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NEW CLADIELLANE DITERPENES FROM THE SOFT CORAL *CLADIELLA AUSTRALIS* OF THE ANDAMAN AND NICOBAR ISLANDS

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ABSTRACT.—Five new cladiellane diterpenes, (1*R**,2*R**,3*R**,6*S**,7*S**,9*R**,10*R**,14*R**)-3-acetoxy-6-(3-methylbutanoyloxy)cladiell-11(17)-en-7-ol [**2**], (1*R**,2*R**,3*R**,6*S**,7*S* *,9*R**,10*R**,14*R**)-3-butanoyloxycladiell-11(17)-en-6,7-diol [**3**], (1*R**,2*R**,3*R**,6*S**,9*R**10*R**,14*R**)-3-acetoxycladiell-7(16),11(17)-dien-6-ol [**4**], 3-acetoxycladiell-11(17)-en-6-one [**5**], and its stereoisomer [**6**], have been isolated from the soft coral *Cladiella australis* collected on the coasts of the Andaman and Nicobar Islands of the Indian Ocean. In addition, sclerophytins C [**7**] and E [**8**], reported earlier from *Sclerophytum capitalis*, were also isolated. The structures of these metabolites were elucidated by interpretation of spectral data.

Soft corals have a reputation as prolific producers of terpenoid metabolites, mostly diterpenes (1–4). Diterpenes possessing the tricyclic skeleton of cladiellin [**1**] (5) are comparatively rare in soft corals and only a few have been reported (6–13). *Cladiella australis* from the Andaman and Nicobar Islands, Indian Ocean, was examined and we report in this paper the isolation and structural elucidation of five new cladiellanes.

RESULTS AND DISCUSSION

The EtOH extract of *C. australis* Macfadyen, 1936 (Alcyoniidae) was digested in EtOAc and the soluble portion was chromatographed on Si gel using solvents with increasing polarity from petroleum ether to EtOAc to obtain several fractions, which on exhaustive rechromatography yielded nine pure compounds. Two compounds were identified as sclerophytins -C [**7**] and -E [**8**], by comparison of spectral data with literature values for metabolites of *Sclerophytum capitalis* (7–8).[2] Two metabolites, sclerophytin-C 6-ethyl ether [**9**], and sclerophytin-E 6-ethyl ether [**10**] were characterized and considered artifacts because EtOH had been used in the extraction process. The structures of five compounds, (1*R**,2*R**,3*R**,6*S**,7*S**,9*R**,10*R**,14*R**)-3-acetoxy-6-(3-methylbutanoyloxy)cladiell-11(17)-en-7-ol [**2**], (1*R**,2*R**,3*R**,6*S**,7*S**,9*R**,10*R**,14*R**)-3-butanoyloxycladiell-11(17)-en-6,7-diol [**3**], (1*R**,2*R**,3*R**,6*S**,9*R**,10*R**,14*R**)-3-acetoxycladiell-7(16),11(17)-dien-6-ol [**4**],3-acetoxycladiell-11(17)-en-6-one [**5**], and its stereoisomer [**6**] were elucidated by interpretation of high-resolution nmr spectral data as detailed below.

Compound **2** was obtained as an oil and the hrfab mass spectrum established its molecular formula as $C_{27}H_{44}O_6$ (*m/z* 447.3110, [MH^+-H_2O]). The ^1H and ^{13}C-nmr and mass spectral data indicated the following moieties: an acetoxyl [δ_H 2.11 (3H, s); δ_C 169.6, 22.9; eims, *m/z* 386 (M^+-H_2O-CH_3CO_2H)], a 3-methylbutanoyloxy [δ_H 2.14 (2H, m), 2.12 (1H, m), 0.96 (6H, d, J=6.1 Hz); δ_C 173.9, 43.8, 25.8, 22.4 (2 carbons); eims, *m/z* 344 ($M^+-H_2O-C_4H_9COOH$), an exomethylene [δ_H 4.68 (1H, br s), 4.62

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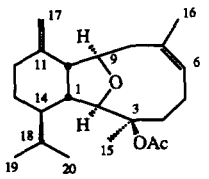
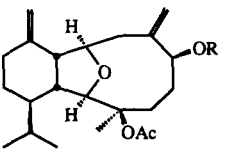
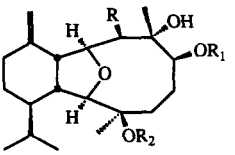
[2]We thank Dr. Alam for providing authentic ^1H- and ^{13}C-nmr spectra, but have noticed some typographical errors in the data reported by Sharma and Alam (7).



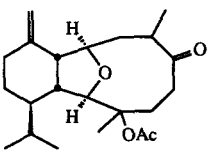
1



4 R=H
12 R=Ac



2 R=H, R_1=$COCH_2CHMe_2$, R_2=Ac
3 R=R_1=H, R_2=$COCH_2CH_2CH_3$
7 R=OH, R_1=H, R_2=Ac
8 R=R_1=H, R_2=Ac
9 R=OH, R_1=Et, R_2=Ac
10 R=H, R_1=Et, R_2=Ac
11 R=H, R_1=Ac, R_2=$COCH_2CH_2CH_3$



5,6 stereoisomers

(1H, br s); δ_C 147.6, 109.5], an isopropyl [δ_H 0.78 (3H, d, J=6.5 Hz), 0.97 (3H, d, J=6.5 Hz), 1.71 (1H, m); δ_C 29.0, 21.9, 15.4] and two tertiary methyls [δ_H 1.20 (3H, s), 1.39 (3H, s); δ_C 23.8, 22.9]. There were three methine protons [δ_H 3.63 (1H, br s), 4.17 (1H, ddd, J=12.0, 7.5, and 4.5 Hz), 5.62 (1H, d, J=5.6 Hz); δ_C 92.1, 84.5, 78.1] and two quarternary carbons bearing oxygen (δ_C 86.7, 75.5). Comparison of the above data with those of sclerophytin-E [**8**] revealed that a 3-methylbutanoyloxy group was present on C-6 in **2**, replacing the C-6 hydroxyl in **8**. This change was supported by the chemical shifts of H-6 at δ 4.58 (d, J=6.4 Hz) and C-6 at δ 79.7 in **8** which were found at δ 5.62 (d, J=5.6 Hz) and δ 84.5, respectively, in **2**. The other possible alternative, i.e., an acetoxyl at C-6 and a 3-methylbutanoyloxy moiety at C-3 in **2**, was ruled out by the correlation observed between the 3-methylbutanoyloxy carbonyl (δ 173.9) and H-6 (δ 5.62) in the HMBC (heteronuclear multiple-bond connectivity) spectrum of **2** (14). Assignments of other proton and carbon chemical shifts were supported by ^{1}H-^{1}H COSY and HMBC spectra. The stereochemistry at various chiral centers in **2** was assigned to be that of **8** by a careful scrutiny of ^{1}H- and ^{13}C-nmr data of both the compounds. Compound **2** may be semi-systematically (9) named (1*R**,2*R**,3*R**,6*S**,7*S**,9*R**, 10*R**,14*R**)-3-acetoxy-6-(3-methylbutanoyloxy)cladiell-11(17)-en-7-ol. This is the first report of a 3-methylbutanoate ester of a diterpene from a soft coral, though some gorgonian diterpenes possess this functionality (15).

Compound **3** was obtained as an oil of molecular formula $C_{24}H_{40}O_5$. Comparison of its ^{1}H-nmr (Table 1) and ^{13}C-nmr (Table 2) data with those of sclerophytin-E [**8**] suggested the replacement of a C-3 acetoxyl in **8** by an *n*-butanoyloxy group [δ 0.99, (3H, t, J=6.8 Hz), 1.68 (2H, sext, J=6.8 Hz), 2.34 (2H, t, J=6.8 Hz); δ_C 13.7, 18.3, 37.3, 172.5] in **3**. The presence of the butanoyloxy moiety is also supported by a fragment ion at *m/z* 320 (32%, $M^+-C_3H_7COOH$) in the mass spectrum of **3**. The location of the butanoyloxy moiety at C-6 in **3** was discounted because (a) the chemical shifts of H-6 in **3** [δ 4.58 (d, J=6.4 Hz)] and **8** [δ 4.58 (d, J=6.4 Hz)] are identical, (b) the C-6 hydroxyl in **3** could be acetylated with Ac_2O/pyridine to yield **11**, in which the corresponding acetoxymethine proton resonated at δ 5.32, and (c) the carbon chemical

TABLE 1. ^{1}H-Nmr Data ($CDCl_3$, 500 MHz) of Compounds **2–10**.[a]

Proton	Compound								
	2[b]	**3**[b]	**4**[b]	**5**[b]	**6**	**7**[b]	**8**[c]	**9**[c]	**10**[b]
1	2.19 (m)	2.20 (m)	2.25 (m)	2.20 (m)	2.28 (m)	2.28 (m)	2.21 (m)	2.25 (m)	2.18 (m)
2	3.63 (br s)	3.58 (br s)	3.72 (br s)	3.59 (br s)	3.66 (br s)	3.60 (br s)	3.58 (br s)	3.58 (br s)	3.65 (br s)
4	2.61 (dd, 14, 8)	2.62 (dd, 11, 4)		2.73 (ddd, 14, 10, 4)	2.52 (m, 13, 11, 8)	2.52 (dd, 14, 9)	2.60 (m)	2.55 (m)	2.65 (dd, 14, 8)
	1.52 (m)	1.61 (m)		2.00 (m)	2.24 (m)	1.87 (m)			1.78 (m)
5	2.02 (m)	1.82 (m)	2.16 (m)	2.48 (m)	2.42 (m, 13, 11, 3)	1.64 (dd, 14, 9)			1.71 (m)
	1.46 (m)	1.42 (m)	1.72 (m)	1.84 (m)	2.18 (m)	1.43 (m)			1.60 (m)
6	5.62 (d, 6)	4.58 (d, 6)	4.39 (dd, 12, 4)			4.62 (d, 6)	4.58 (d, 6)	4.21 (d, 6)	4.20 (d, 7)
7				2.57 (m)	2.69 (m)				
8	2.08 (m)	1.91 (m)	2.77 (dd, 14, 3)	1.96 (m)	2.20 (m)	3.58 (d, 10)		3.50 (m)	1.82 (m)
	1.85 (m)	1.86 (m)	2.23 (m)	1.96 (m)	1.89 (m)				1.82 (m)
9	4.17 (m, 12, 7, 5)	4.14 (m)	4.13 (dd, 11, 3)	3.90 (m)	3.97 (m, 10, 5, 2)	3.89 (dd, 9, 6)	4.15 (m)	3.91 (m)	4.16 (m)
10	2.98 (t, 7)	2.98 (t, 7)	3.05 (dd, 11, 8)	3.08 (t, 8)	3.02 (dd, 10, 7)	3.29 (t, 7)	2.94 (t, 7)	3.27 (t, 5)	2.93 (t, 7)
12	2.27 (m)	2.27 (m)	2.27 (m)	2.26 (m)	2.28 (m)	2.31 (m)	2.28 (m)	2.28 (m)	2.27 (m)
	2.02 (m)	2.06 (m)	2.04 (m)	2.01 (m)	2.03 (m)	2.04 (m)	2.03 (m)	2.04 (m)	2.05 (m)
13	1.72 (m)	1.74 (m)	1.76 (m)	1.70 (m)	1.73 (m)	1.75 (m)			1.72 (m)
	1.00 (m)	1.03 (m)	1.04 (m)	1.00 (m)	1.02 (m)	1.00 (m)			1.03 (m)
14	1.28 (m)	1.28 (m)	1.30 (m)	1.26 (m)	1.29 (m)	1.25 (m)			1.26 (m)
15	1.39 (s, 3H)	1.40 (s, 3H)	1.62 (s, 3H)	1.39 (s, 3H)	1.45 (s, 3H)	1.42 (s, 3H)	1.41 (s, 3H)	1.42 (s, 3H)	1.40 (s, 3H)
16	1.20 (s, 3H)	1.16 (s, 3H)	5.44 (br s)	1.06 (s, 3H)	1.07 (d, 3H)	1.28 (s, 3H)	1.17 (s, 3H)	1.25 (s, 3H)	1.14 (s, 3H)
			5.12 (br s)						
17	4.68 (br s)	4.69 (br s)	4.81 (br s)	4.72 (br s)	4.77 (br s)	4.87 (br s)	4.70 (br s)	4.89 (br s)	4.68 (br s)
	4.62 (br s)	4.65 (br s)	4.68 (br s)	4.68 (br s)	4.67 (br s)	4.78 (br s)	4.64 (br s)	4.78 (br s)	4.62 (br s)
18	1.72 (m)	1.74 (m)	1.90 (m)	1.70 (m)	1.73 (m)	1.74 (m)	1.74 (m)	1.71 (m)	1.71 (m)
19	0.78 (d, 3H, 7)	0.79 (d, 3H, 7)	0.76 (d, 3H, 7)	0.76 (d, 3H, 7)	0.75 (d, 3H, 7)	0.81 (d, 3H, 7)	0.79 (d, 3H, 7)	0.78 (d, 3H, 7)	0.78 (d, 3H, 7
20	0.97 (d, 3H, 7)	0.97 (d, 3H, 7)	0.97 (d, 3H, 7)	0.93 (d, 3H, 7)	0.95 (d, 3H, 7)	0.98 (d, 3H, 7)	0.97 (d, 3H, 7)	0.96 (d, 3H, 7)	0.96 (d, 3H, 7)
R_1	2.22 (d, 2H, 7)							3.62 (m)	3.61 (m)
	2.12 (m)							3.40 (m)	3.37 (m)
	0.96 (d, 6H, 6)							1.19 (t, 3H, 7)	1.19 (t, 3H, 7)
R_2	2.11 (s, 3H)	2.34 (t, 2H, 7)	1.93 (s, 3H)	2.19 (s, 3H)	2.12 (s, 3H)	2.12 (s, 3H)	2.10 (s, 3H)	2.09 (s, 3H)	2.11 (s, 3H)
		1.68 (m)							
		0.99 (t, 3H, 7)							

[a]Assignments based on ^{1}H-^{1}H COSY and HMBC data.
[b]Assignments based on ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY data.
[c]Assignments by comparison with literature data in Alam *et al.* (8).

TABLE 2. ^{13}C-Nmr Data for Compounds **2–10**.[a]

Carbon	Compound								
	2[b]	**3**[b]	**4**[b]	**5**[b]	**6**	**7**[b]	**8**[c]	**9**[c]	**10**[c]
1	45.8	45.4	47.2	46.7	43.0	45.3	45.5	45.5	45.3
2	92.1	92.0	90.9	91.3	91.4	91.8	91.9	90.4	92.1
3	86.7	86.4	84.8	84.7	84.7	86.3	86.7	87.0	86.4
4	35.7	36.1	35.6	33.1	38.1	35.1	36.0	36.2	36.6
5	29.3	30.4	28.4	30.1	32.6	29.6	30.6	29.6	27.5
6	84.5	80.1	72.2	214.8	214.5	77.4	79.8	74.6	88.3
7	75.5	76.8	150.8	48.3	45.8	79.9	76.8	78.9	75.9
8	45.8	45.8	38.9	42.3	38.3	79.5	46.0	79.8	44.9
9	78.1	78.2	80.1	80.2	77.7	81.2	78.4	80.7	78.5
10	53.8	53.6	44.1	53.7	50.9	53.1	53.6	53.1	53.9
11	147.6	147.6	146.2	146.8	146.3	149.0	147.7	148.6	147.8
12	31.5	31.4	31.7	31.4	31.4	31.7	31.5	31.3	31.5
13	24.6	24.6	25.2	24.6	24.9	24.9	24.7	24.7	24.6
14	43.8	43.9	44.6	43.0	40.8	43.9	44.0	43.5	44.0
15	22.9	23.2	22.0	22.4	22.4	23.0	23.2	23.0	23.1
16	23.8	22.6	116.5	16.9	15.4	17.8	22.3	17.5	23.8
17	109.5	109.3	111.3	110.0	110.7	110.2	109.4	109.2	109.5
18	29.0	29.0	27.4	28.7	28.0	29.1	29.1	29.1	29.0
19.....	15.4	15.6	15.5	15.2	15.3	16.1	15.8	16.2	15.5
20	21.9	21.9	21.9	21.7	21.8	22.0	22.0	21.6	21.9
R_1	173.9							64.2	64.6
	43.8							15.6	15.5
	25.8								
	22.4								
	(2 C)								
R_2	169.6	172.5	169.8	169.7	169.9	169.5	169.6	169.2	169.9
	22.9	37.3	22.5	22.2	22.6	22.5	22.7	22.5	22.3
		18.3							
		13.7							

[a]Spectra recorded in $CDCl_3$; **2–7** and **10** at 125 MHz and **8–9** at 22.5 MHz.
[b]Assignments confirmed by DEPT, ^{1}H-^{13}C COSY, or HMBC experiments.
[c]Assignments made by comparison with literature data in Alam *et al.* (8).

shifts of C-1 through C-20 of **3** compare well with those of **8**, which contains an ester group at C-3. The stereochemistry of the eight chiral carbons in **3** is assigned to be that of **8** by comparison of their ^{1}H- and ^{13}C-nmr data (Tables 1 and 2). Thus, **3** could be described as (1*R**,2*R**,3*R**,6*S**,7*S**,9*R**,10*R**,14*R**)-3-butanoyloxycladiell-11(17)-en-6,7-diol [**3**].

Compound **4** was obtained as an oil whose molecular formula, $C_{22}H_{34}O_4$, was ascertained by hrfab mass spectrometry (*m/z* 363.2535 [MH^+]). The ir spectrum exhibited bands due to hydroxyl (3450 cm^{-1}) and acetate (1730 cm^{-1}) groups. The ^{1}H- and ^{13}C-nmr spectral data, while revealing characteristic structural features of a cladiellane system, indicated an additional exocyclic double bond [δ_H 5.12 (1H, br s), 5.44 (1H, br s); δ_C 150.8, 116.5] besides the usual signals for $\Delta^{11(17)}$ [δ_H 4.81 (1H, br s), 4.68 (1H, br s); δ_C 146.2, 111.3]. The ^{1}H-^{1}H COSY spectrum showed coupling between the exocyclic methylene proton at δ 5.12 and H-8 (δ 2.77), which was in turn coupled to H-9 (δ 4.13). This sequence of couplings suggests that the new exocyclic double bond is at C-7. The ^{1}H-^{1}H COSY spectrum indicated coupling between the proton at δ 4.39 (H-6) and one of the methylene protons at δ 1.72 (H-5), which was in turn coupled to another methylene proton at δ 2.62 (H-4), suggesting the placement of the hydroxyl on

C-6. On the basis of the multiplicity of H-6, the hydroxyl is assumed to be β, as found in analogous compounds (7,8). Compound **4** formed a monoacetyl derivative on treatment with Ac_2O/pyridine at room temperature and the corresponding oxymethine proton shifted to δ 5.25 from 4.39. Further, the appearance of CH_3-15 at a rather deshielded position (δ 1.62) in the ^{1}H-nmr spectrum suggests the placement of the acetoxyl group [δ_H 1.93 (3H, s); δ_C 169.8, 22.5] on C-3. The stereochemistry of **4** at varous chiral centers is assigned to be the same as that of **8** by a careful examination of ^{1}H- and ^{13}C-nmr data (Tables 1 and 2). Thus, compound **4** could be described as (1*R**,2*R**,3*R**,6*S**,9*R**,10*R**,14*R**)-3-acetoxycladiell-7(16),11(17)-dien-6-ol.

Compound **5** was obtained as an oil of molecular formula $C_{22}H_{34}O_5$. The ir spectrum showed no hydroxyl bands but showed strong absorption bands for carbonyl groups (1720 and 1690 cm^{-1}). The ^{1}H- and ^{13}C-nmr spectral data indicated the presence of an acetate [δ_H 2.19 (3H, s); δ_C 22.2, 169.7] and a ketone group [δ_C 214.8], in addition to common structural features of a cladiellane which are supported by ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY data. The acetate is located on C-3, as found in the analogous compounds, by comparison of the spectral data. The ^{1}H-^{1}H COSY spectral data indicated that the methyl protons at δ 1.06 (CH_3-16) are coupled to a proton at δ 2.57 (H-7), which is further coupled to the proton at δ 1.96 (H-8), and that there is also coupling between H-8 (δ 1.96) and H-9 (δ 3.90). This chain of couplings supported the secondary nature of CH_3-16 and suggested the location of the keto group at C-6. The stereochemistry of **5** could not be determined completely and the compound may be described as 3-acetoxycladiell-11(17)-en-6-one [**5**].

Compound **6** was obtained as an oil of molecular formula $C_{22}H_{34}O_4$. The ^{1}H- and ^{13}C-nmr (Tables 1 and 2) and other analytical data indicated that **6** is a stereoisomer of **5** at one or more chiral centers. Initially, it was proposed that **5** and **6** were epimers at C-7, but on further examination, the possibility of isomerization at C-3 could not be eliminated. Thus ketone **6** must also be described as 3-acetoxycladiell-11(17)-en-6-one [**6**].

EXPERIMENTAL

COLLECTION, EXTRACTION AND PURIFICATION.—The soft coral *Cladiella australis* (dry wt ca. 3.2 kg) was collected in the intertidal rocky region of the Little Andaman coast (91°31′E, 10°30′N) in the Indian Ocean in December 1986. Voucher specimens are on deposit at the School of Chemistry, Andhra University, Visakhapatnam (MF-CBR-37) and at the Northern Territory Museum of Arts and Sciences, Australia (NTM C10961). The animals were cut into very thin slices and stored in EtOH at room temperature. The EtOH extract was concentrated under reduced pressure, digested in EtOAc, which , after drying over anhydrous $MgSO_4$ and removal of the solvent, yielded a dark greenish gum (58 g) that was chromatographed repeatedly on Si gel using solvent mixtures of increasing polarity from petroleum ether (bp 60–80°) through C_6H_6 to EtOAc. Exhaustive rechromatography of selected fractions from suitable solvent mixtures yielded pure samples of **3** and **6–9** and, after further separation on hplc using C_{18} reversed-phase [(MeOH-H_2O-CH_2Cl_2 (8:1:1)] and normal-phase [isooctane-Et_2O-CH_2Cl_2 (1:1:1)] columns, **2**, **4**, **5**, and **10** were also purified.

(1*R**,2*R**,3*R**,6*S**,7*S**,9*R**,10*R**,14*R**)-3-ACETOXY-6-(3-METHYLBUTANOYLOXY)-CLADIELL-11(17)-EN-7-OL [**2**].—Oil; ir ν max ($CHCl_3$) 3450, 2960, 1730, 1640, 1320, 1110, 920, 710 cm^{-1}; ^{1}H nmr ($CDCl_3$), see Table 1; ^{13}C nmr, ($CDCl_3$) see Table 2; eims *m/z* 446 (5) $[M-H_2O]^+$, 428 (8), 386 (16), 368 (18), 344 (24), 284 (36), 85 (36), 57 (4), 68 (40); hrfabms *m/z* 447.3110 $[MH-H_2O]^+$, $C_{27}H_{43}O_5$ requires 447.3123.

(1*R**,2*R**,3*R**,6*S**,7*S**,9*R**,10*R**,14*R**)-3-BUTANOYLOXYCLADIELL-11(17)-EN-6,7-DIOL [**3**].—Oil; $[\alpha]^{28}D$ +7.1° (*c*=0.7, $CHCl_3$); ir ν max ($CHCl_3$) 3450, 2950, 1740, 1640, 1448, 1360, 1108, 710 cm^{-1}; ^{1}H nmr ($CDCl_3$), see Table 1; ^{13}C nmr ($CDCl_3$), see Table 2; eims *m/z* 408 (2) [M^+], 390 (6), 320 (24), 302 (26), 274 (12), 71 (68), 43 (100); *anal.* found C 70.4, H 9.9; $C_{24}H_{40}O_5$ requires C 70.7, H 9.8%.

Acetylation of **3** was accomplished by treatment with Ac_2O (300 μl) and pyridine (300 μl) at room temperature overnight. Si gel cc of the reaction mixture after the usual workup yielded the monoacetate **11** (6 mg) as colorless oil. Ir ν max ($CHCl_3$) 3450, 2980, 1735, 1648, 890 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.80 (3H, d, *J*=7.0 Hz), 0.98 (3H, d, *J*=7.0 Hz), 1.05 (3H, t, *J*=7.0 Hz), 1.24 (3H, s), 1.42 (3H, s), 2.01 (3H, s),

2.34 (2H, t, J=6.5 Hz), 2.89 (1H, t, J=7.1 Hz), 3.60 (1H, br s), 4.18 (1H, m), 4.71 (1H, br s), 4.81 (1H, br s), 5.32 (1H, d, J=6.5 Hz).

(1*R**,2*R**,3*R**,6*S**,9*R**,10*R**,14*R**)-3-ACETOXYCLADIELL-7(16),11(17)-DIEN-6-OL [**4**].—Colorless oil; $[\alpha]^{28}D$ −58.8° (c=0.17, $CHCl_3$); ir ν max ($CHCl_3$) 3450, 1730, 1640, 1370, 1090, 1065, 990 cm^{-1}; ^1H nmr ($CDCl_3$), see Table 1; ^{13}C nmr ($CDCl_3$), see Table 2; eims *m/z* 344 (6) [M^+-H_2O], 302 (32), 284 (8), 242 (2), 176 (50), 147 (2), 132 (21), 91 (48), 70 (41), 48 (58), 43 (100); hrfabms *m/z* 363.2535 [MH^+], $C_{22}H_{34}O_4$ requires 362.2540.

Acetylation of **4** (9 mg) was performed by treatment with Ac_2O (300 μl) and pyridine (300 μl) at room temperature for about 5 h. The residue obtained after the usual workup was chromatographed on Si gel which gave pure monoacetate [**12**] as a colorless oil (7.5 mg). Ir ν max ($CHCl_3$) 2950, 1735, 1645, 1090, 1060, 900 cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.78 (3H, d, J=7.8 Hz), 0.92 (3H, d, J=7.8 Hz), 2.58 (3H, s), 2.01 (3H, s), 2.10 (3H, s), 3.10 (1H, t, J=8.5 Hz), 3.78 (1H, m), 4.20 (1H, m), 4.65 (1H, br s), 4.80 (1H, br s), 5.10 (1H, br s), 5.25 (1H, br m, $W_{1/2}$=10.0 Hz), 5.42 (1H, br s).

3-ACETOXYCLADIELL-11(17)-EN-6-ONE [**5**].—Oil; $[\alpha]^{28}D$ −8.5° (c=0.97, $CHCl_3$) ir ν max ($CHCl_3$) 2990, 1735, 1715, 1640, 1108, 1065, 900 cm^{-1}; ^1H nmr ($CDCl_3$), see Table 1; ^{13}C nmr ($CDCl_3$), see Table 2; *anal.* found, C 72.9, H 9.2, $C_{22}H_{34}O_4$ requires C 72.8, H 9.4%.

3-ACETOXYCLADIELL-11(17)-EN-6-ONE [**6**].—Oil; $[\alpha]^{28}D$ −8.5° (c=0.97, $CHCl_3$); ir ν max ($CHCl_3$) 2998, 1735, 1712, 1645, 1112, 880 cm^{-1}; ^1H nmr ($CDCl_3$), see Table 1; ^{13}C nmr ($CDCl_3$), see Table 2; *anal.* found, C 72.9, H 9.5, $C_{22}H_{34}O_4$ requires C 72.8, H 9.88%.

SCLEROPHYTIN-C 6-ETHYL ETHER [**9**].—Oil; $[\alpha]^{28}D$ −8.5° (c=0.48, $CHCl_3$); ir ν max ($CHCl_3$) 3550, 2960, 1730, 1640, 1112, 1025, 890 cm^{-1}; ^1H nmr ($CDCl_3$), see Table 1; ^{13}C nmr ($CDCl_3$), see Table 2; hrms *m/z* 424.2825, $C_{24}H_{40}O_6$ requires 424.2818.

SCLEROPHYTIN-E 6-ETHYL ETHER [**10**].—Oil; ir ν max ($CHCl_3$) 3550, 2940, 1725, 1640, 1110, 890 cm^{-1}; ^1H nmr ($CDCl_3$), see Table 1, ^{13}C nmr ($CDCl_3$), see Table 2; *anal.* found, C 70.4, H 9.98 $C_{24}H_{40}O_5$ requires C 70.5, H 9.8%.

SCLEROPHYTIN-C [**7**].—Colorless cubes; mp 94–95°; $[\alpha]^{28}D$ −16.1° (c=0.32, $CHCl_3$); ir ν max ($CHCl_3$) 3450, 2960, 1730, 1640, 1440, 1360, 1117, 1112, 710 cm^{-1}; ^1H nmr ($CDCl_3/CD_3OD$), see Table 1; ^{13}C nmr ($CDCl_3/CD_3OD$), see Table 2; cims *m/z* 379 (100) [MH^+-H_2O], 361 (20), 337 (17), 319 (18), 301 (5); eims *m/z* 318 (36) [$M^+-H_2O-AcOH$], 300 (12), 219 (32), 117 (62), 134 (60), 127 (74), 94 (80), 83 (100); *anal.* found, C 66.8, H 9.2, $C_{22}H_{36}O_6$ requires C 66.6, H 9.1%.

SCLEROPHYTIN-E [**8**].—Gummy oil; $[\alpha]^{28}D$ +10.4° (c=0.48, $CHCl_3$); ir ν max ($CHCl_3$) 3550, 2950, 1730, 1645, 1110, 1070, 1020, 890 cm^{-1}; ^1H nmr ($CDCl_3$), see Table 1; ^{13}C nmr ($CDCl_3$), see Table 2; eims *m/z* 364 (9) [M^+-H_2O], 348 (30), 320 (10), 290 (25), 275 (35), 224 (22), 190 (25), 68 (50), 57 (100); *anal.* found, C 69.5, H 9.7, $C_{22}H_{36}O_5$ requires C 69.4, H 9.5%.

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