	19.5,20.4	19.4,20.4	19.1,20.6	18.9,20.3	19.6,20.3	19.6,20.4	18.8,20.7	20.3×2	19.5,20.2	19.9,20.1[a]
18	28.3	22.3	28.4	28.1	28.7	28.1	21.3	29.1	28.4	20.2[a]
19	16.3	16.3	16.5	18.0	25.6	26.5	18.0	16.6	17.2	15.7
20	14.7	14.8	17.7	23.9	23.2	23.1	24.1	16.1	21.4[a]	20.9[a]
MeO		50.1					49.9			51.8
MeCOO									20.8[a]	
MeCOO									170.9	

a), b), c) These values may be interchangeable in any vertical column.

of H-1 (δ = 1.56; 1H, m), H-7 (δ = 5.20; 1H, br t, J = 7.1 Hz), and H-11 (δ = 5.29; 1H, d, J = 8.2 Hz) respectively, while the irradiation of H-7 induced a 3.0 and 3.5% enhancement of H-6β (δ = ca. 2.45; 1H, overlapped) and H-9β (δ = 2.34; 1H, dd, J = 8.2 and 13.2 Hz), respectively, as well as a 4.3% enhancement of H-3. Similarly, NOEs obtained between H-11 and H-9β (3.2%), H-10 (1.6%), and H-13β (δ = ca. 2.00; 1H, m, 4.9%) were observed. The α-configuration of the methyl group at C-4 was concluded from the NOE of Me-18 (δ = 1.24; 3H, s) to H-2 (δ = 5.13, dd, 1H, J = 9.2 and 15.5 Hz, 3.8%) and to H-3 (0.8%). The absolute configuration of the chiral center at C-10 was determined as R on the ba-

sis of the exciton chirality method of the allylic benzoate,[6] because the *p*-bromobenzoyl ester **15**, derived from **1**, exhibited a negative Cotton effect in the CD spectrum [λ_{ext} 245 nm ($\Delta\varepsilon$ −15.77) and 216 nm ($\Delta\varepsilon$ +2.08)], indicating the negative chirality due to the double bond at C-11 and *p*-bromobenzoate chromophores (Fig. 3). Therefore, the absolute structure of sartol A is shown in structure **1**.

The ^{1}H and ^{13}C NMR spectra of compound **2** were similar to those of **1**, except for an additional resonance assigned to the methoxy group (δ_H = 3.12; 3H, s, δ_C = 50.1, s). The location of the methoxy group was determined to be C-4 from the downfield shift (Δ 4.2 ppm) of C-4 (δ = 76.7) compared with that of **1**. The NOE experiments of **2** in C_6D_6 were as follows (Fig. 4): H-3⟷H-1 (5.2%), H-6β (2.4%), H-7 (3.2%), Me-19 (2.3%), and MeO (2.0%), H-7⟷H-6β (1.0%), H-9β (3.6%), and H-9α (1.5%), and H-10⟷H-9β (0.7%), H-9α (3.5%), and Me-20 (6.7%). The observation of the NOEs from H-3 to H-7 and Me-19 indicated that H-3 is close to both H-7 and H-19, unlike in the case of **14**. Based on these results, **2** was identified as 4-*O*-methylsartol A.

Sartone A (**3**), $C_{20}H_{32}O_2$, showed absorption bands indicative of a hydroxy group (3410 cm^{-1}) and an α, β-unsaturated carbonyl moiety (1680 and 1614 cm^{-1}) in the IR spectrum. The ^{13}C NMR spectrum was similar to that of **1**, except that the resonances for C-9 to C-12 were shifted downfield (Δ 8.8 and 18.8 ppm, respectively), and the methine carbon bearing oxygen in **1** was replaced by a signal assigned to a carbonyl carbon (δ = 199.9). In the ^{1}H NMR spectra, resonances due to isopropyl protons (δ = 0.80 and 0.83; 3H each, d, J = 6.6 Hz, Me-16 and Me-17; δ = ca. 1.50; 1H, overlapped, H-15), two olefinic methyl groups (δ = 1.65; 3H, br s, Me-19 and 2.09; 3H, br s, Me-20), and a tertiary methyl group on a carbon carrying oxygen (δ = 1.40; 3H, s) were observed. As observed for **1**, a double doublet at δ = 5.27 (1H, J = 9.5 and 15.8 Hz, H-2) and a doublet at δ = 5.63 (1H, J = 15.8 Hz, H-3) were seen. Based on the values of the chemical shifts and coupling patterns, the methylene protons (δ = 2.87 and 3.04; J = 13.6 Hz, H-9) were assumed to be located between a double bond and a carbonyl group. Resonances due to *trans*-olefinic protons appeared at δ = 5.27 (1H, dd, J = 9.5 and 15.8 Hz, H-2) and δ = 5.63 (1H, d, J = 15.8 Hz, H-3), and the H-2 was further coupled with H-1 (δ = 1.55; 1H, m). COLOC correlations of Me-18 to C-3 (δ_C = 137.4), C-4 (δ_C = 72.4), and C-5 (δ_C = 42.4) (Fig. 5) and the ^{13}C–^{1}H COSY data established the chemical shifts of H-5 (δ_H = ca. 1.55; 1H, overlapped and δ_H = ca. 2.03; 1H, overlapped). One of the H-5 protons (δ_H = ca. 2.03) was coupled to one of the H-6 protons (δ = 2.57; 1H, dt, J = 9.5 and 15.4 Hz), which in turn was coupled to H-7 (δ = 5.38; 1H, dd, J = 4.8 and 9.9 Hz). An olefinic proton in the α, β-unsaturated carbonyl group (δ = 6.23; 1H, br s, H-11) was weakly coupled to olefinic methyl protons (δ = 2.09; 3H, br s, Me-20). This was supported by the COLOC experiments. Thus, Me-20 displayed correlations with C-10 (δ = 199.9) and C-11 (δ = 122.1), highlighting the α, β unsaturated group. The *E*-configurations at C-7 and C-11 were determined by the chemical shifts of the methyl groups at C-19 (δ = 16.5) and at C-20 (δ = 17.7) in the ^{13}C NMR spectrum. Further structural proof and stereochemical details were obtained from the NOE experiments (Fig. 6). Irradiation of H-11 induced a 2.8, 3.2, 2.6, 8.3% peak enhancement of H-3, H-7, H-9β, and H-13β [δ = ca. 2.03 (1H, overlapped)], respectively. On irradiation of H-3, peak enhancements of H-1 (6.9%), H-6β (δ = 2.57; 1H, dt, J = 9.5 and 15.4 Hz, 2.9%), and H-7 (1.9%), as well as H-11 (2.2%) were observed. These results suggested that H-1, H-3, H-7, H-9β, and H-11 were in β-configuration. NOEs from H-2 to H-14*endo* [δ = ca. 1.69 (1H, overlapped), 1.7%] and from Me-18 to H-2 (4.7%), and from Me-19 to H-9α (1.5%) showed that H-2, H-9α, Me-18, and Me-19 were on the opposite face to H-1. The absolute stereochemistry of **3** was established as follows: Reduction of **3** with sodium borohydride yielded an alcohol **16** ($C_{20}H_{34}O_2$; $[\alpha]_D$ +13.4°) and its isomer **17** ($[\alpha]_D$ −64.3°) in 25 and 75% yields, respectively. The minor alcohol **16** had the same NMR spectral data and optical rotation as those of sartol A (**1**), $[\alpha]_D$ +24.7°, which was isolated from the same source. The absolute structure of **3** was therefore shown as depicted.

Sartone B (**4**) was identified as an isomer of **3**. The

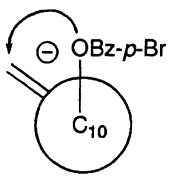

Fig. 3. Conformation of C-10 of **15**.

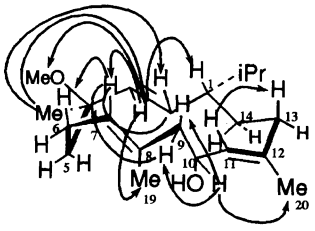

Fig. 4. NOEs observed for **2**.

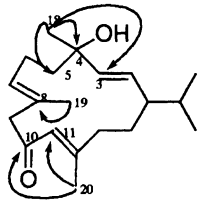

Fig. 5. COLOC correlation for **3**.

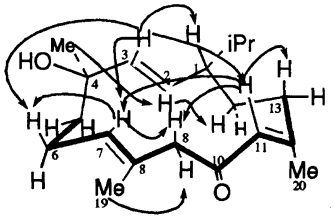

Fig. 6. NOEs observed for **3**.

^{1}H NMR spectrum showed signal patterns similar to those of **3**, and resonances due to the following protons were readily assigned by the usual NMR techniques: H-2 (δ = 5.29; 1H, dd, J = 8.1 and 15.9 Hz), H-3 (δ = 5.46; 1H, d, J = 15.9 Hz), H-7 (δ = 5.14; 1H, br t, J = 6.1 Hz), H-9 (δ = 2.96; 1H, br d, J = 13.9 Hz, δ = 3.08; 1H, br d, J = 13.9 Hz), and H-11 (δ = 5.99; 1H, br s), as well as isopropyl protons (δ = 0.82 and 0.85; 3H each, d, J = 6.6 Hz, Me-16 and Me-17, ca. 1.62; 1H, overlapped, H-15) and three methyl protons (δ = 1.31; 3H, s, Me-18, δ = 1.71; 3H, br s, Me-19, and δ = 1.84; 3H, d, J = 1.1 Hz, M-20). The *E*-configuration at C-7 and the *Z*-configuration at C-11 were suggested by the absence of NOE between H-7 and Me-19 and the presence of NOE (3.7%) between H-11 and Me-20. This was further supported by the chemical shift data for the methyl resonances at δ = 18.0 (C-19) and 23.9 (C-20) in the ^{13}C NMR spectrum. Therefore, sartone B was identified as the 11*Z* isomer of sarton A.

A fifth compound, sartone C (**5**), was also isomeric with **3** and **4**. The ^{1}H and ^{13}C NMR spectra showed close similarity with those of **4**, except that the resonance for C-19 appeared at a lower field (δ_C = 25.6), implying that the C-7 double bond is the *Z*-configuration. Thus, sartone C was identified as 7*Z*, 11*Z*-sartone A.

It appeared that sartone A (**3**) is photo-labile and could be isomerized in light to produce sartones B (**4**) and C (**5**), since HPLC analysis of sartone A exposed to the light in a room showed peaks corresponding to sartones B and C.

Sartone D (**6**) displayed a UV maximum at 272 nm, suggesting a cross-conjugated system. The IR spectrum indicated absorption bands corresponding to a hydroxy group (3420 cm^{-1}) and a conjugated carbonyl (1667 and 1620 cm^{-1}). By comparison of the ^{1}H NMR data with those of **3**—**5**, the resonances due to an isopropyl group (δ = 0.83 and 0.87; 3H each, d, J = 6.8 Hz, Me-16 and Me-17), a tertiary methyl group (δ = 1.25; 3H, s, Me-18) on a carbon carrying oxygen, and two olefinic methyl groups (δ = 1.81; 3H, d, J = 1.1 Hz, Me-19, δ = 1.89; 3H, d, J = 1.5 Hz, Me-20) were readily assigned. The lowfield chemical shift (δ = 6.00; 2H, br s) of the two olefinic protons suggested that the double bonds were conjugated with a carbonyl. This implied that there was a double bond at C-8 rather than at C-7 as in **3**—**5**, and this was supported by the absence of the signal for the methylene protons H-9 observed in the NMR spectra of **3**—**5**. The *Z* geometry of the two double bonds was indicated by the chemical shifts of the olefinic methyls C-19 (δ = 26.5) and C-20 (δ = 23.1), and by the NOE from Me-19 to H-9 (3.1%) and from Me-20 to H-11 (3.0%). The stereochemistry at C-1 and C-4 was established by NOEs between Me-18 and H-2 (2.7%) and between H-1 (δ = ca. 1.57; 1H, overlapped) and H-3 (12.2%) as observed for **3**—**5**, suggesting that H-1 and Me-18 were α- and β-configurations, respectively.

Compound **7**, containing an additional CH_3 group, was isolated as an oil. The ^{1}H NMR spectrum was similar to that of **4**, except for a sharp resonance at δ = 3.12 (3H, s, MeO-4) assigned to a methyoxy group. Placement of the methoxy group at C-4 was indicated by the downfield shift of C-4 (δ = 77.1, Δ 4.3 ppm) compared to the same position of **4**. The stereochemistry of the methoxy group was deduced to be β by an NOE between H-3 (δ = 5.31; 1H, d, J = 16.1 Hz) and H-1 (δ = ca. 1.63; 1H, overlapped, 2.1%), H-7 (5.13; 1H, br t, J = 6.0 Hz, 2.2%), and the methoxy protons (1.0%) were observed. Irradiation of Me-18 resulted in an enhancement of H-2 (3.4%). Therefore, compound **5** was assigned as 4-*O*-methoxylsartone B.

Epoxysartone A (**8**) was isolated as an oil with a molecular formula $C_{20}H_{32}O_3$, indicating that **8** had one more oxygen than **3**. Comparison of the ^{1}H and ^{13}C NMR spectra of **8** with those of **3** showed that the C-11 double bond had been replaced by an epoxide [δ_H = 3.67 (s), H-11; δ_C = 62.0 (d), C-11 and δ_C = 64.8 (s), C-12]. The stereochemistry of the epoxide was determined to be 11-α and 12-β from the observation of a series of NOE experiments (Fig. 7). In summary, the irradiation of H-11 resulted in an enhancement of H-7 (δ = 5.52, br t, J = 5.9 Hz, 2.1%), H-9β (δ = 3.19, AB, J = 14.3 Hz, 2.4%), and H-13β (δ = ca. 1.39; 1H, overlapped, 8.3%). NOEs between H-3 (δ = 5.73, d, J = 15.8 Hz) and H-11 (2.1%) and between Me-20 and H-14*exo* (δ = ca. 1.39; 1H, overlapped, 0.7%) were further observed. The remainder of the NOEs was similar to those of **3**. Therefore, compound **8** was identified as 11α, 12β-epoxysartone A. Epoxysartone A could be a potential precursor for the 13-membered carbocyclic cembranoids which would be formed by a ring contraction mechanism of **8**.[4)]

The IR data of **9**, $C_{22}H_{36}O_5$, indicated the presence of a hydroxy group (3378 cm^{-1}), an ester carbonyl (1742 and 1242 cm^{-1}), and a double bond (1663 cm^{-1}). The ^{1}H NMR data for **9** were similar to those of sarcotol acetate (**12**),[4)] except for a resonance at δ = 4.76 (dt, J = 2.4 and 8.6 Hz, H-6), which led to the assumption that **9** might possess an additional hydroxy group at an allylic position. This was confirmed by the ^{1}H–^{1}H COSY data which showed coupling between H-6 and H-7 (δ = 5.25; 1H, overlapped). The configuration of H-6 was determined to be α from NOE experiments, in which the irradiation of the H-6 resulted in a 9.9% enhancement of Me-19 (δ = 1.76; 3H, br s), as observed in **11**. Irradiation of H-9α (δ = 3.27; 1H, d, J = 12.5 Hz) caused a 3.3% enhancement of Me-19. Together these data suggested that **9** was 18-β-hydroxysarcotol acetate.

The ^{1}H NMR spectrum of compound **10**, $C_{21}H_{36}O_3$, was similar to that of sarcotol (**11**), except for an additional resonance assigned to the methoxy protons (δ = 3.15; 3H, s). The location of the methoxy group was concluded to be at C-4 on th basis of an NOE between Me-18 (1.21; 3H, s) and the methoxy protons (2.8%). This was confirmed by the downfield shift of C-4 (δ = 77.5) compared to that of **11**

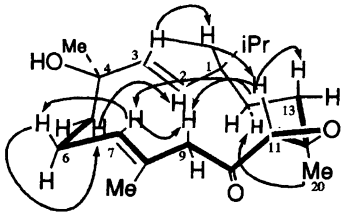

Fig. 7. NOEs observed for **8**.

(δ = 73.1). Therefore, compound **10** was identified as 4-*O*-methylsarcotol.

Ichthyotoxicity tests were performed for sartol A (**1**), sartones A (**3**), B (**4**), C (**5**), D (**6**), 4-*O*-methylsartone B (**7**), 4-*O*-methylsarcotol (**10**), 10-episartol A (**17**), and sartol A acetate (**14**). Compounds **3**, **4**, **5**, **6**, **7**, and **14** showed ichthyotoxicity at 20 ppm to killifish, *Oryzia latipes*, which died within 24 h, while compounds **1**, **10**, and **17** were not toxic at 20 ppm.

Experimental

Extraction and Isolation The CH_2Cl_2 soluble portion (8.1 g) of the MeOH extract of *Sarcophyton* sp. described in Ref. 4 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, 4 : 1), 3-4 (CH_2Cl_2), 5-6 (MeOH–CH_2Cl_2, 1 : 49), 7-9 (MeOH–CH_2Cl_2, 1 : 19), 10-11 (MeOH–CH_2Cl_2, 1: 9), 12-13 (MeOH-CH_2Cl_2, 1 : 4), 14-15 (MeOH–CH_2Cl_2, 1 : 1), and 16 (MeOH). Fraction 1 (1.7g) was again chromatographed on silica-gel using CH_2Cl_2 with acetone (98.5 : 1.5), (97 : 3), and (93 : 7) as eluents to give fractions 1a, 1b, and 1c, respectively. Reversed-phase C_{18} chromatography (ODS-HPLC) of fr. 1a with MeOH–H_2O (4 : 1) yielded **7** (2.1 mg). Compounds **3** (14.1 mg), **4** (3.2 mg), and **2** (13.6 mg) were purified by HPLC of fr. 1b with MeOH–H_2O (7 : 3). From fr. 1c compound **12** (3.7 mg) was obtained using HPLC with MeOH–H_2O (3 : 2). Fractions 2-5 (0.9 g) were subjected to HPLC chromatography with MeOH–H_2O (4 : 1) and MeOH–H_2O (3 : 2), respectively, yielding **13** (8.2 mg), **9** (1.1 mg), and **12** (9.3 mg). Fractions 6-8 (2.78 g) were further chromatographed on silica-gel using ether–hexane (3 : 2), followed by HPLC with MeOH–H_2O (4 : 1), resulted in **1** (70.9 mg), **4** (4.7 mg), **5** (1.7 mg), **6** (2.6 mg), **8** (9.8 mg), **10** (2.9 mg), and **12** (16.0 mg). Compound **11** (67.0 mg) was isolated as crystals from an eluant obtained by the silica-gel chromatography of fractions 6-8 with ether–hexane (3 : 1).

Sartol A (1). Oil, $[\alpha]_D^{27}$ +24.7° (*c* 0.75, MeOH); UV λ_{max}^{MeOH} 208 nm (ε 5370); IR (film) 3385 and 1667 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.82 and 0.85 (3H each, d, *J* = 6.4 Hz, Me-16 and Me-17), ca. 1.32 (1H, overlapped, H-14*exo*), 1.36 (3H, s, Me-18), ca. 1.51 (3H overlapped, H-1, H-5, and H-15), ca. 1.64 (1H, overlapped, H-14), 1.64 (3H, br s, Me-19), 1.67 (3H, br s, Me-20), ca. 1.97 (2H, overlapped, H-5 and H-13β), ca. 2.10 (2H, overlapped, H-6α and H-13α), 2.15 (1H, dd, *J* = 8.2 and 12.6 Hz, H-9β), ca. 2.44 (2H, overlapped, H-6β and H-9α), 4.53 (1H, dt, *J* = 4.8 and 8.2 Hz, H-10), ca. 5.20 (1H, overlapped, H-7), 5.20 (1H, br d, *J* = 8.2 Hz, H-11), 5.24 (1H, dd, *J* = 9.2 and 15.8 Hz, H-3), and 5.60 (1H, d, *J* = 15.8 Hz, H-2). HREIMS Found: *m/z* 306.2554 (M^+). Calcd for $C_{20}H_{34}O_2$: M, 306.2557.

4-*O*-Methylsartol A (2). Oil, $[\alpha]_D^{27}$ +16.7° (*c* 0.87, MeOH); IR (film) 3387 and 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85 and 0.87 (3H each, d, *J* = 6.8 Hz, Me-16 and Me-17), 1.24 (3H, s, Me-17), ca. 1.34 (1H, overlapped, H-14*exo*), ca. 1.38 (1H, overlapped, H-5*endo*), ca. 1.55 (2H, overlapped, H-1 and H-15), 1.62 (3H, br s, Me-19), ca. 1.63 (2H, overlapped, H-14*endo*, H-15), 1.67 (3H, br s, Me-20), ca. 1.97 (2H, overlapped, H-5*exo* and H-13β), ca. 2.11 (2H, H-6α and H-13α), 2.14 (1H, dd, *J* = 9.0 and 12.6 Hz, H-9β), ca. 2.45 (2H, overlapped, H-6β and H-9α), 3.12 (3H, s, OMe), 4.53 (1H, m, H-10), 5.20 (1H, dd, *J* = 8.8 and 15.8 Hz, H-7), 5.20 (1H, overlapped, H-7), and 5.34 (1H, d, *J* = 15.8 Hz, H-3); ^1H NMR (C_6D_6) δ = 0.85 and 0.88 (3H each, d, *J* = 7.0 Hz, Me-16 and Me-17), ca. 1.20 (1H, overlapped, H-14*exo*), 1.20 (3H, s, Me-18), ca. 1.35 (1H, m, H-5*endo*), ca. 1.49 (2H, overlapped, H-14*endo* and H-15), 1.58 (3H, br s, Me-20), 1.61 (3H, br s, Me-19), ca. 1.67 (1H, m, Me-1), ca. 2.02 (2H, overlapped, H-13), ca. 2.05 (1H, overlapped, H-6α), ca. 2.07 (1H, overlapped, H-5*exo*), 2.20 (1H, dd, *J* = 8.3 and 12.8 Hz, H-9β), 2.37 (1H, dd, *J* = 4.6 and 12.8 Hz, H-9α), 2.70 (1H, dt, *J* = 9.2 and 13.6 Hz, H-6β), 3.12 (3H, OMe), 4.45 (1H, dt, *J* = 4.6 and 8.3 Hz, H-10), 5.13 (1H, *J* = 9.5 and 15.8 Hz, H-2), 5.22 (1H, m, H-7), 5.29 (1H, br d, *J* = 8.3 Hz, H-11), and 5.52 (1H, d, *J* = 15.8 Hz, H-2). HREIMS Found: *m/z* 320.2762 (M^+). Calcd for $C_{21}H_{36}O_2$: M, 320.2715.

Sartone A (3). Oil, $[\alpha]_D^{27}$ +134.6° (*c* 0.69, MeOH); UV λ_{max}^{MeOH} 246 nm (ε 7300); IR (film) 3410, 1680, and 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.80 and 0.83 (3H each, d, *J* = 6.6 Hz, Me-16 and Me-17), 1.40 (3H, s, Me-18), ca. 1.45 (1H, m, H-14), ca. 1.50 (1H, overlapped, H-15), ca. 1.55 (2H, overlapped, H-1 and H-5), 1.65 (3H, br s, Me-19), 1.69 (1H, overlapped, H-14), ca. 2.03 (2H, overlapped, H-5 and H-13β), 2.09 (3H, br s, Me-20), ca. 2.17 (2H, overlapped, H-6α and H-13α), 2.57 (1H, dt, *J* = 9.5 and 15.4 Hz, H-6β), 2.87 (1H, br d, *J* = 13.6 Hz, H-9α), 3.04 (1H, d, *J* = 13.6 Hz, H-9β), 5.27 (1H, dd, *J* = 9.5 and 15.8 Hz, H-2), 5.38 (1H, br dd, *J* = 4.8 and 9.9 Hz, H-7), 5.63 (1H, d, *J* = 15.8, H-3), and 6.23 (1H, br s, H-11). HREIMS Found: *m/z* 304.2380 (M^+). Calcd for $C_{20}H_{32}O_2$: M, 304.2400.

Sartone B (4). Oil, $[\alpha]_D^{27}$ −2.7° (*c* 0.22, MeOH); UV λ_{max}^{MeOH} 245 nm (ε 5380); IR (film) 3740, 1680, and 1618 cm^{-}; ^1H NMR ($CDCl_3$) δ = 0.82 and 0.85 (3H each, d, *J* = 6.6 Hz, Me-16 and Me-17), 1.31 (3H, s, Me-18), ca. 1.41 (1H, m, H-14*endo*), ca. 1.52 (1H, overlapped, H-5), ca. 1.62 (3H, overlapped, H-5, H-15, and H-14*exo*), 1.65 (1H, overlapped, H-1), 1.71 (3H, br s, Me-19), 1.84 (1H, overlapped H-5), 1.84 (1H, d, *J* = 1.1 Hz, Me-20), ca. 1.85 (1H, overlapped, H-6), ca. 2.09 (1H, m, H-6α), 2.31 (1H, br dt, H-6β), 2.56 (2H, t, *J* = 6.8 Hz, H-13), 2.96 (1H, br d, *J* = 13.9 Hz, H-9α, 3.08 (1H, br d, *J* = 13.9 Hz, H-9β), 5.14 (1H, br t, *J* = 6.1 Hz, H-7), 5.29 (1H, dd, *J* = 8.1 and 15.9 Hz, H-2), 5.46 (1H, d, *J* = 15.9 Hz, H-3), and 5.99 (1H, br s, H-11). HREIMS Found: *m/z* 286.2280 (M^+-H_2O). Calcd for $C_{20}H_{30}O$: M^+-H_2O, 286.2295.

Sartone C (5). Oil, $[\alpha]_D^{27}$ −8.2° (*c* 0.085, MeOH), UV λ_{max}^{MeOH} 239 nm (ε 5100); IR (film) 3445, 1692, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.83 and 0.87 (3H each, d, *J* = 6.6 Hz, Me-16 and Me-17), 1.24 (1H, m, H-14*endo*), 1.30 (3H, s, Me-18), 1.52 (1H, overlapped, H-5), 1.55 (1H, overlapped, H-15), 1.58 (1H, overlapped, H-1), 1.73 (3H, br d, *J* = 1.1 Hz, Me-19), 1.77 (1H, m, H-14*exo*), 1.83 (3H, d, *J* = 1.1 Hz, Me-20), 2.44 (1H, m, H-13α), 1.85 (1H, overlapped, H-6β), 2.75 (1H, ddd, *J* = 7.3, 10.6, and 14.5. Hz, H-13β), 3.02 (1H, d, *J* = 18.7 Hz, H-9α), 3.34 (1H, br d, *J* = 18.3 Hz, H-9β), 5.18 (1H, dd, *J* = 8.6 and 16.1 Hz, H-3), 5.44 (1H, br t, *J* = 7.7 Hz, H-7), 5.52 (1H, d, *J* = 16.1 Hz, H-2), and 6.01 (1H, br s, H-11). HREIMS Found: *m/z* 286.2298 (M^+-H_2O). Calcd for $C_{20}H_{30}O$: M−H_2O, 286.2297.

Sartone D (6). Oil, $[\alpha]_D^{27}$ +39.6° (*c* 0.13, MeOH); UV λ_{max}^{MeOH} 272 nm (ε 7500); IR (film) 3420, 1667, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.83 and 0.87 (3H each, d, *J* = 6.8 Hz, Me-16 and Me-17), ca. 1.21 (1H, overlapped, H-14*endo*), 1.25 (3H, s, Me-18), ca. 1.55 (1H, overlapped, H-15), ca. 1.57 (1H, overlapped, H-1), ca. 1.73 (1H, m, H-14*exo*), 1.81 (3H, d, *J* = 1.1 Hz, Me-19), 1.89 (3H, d, *J* = 1.5 Hz, Me-20), ca. 2.46 (1H, m, H-13β), ca. 2.56 (2H, overlapped, H-7×2 and H-13α), 5.20 (1H, dd, *J* = 9.0 and 15.8 Hz, H-2), 5.35 (1H, d, *J* = 15.8 Hz, H-3), and 6.00 (2H, br s, H-9 and H-11). HREIMS Found: *m/z* 286.2293 (M^+-H_2O). Calcd for $C_{20}H_{30}O$: M−H_2O, 286.2295.

4-*O*-Methylsartone A (7). Oil, $[\alpha]_D^{27}$ −6.4° (*c* 0.09, MeOH); UV λ_{max}^{MeOH} 245 nm (ε 5600); IR (film) 1684 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85 and 0.88 (3H each, d, *J* = 6.6 Hz, Me-16

and Me-17), 1.21 (3H, s, Me-18), 1.41 (1H, overlapped H-14*endo*), ca. 1.49 (1H, ddd, J = 1.5, 9.2, and 13.8 Hz, H-5), ca. 1.63 (2H, overlapped, H-1 and H-15), 1.68 (1H, overlapped, H-14*exo*), 1.70 (3H, br s, Me-19), 1.84 (3H, br s, Me-20), ca. 1.90 (1H, ddd, J = 1.5, 9.7, and 13.8 Hz, H-5), ca. 2.05 (1H, m, H-6β), 2.33 (1H, br dt, J = 8.1 and 16.5 Hz, H-6α), 2.54 (1H, m, H-13β), 2.61 (1H, br d, J = 6.6 and 15.0 Hz, H-13α), 2.93 (1H, br d, J = 13.6 Hz, H-9α), 3.07 (1H, br d, J = 13.6 Hz, H-9β), 3.12 (3H, s, OMe), 5.13 (1H, br t, J = 6.0 Hz, H-7), 5.21 (1H, dd, J = 8.6 and 16.1 Hz, H-2), 5.31 (1H, d, J = 16.1 Hz, H-3), and 6.00 (1H, br s, H-11). HREIMS Found: *m/z* 318.2577 (M^+). Calcd for $C_{21}H_{34}O_2$: M, 318.2559.

Epoxysartone A (8). Oil, $[\alpha]_D^{27}$ +30.4° (*c* 0.49, MeOH); UV λ_{max}^{MeOH} 206 nm (ε 3840); IR (film) 3459, 1717 and 1659 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.84 and 0.90 (3H each, d, J = 6.6 Hz, Me-16 and Me-17), 1.20 (3H, s, Me-20), 1.35 (3H, s, Me-18), ca. 1.39 (3H, overlapped, H-13β and H-14), 1.54 (1H, hept, J = 6.6 Hz, H-15), 1.61 (3H, br s, Me-19), ca. 1.66 (1H, m, H-5*endo*), 1.81 (1H, ddd, J = 2.7, 7.6, and 10.4 Hz, H-1), ca. 1.94 (1H, overlapped, H-13α), ca. 2.00 (1H, overlapped, H-5*exo*), 2.28 (2H, m, H-6), 3.01 (1H, br d, J = 14.3 Hz, H-9α), 3.19 (1H, br d, J = 14.3 Hz, H-9β), 3.67 (1H, s, H-11), 5.47 (1H, dd, J = 8.1 and 15.9 Hz, H-2), 5.52 (1H, br t, J = 5.9 Hz, H-7), and 5.73 (1H, d, J = 15.9 Hz, H-3). HREIMS Found: *m/z* 320.2367 (M^+). Calcd for $C_{20}H_{32}O_3$: M, 320.2352.

6β-Hydroxysarcotol Acetate (9). Oil, $[\alpha]_D^{27}$ −80.0° (*c* 0.06, MeOH); UV λ_{max}^{MeOH} 206 nm (ε 2740); IR (film) 3378, 1742, 1703, 1663, and 1242 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.80 and 0.82 (3H each, d, J = 6.6 Hz, Me-16 and Me-17), ca. 0.89 (1H, m, H-14*endo*), 1.22 (3H, s, Me-20), ca. 1.34 (1H, overlapped, H-13α), 1.36 (3H, s, Me-18), ca. 1.42 (1H, m, H-14*exo*), ca. 1.51 (1H, overlapped, H-15), ca. 1.81 (1H, m, H-13β), 1.83 (3H, br s, Me-19), 2.02 (3H, s, OAc), 2.03 (3H, dd, J = 2.4 and 13.7 Hz, H-5α), 2.13 (1H, dd, J = 8.6 and 13.7 Hz, H-5β), 2.71 (1H, br d, J = 12.8 Hz, H-9β), 3.69 (1H, d, J = 12.8 Hz, H-9α), 4.09 and 4.21 (1H each, d, J = 11.0 Hz, H-11), 4.76 (1H, dt, J = 2.4 and 8.6 Hz, H-6), 5.25 (1H, dd, J = 8.6 and 16.1 Hz, H-2), 5.25 (1H, overlapped, H-7), and 5.47 (1H, d, J = 16.1 Hz, H-3); ^1H NMR (C_6D_6) δ = 0.73 and 0.78 (3H each, d, J = 6.6 Hz, Me-16 and Me-17), ca. 0.88 (1H, overlapped, H-14*endo*), 0.91 (3H, s, Me-20), ca. 1.03 (1H, m, H-13α), 1.12 (3H, s, Me-18), ca. 1.20 (1H, m, H-14*exo*), ca. 1.33 (2H, overlapped, H-1 and H-15), 1.58 (1H, ddd, J = 3.3, 13.6, and 13.6 Hz, H-13β), 1.64 (3H, s, OCOMe), 1.76 (1H, br s, Me-19), 1.94 (1H, dd, J = 2.3 and 13.9 Hz, H-5α), 2.05 (1H, dd, J = 8.4 and 13.9 Hz), 2.40 (1H, br d, J = 12.5 Hz, H-9β), 3.27 (1H, d, J = 12.5 Hz, H-9α), 4.30 and 4.38 (1H each, d, J = 11.0 Hz, H-11), 4.64 (1H, dt, J = 2.2 and 8.4 Hz, H-6), 5.08 (1H, br d, J = 8.4 Hz, H-7), 5.09 (1H, dd, J = 8.2 Hz, H-2), and 5.33 (1H, d, J = 16.1 Hz, H-3). HREIMS Found: *m/z* 380.2526 (M^+). Calcd for $C_{22}H_{36}O_5$: M, 380.2561.

4-*O*-Methylsarcotol (10). Oil, $[\alpha]_D^{27}$ −67.8° (*c* 0.15, MeOH); UV λ_{max}^{MeOH} 207 nm (ε 2800); IR (film) 3447, 1696, and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85 and 0.89 (3H each, d, J = 6.6 Hz, Me-16 and Me-17), ca. 1.04 (1H, m, H-14*endo*), 1.13 (3H, s, Me-20), 1.21 (3H, s, Me-18), ca. 1.33 (1H, m, H-13α), ca. 1.43 (1H, m, H-14*exo*), ca. 1.54 (1H, overlapped, H-15), 1.61 (3H, br s, Me-19), ca. 1.63 (1H, overlapped, H-5), ca. 1.73 (1H, m, H-13β), 1.87 (1H, ddd, J = 3.3, 8.8, and 8.9 Hz, H-5), ca. 2.16 (2H, overlapped, H-6), 2.64 (1H, br d, J = 11.7 Hz, H-9α), 3.15 (3H, s, OMe), 3.53 (1H, d, J = 11.7 Hz, H-9β), 3.53 and 3.63 (1H each, br d, J = 11.4 Hz, H-11), 5.14 (1H, dd, J = 9.7 and 15.8 Hz, H-2), 5.30 (1H, overlapped, H-7), and 5.33 (1H, d, J = 15.8 Hz). HREIMS Found: *m/z* 336.2662 (M^+). Calcd for $C_{21}H_{36}O_3$: M, 336.2663.

Acetylation of 1. Sartol A (**1**) (6.0 mg) was treated with Ac_2O in pyridine to give a monoacetate (**14**) (4.3 mg), oil, $[\alpha]_D^{27}$ +7.2° (*c* 0.18, MeOH); IR (film) 3447, 1732, and 1669 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.82 and 0.85 (3H each, d, J = 6.6 Hz, Me-16 and Me-17), ca. 1.30 (1H, m, H-14*exo*), 1.36 (3H, s, Me-18), ca. 1.52 (2H, overlapped, H-14*endo* and H-15), 1.59 (1H, overlapped, H-1), 1.61 (3H, br s, Me-20), 1.67 (3H, br s, Me-19), ca. 1.94 (1H, m, H-5*exo*), ca. 2.02 (1H, overlapped, H-13β), 2.03 (3H, s, OCOMe), ca. 2.11 (2H, overlapped, H-6α and H-13α), 2.25 (1H, dd, J = 8.8 and 13.2 Hz, H-9β), ca. 2.41 (2H, overlapped, H-6β and H-9α), 5.13 (1H, br d, J = 8.8 Hz, H-11), 5.25 (1H, dd, J = 9.0 and 15.8 Hz, H-2), ca. 5.25 (1H, overlapped, H-7), 5.65 (1H, d, J = 15.8 Hz, H-3), and 5.68 (1H, dt, J = 4.8 and 8.8 Hz, H-10); ^{13}C NMR ($CDCl_3$) δ = 14.9 (C-20), 16.2 (C-19), 19.5 and 20.4 (C-16 and C-17), 21.4 (OCOMe), 22.3 (C-6), 27.2 (C-14), 28.2 (C-18), 33.0 (C-15), 36.6 (C-13), 42.7 (C-5), 44.9 (C-9), 46.2 (C-1), 68.8 (C-10), 72.5 (C-4), 123.9 (C-11), 129.3 (C-8), 129.4 (C-2), 131.7 (C-7), 137.7 (C-3), 140.7 (C-12), and 170.4 (OCOMe); ^1H NMR (C_6D_6) δ = 0.81 and 0.84 (3H each, d, J = 6.8 Hz, Me-16 and Me-17), ca. 1.10 (1H, m, H-14*exo*), 1.24 (3H, s, Me-18), ca. 1.35 (1H, overlapped, H-15), ca. 1.38 (1H, overlapped, H-5*endo*), ca. 1.45 (1H, overlapped, H-14*endo*), ca. 1.56 (1H, m, H-1), 1.63 (3H, br s, Me-19 or Me-20), 1.65 (3H, br s, Me-20 or Me-19), 1.73 (3H, s, OCOMe), 1.84 (1H, ddd, J = 1.8, 9.5, and 13.9 Hz, H-5*exo*), ca.2.00 (2H, m, H-13β), 2.04 (1H, overlapped, H-6α), 2.34 (1H, dd, J = 8.2 and 13.2 Hz, H-9β), ca. 2.45 (2H, overlapped, H-6β and H-9α), 5.13 (1H, dd, J = 9.2 and 15.5 Hz, H-2), 5.20 (1H, br t, J = 7.1 Hz, H-7), 5.29 (1H, d, J = 8.2 Hz, H-11), 5.71 (1H, d, J = 15.5 Hz, H-3), and 5.95 (1H, dt, J = 5.0 and 8.2 Hz, H-10). EIMS: *m/z* 288 ($M^+ - H_2O - AcOH$).

***p*-Bromobenzoylation of 1.** A mixture of **1** (9.1 mg), *p*-BrBzCl (9 mg), DMAP (catalytic amount), and pyridine (2 ml) was stirred at r.t. for 24 h. After the usual work-up, the crude residue was subjected to silica-gel chromatography with AcOEt–hexane (3 : 7) and then purified by a C_{18} reversed phase column with CH_3OH–H_2O (9 : 1) to afford the mono-*p*-bromobenzoate **15** (4.9 mg); oil, UV λ_{max}^{MeOH} 244 nm (ε 18300); CD (MeOH) 216 nm ($\Delta\varepsilon$ +2.08) and 245 nm ($\Delta\varepsilon$ −9.97); IR (film) 3472, 1715, 1667, 1591, and 847 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.83 and 0.86 (3H each, d, J = 6.8 Hz, Me-16 and Me-17), 1.31 (1H, m, H-14*exo*), 1.38 (3H, s, Me-18), 1.56 (2H, overlapped, H-14 and H-15), ca. 1.66 (1H, overlapped, H-1), 1.66 (3H, br s, Me-20), 1.75 (3H, br s, Me-19), 1.96 (1H, ddd, J = 1.8, 9.5, and 13.9 Hz, H-5*exo*), 2.04 (1H, dd, J = 3.8 and 13.0 Hz, H-13β), ca. 2.16 (2H, overlapped, H-6α and H-13α), ca. 2.41 (1H, overlapped, H-6β), 2.41 (1H, dd, J = 7.3 and 13.6 Hz, H-9β), 2.49 (1H, dd, J = 4.6 and 13.6 Hz, H-9α), 5.22 (1H, partially overlapped, d, J < 7.3 Hz, H-11), 5.27 (1H, dd, J = 8.8 and 15.8 Hz, H-2), 5.32 (H, br t, J = 7.8 Hz, H-7), 5.71 (1H, d, J = 15.8 Hz, H-3), 5.93 (1H, m, H-10), 7.56 and 7.89 (2H each, d, J = 8.6 Hz, ArH). EIMS Found: *m/z* 470 ($M^+ - H_2O$).

Reduction of 3. A solution of **3** (9.4 mg) in MeOH (2 ml) was treated with $NaBH_4$ (10 mg). After the usual work-up, the mixture was subjected to chromatography on silica-gel with acetone–CH_2Cl_2 (1 : 24) and on an ODS with CH_3OH–H_2O (3 : 2) to give **16** (2.4 mg) and **17** (7.1 mg). The spectral data of **16** were identical with those of **1**. **16**: Oil, $[\alpha]_D^{27}$ +13.4° (*c* 0.13, MeOH); EIMS *m/z* 288 $(M - H_2O)^+$. **17**: Oil, $[\alpha]_D^{27}$ −64.3° (*c* 0.38, MeOH); UV λ_{max}^{MeOH} 208 nm (ε 5360); IR (film) 3355 and 1667 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.82 and 0.85 (3H each, d, J = 6.8 Hz, Me-16 and Me-17), 1.32 (3H, s, Me-18), ca. 1.37 (1H, m, H-14*exo*), ca. 1.54 (1H, m, H-5*endo*), ca. 1.64 (1H, overlapped, H-14*endo*), 1.64 (3H, d, J = 1.1 Hz, Me-20), 1.68 (3H, br s, Me-19), 1.78 (1H, m, H-1), 1.85 (1H, ddd, J = 1.8, 8.7, and 13.7 Hz, H-5*exo*), ca. 1.98 (1H, overlapped, H-13β), ca. 2.03 (1H, overlapped, H-6α), 2.09 (1H, m, H-13α), 2.22 (1H, dd, J = 8.8 and 14.3 Hz, H-9β), 2.34

(1H, br d, $J = 14.3$ Hz, H-9α), 2.40 (1H, br dt, $J = 8.7$ and 16.5 Hz, H-6β), 4.58 (1H, dt, $J = 2.9$ and 8.8 Hz, H-10), 5.06 (1H, br t, $J = 6.2$ Hz, H-7), 5.24 (1H, dd, $J = 1.1$ and 8.8 H, H-11), 5.32 (1H, dd, $J = 8.4$ and 15.8 Hz, H-2), and 5.57 (1H, d, $J = 15.8$ Hz, H-2); ^{13}C NMR ($CDCl_3$) $\delta = 16.6$ and 17.9 (C-19 and C-20), 19.4 and 20.1 (C-16 and C-17), 22.7 (C-6), 28.1 (C-18), 28.3 (C-14), 33.5 (C-15), 38.7 (C-13), 42.9 (C-5), 46.7 (C-9), 47.0 (C-1), 67.1 (C-10), 72.7 (C-4), 127.8, 128.7, and 130.0 (C-2, C-7, and C-11), 130.3 (C-8), 136.9 (C-3), and 138.2 (C-12). EIMS: m/z 288 ($M^+ - H_2O$).

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References

1) New cembranoids from *Sarcophyton* sp. collected at Bonotsu, Kagoshima prefecture. 3. Part 2. Ref. 4.

2) J. C. Coll, *Chem. Rev.*, **92**, 613 (1992).

3) D. J. Faulkner, *Nat. Prod. Rep.*, **13**, 75 (1996), and references therein.

4) T. Iwagawa, S. Nakamura, T. Masuda, H. Okamura, M. Nakatani, and M. Shiro, *Tetrahedron*, **51**, 5291 (1995).

5) P. A. Couperus, A. D. H. Clague, and J. P. C. M. van-Dongen, *Org. Magn. Reson.*, **8**, 426 (1976).

6) N. C. Gonnella, K. Nakanishi, V. S. Martin, and K. B. Scharpless, *J. Am. Chem. Soc.*, **104**, 3775 (1982).