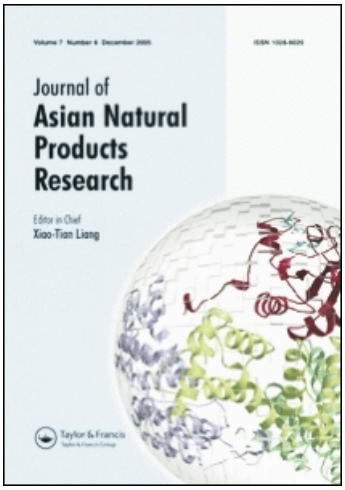


Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Alcyonacean Metabolites VII - Chemical Constituents of *Lobophytum denticulatum* and *Lobophytum strictum* of the Indian Ocean

Mulabagal Vanisree[a]; Gottumukkala V. Subbaraju; Ch. Bheemasankara Rao[b]
[a] Department of Chemistry, Sri Venkateswara University, Tirupati, India [b] School of Chemistry, Andhra University, Visakhapatnam, India

To cite this Article Vanisree, Mulabagal , Subbaraju, Gottumukkala V. and Rao, Ch. Bheemasankara(2000) 'Alcyonacean Metabolites VII - Chemical Constituents of *Lobophytum denticulatum* and *Lobophytum strictum* of the Indian Ocean', Journal of Asian Natural Products Research, 2: 2, 87 — 95
To link to this Article: DOI: 10.1080/10286020008039897
URL: http://dx.doi.org/10.1080/10286020008039897

JANPR, Vol. 2, pp. 87-95
Reprints available directly from the publisher
Photocopying permitted by license only

ALCYONACEAN METABOLITES VII – CHEMICAL CONSTITUENTS OF *LOBOPHYTUM DENTICULATUM* AND *LOBOPHYTUM STRICTUM* OF THE INDIAN OCEAN

MULABAGAL VANISREE[a], GOTTUMUKKALA V. SUBBARAJU[a,*] and CH. BHEEMASANKARA RAO[b]

[a]*Department of Chemistry, Sri Venkateswara University, Tirupati – 517 502, India;* [b]*School of Chemistry, Andhra University, Visakhapatnam – 530 003, India*

(Received 26 April 1999; Revised 28 May 1999; In final form 21 June 1999)

A rare cembranoid diterpene, (7E,11E,1R,2S,3R,4R,14S)-14-acetoxy-3,4-epoxycembra-7,11,15-triene-17,2-olide (**1**), was isolated from *Lobophytum denticulatum* and a new polyhydroxysterol, 7α-hydroxyandamansterol (**9**) has been identified as peracetyl derivative from *Lobophytum strictum*. Several known polyhydroxysterols have also been isolated from these organisms. **1** exhibited moderate antibacterial activity.

Keywords: *Lobophytum denticulatum*; *Lobophytum strictum*; Cembranoid; Polyhydroxysterols; 7α-Hydroxyandamansterol

INTRODUCTION

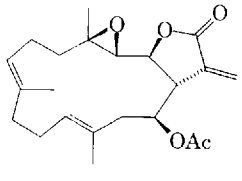
Alcyonaceans (Soft corals, Phylum: Coelenterata) of the genus *Lobophytum* are rich store house of terpenoids and polyhydroxysteroids [1]. About twenty species of the genus have been chemically examined so far [2]. The terpenoid and steroid content of Alcyonaceans, particularly, *Lobophytum* species, vary considerably based on the geographical location and season of collection [3–7]. Earlier chemical investigations on *Lobophytum strictum*

* Corresponding author. Tel.: 91-8574-29757. Fax: 91-8574-27499.

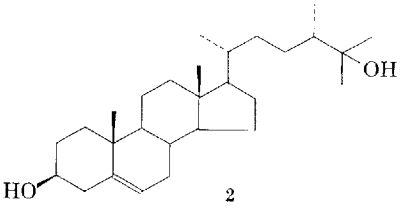
revealed the presence of simple amines [4], terpenoids [6,7] and polyhydroxysterols [3,5]. Denticulatolide and its 7-epimer were obtained from *Lobophytum denticulatum* [8,9]. In continuation of our studies on Alcyonaceans [6,10–14], we have examined *Lobophytum denticulatum* collected from the Mandapam coast and *Lobophytum strictum* of the Car Nicobar Islands of the Indian Ocean and the results are reported in the present paper.

RESULTS AND DISCUSSION

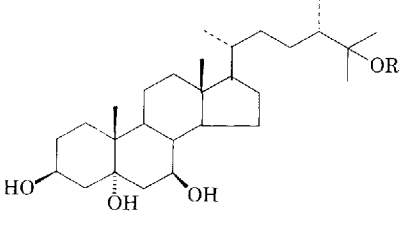
The residue from the ethyl acetate soluble portion of the methanolic extracts of the soft coral, *Lobophytum denticulatum*, on extensive chromatography over silica gel gave compound **A** (**1**), (24S)-ergost-5-en-3β,25-diol (**2**) [15], (24S)-ergostane-3β,5α,6β,25-tetraol 25-monoacetate (**3**) [10], batyl alcohol (**4**) [16] in addition to a mixture of polyhydroxysterols.



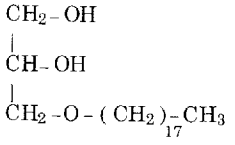
1



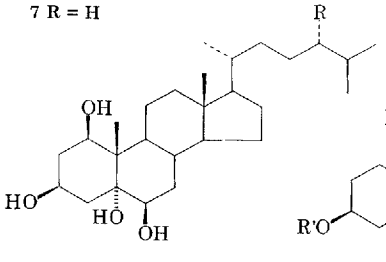
2



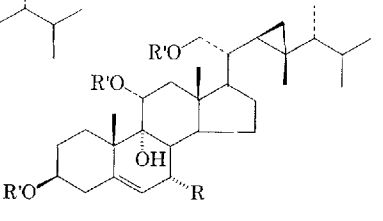
3 R = Ac
7 R = H



4



5 R = CH_3
6 R = H



8 R = H ; R' = Ac
9 R = OH ; R' = H
10 R = OAc ; R' = Ac

Compound **A** (**1**) was obtained as pale yellow needles from methanol, m.p. 145–146°C, $[\alpha]_D$ −254 (C 0.35, $CHCl_3$) and analysed for $C_{22}H_{30}O_5$ (*m/z* 314, $M^+ - AcOH$). Its IR spectrum contained bands at 1769 and 1661 cm^{-1}, suggestive of an α,β-unsaturated-γ-lactone moiety. Its ^1H NMR spectrum showed signals corresponding to two olefinic methyls (δ 1.65 and 1.68, 3H each, s), a geminally oxygenated methyl (δ 1.30, 3H, s) and an α,β-unsaturated-γ-lactone unit (δ 4.12, 1H, dd, $J = 8.8, 2.6$ Hz; 3.42, 1H, m; 6.50, 1H, d, $J = 1.9$ Hz; and 5.80, 1H, d, $J = 1.9$ Hz) characteristic of cembranoid type diterpene [17]. ^{13}C NMR data of compound A indicated the presence of four olefinic carbons (δ 123.6, 136.2, 129.1, 130.4), an epoxide (δ 65.5 and 59.9), an α,β-unsaturated-γ-lactone unit (δ 80.6, 133.5, 125.4 and 169.6) and an acetate functionality (δ 170.6, 20.9). A careful literature survey on cembranoid diterpenes revealed that the physical and spectral data of compound A are in good agreement with those recorded for (7E,11E,1R,2S,3R,4R, 14S)-14-acetoxy-3,4-epoxycembra-7,11,15-triene-17,2-olide (**1**), isolated earlier from *Lobophytum cristigalli* [17] and *Sinularia conferta* [18].

1 was reported to be cytotoxic and a potent inhibitor of Farnasyl Protein Transferase (FPT) [19]. During our bioactivity studies on **1**, we have found that **1** exhibited moderate antibacterial activity [20] against Gram positive (*Bacillus pumilis*, *Bacillus subtilis* and *Staphylococcus epidermis*) and Gram negative (*Escherichia coli* and *Pseudomonas aerogenosa*) bacteria at a concentration of 1 mg/ml. MIC of **1** against *Staphylococcus epidermis* was found to be 50 µg/ml.

The polyhydroxysterol fraction was found to be homogeneous over silica gel thin layers. However, its ^1H NMR spectrum showed more secondary methyl signals than expected for a cholestane or ergostane type steroid. Duplicated carbon resonances found in ^{13}C NMR spectrum also suggested that it could be a mixture of polyhydroxysterols. A careful scrutiny of ^1H and ^{13}C NMR data revealed that this fraction contained two polyhydroxysterols having common ($1\beta,3\beta,5\alpha,6\beta$-tetrahydroxysteroid) nucleus and differed only in their side chains. Further analysis of the NMR data showed that the fraction is a mixture (2 : 1) of ergostane-$1\beta,3\beta,5\alpha,6\beta$-tetraol (**5**) and cholestane-$1\beta,3\beta,5\alpha,6\beta$-tetraol (**6**). Such an inseparable mixture of **5** and **6** was also isolated by Kobayashi *et al.* [21] from *Sarcophyton glaucum*. Raju *et al.* [12] reported that such a mixture obtained from *Lobophytum hirsutam* could not be separated even after acetylation. Since the NMR spectral data for such a mixture have not been interpreted completely so far, we have interpreted the NMR data and details are noted in the experimental section.

The residue from the ethyl acetate solubles of the methanolic extracts of *Lobophytum strictum* on repeated chromatography over silica gel gave (24S)-ergostane-3β,5α,6β,25-tetraol 25-monoacetate (**3**) [10], (24S)-ergostane-3β,5α,6β,25-tetraol (**7**) [10] and a polyhydroxysterol fraction.

The polyhydroxysterol fraction was found to contain two polyhydroxysterols and its ^{1}H NMR revealed that these sterols contained no acetoxyl groups. Therefore, the sterol fraction was acetylated with Py/Ac_2O

TABLE I NMR data of gorgost-5-en-3β,7α,9α,11α,21-pentaol 3,7,11,21-tetraacetate (**10**) (500 MHz for ^{1}H and 125 MHz for ^{13}C in $CDCl_3$)

Position	δ_H*	δ_C*	*HMBC*
1		30.4	
2	1.60–1.66 (2H, m)	27.8	
3	4.67 (1H, m)	72.2	
4	2.42–2.46 (1H, m) and 2.31–2.34 (1H, m)	38.6	
5		144.7	
6	5.67 (1H, dd, J = 5.3, 2.0 Hz)	119.8	C-4, C-7, C-10
7	5.11 (1H, brs, $W\frac{1}{2}$ = 11 Hz)	68.2	C-5, C-6, C-9 C-14, C-7-OAc
8	1.97 (1H, m)	44.5	
9		75.5	
10		44.0	
11	5.34 (1H, dd, J = 11.4, 4.8 Hz)	72.2	C-13, C-11-OAc
12	1.70–1.85 (2H, m)	42.5	
13		40.6	
14		38.1	
15		23.5	
16		27.5	
17		51.5	
18	0.80 (3H, s)	12.3	C-12, C-17
19	1.15 (3H, s)	21.0	C-1, C-5, C-9, C-10
20	1.16–1.21 (1H, m)	38.9	
21	4.08 (1H, dd, J = 11.2, 3.0 Hz) 4.17 (1H, dd, J = 11.2, 2.9 Hz)	67.9	C-17, C-20, C-22, C-21-OAc
22	0.37 (1H, td, J = 9.4, 5.8 Hz)	26.8	C-24
23		25.7	
24	0.29 (1H, dq, J = 8.7, 6.8 Hz)	50.6	C-23, C-25, C-30
25		32.1	
26	0.94 (3H, d, J = 7.0 Hz)	22.1	C-24, C-25
27	0.86 (3H, d, J = 6.6 Hz)	21.3	C-24, C-25
28	0.94 (3H, d, J = 7.0 Hz)	15.3	C-23, C-25
29	0.53 (1H, dd, J = 9.1, 4.6 Hz and 0.01 (1H, t, J = 6.3 Hz)	20.8	C-20, C-22, C-24, C-30
30	0.90 (3H, s)	14.1	C-22, C-23, C-24 C-29
OAc	2.06 (3H, s)	169.9, 21.8	C-11
OAc	2.11 (3H, s)	169.6, 21.4	C-7
2 × OAc	2.03 (6H, s)	171.1, 170.4, 21.0, 21.3	C-3, C-21

*Assignments are supported by ^{1}H–^{1}H COSY and HMQC data.

and chromatographic isolation of the acetyl derivatives gave andamansterol triacetate (**8**) [22] and compound **B**.

Compound **B** (**10**) was obtained as a semisolid and analysed for $C_{38}H_{58}O_9$ (FABMS: *m/z* 621, $M^+ - AcOH + Na$). Its ^1H NMR (Table I) spectrum showed signals corresponding to three tertiary methyls (δ 0.80, 0.90 and 1.15, 3H each, s) and three secondary methyls (δ 0.94, 6H, d, $J = 7.0$ Hz and 0.86, 3H, d, $J = 6.6$ Hz) and signals at δ 0.53 (1H, dd, $J = 9.1, 4.6$ Hz), 0.01 (1H, t, $J = 6.3$ Hz), 0.37 (1H, td, $J = 9.4, 5.8$ Hz) and 0.29 (1H, dq, $J = 8.7, 6.8$ Hz) suggestive of a cyclopropane moiety.

The ^1H NMR also exhibited signals corresponding to three acetoxymethines [δ 4.67 (1H, m), 5.34 (1H, dd, $J = 11.4, 4.8$ Hz) and 5.11 (1H, m)], an acetoxymethylene [δ 4.08 (1H, dd, $J = 11.2, 3.0$ Hz) and 4.17 (1H, dd, $J = 11.2, 2.9$ Hz)] and an olefinic methine [δ 5.67 (1H, dd, $J = 5.3, 2.0$ Hz)]. A careful comparison of the above spectral data with those of **8** revealed that compound **B** contained an additional acetoxyl group.

The ^{13}C NMR spectral data (Table I) of compound **B** supported the presence of four acetoxyl groups [δ 171.1, 170.4, 169.9, 169.6, 21.0, 21.3, 21.4 and 21.8] and two olefinic carbons [δ 144.7 and 119.8].

Vicinal coupling of olefinic proton (H-6) with the acetoxymethine proton (H-7), observed in ^1H–^1H COSY spectrum of compound **B**, led to the placement of the additional acetoxyl at C-7. The position of the acetoxyl at C-7 received further support from the HMBC data (Table I) in which H-7 showed connectivity to C-5, C-6, C-9, C-14 and C-7 OAc. The orientation of the acetoxyl group was deduced as 7α based on the multiplicity of H-7 (δ 5.11, 1H, brs, $W\frac{1}{2} = 11$ Hz) [23].

Thus compound **B** was deduced as gorgost-5-en-3β,7α,9α,11α,21-pentaol 3,7,11,21-tetracetate (**10**) and the original sterol as gorgost-5-en-3β,7α,9α,11α,21-pentaol (7α-hydroxyandamansterol, **9**).

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined on a Mel-Temp apparatus and are uncorrected. UV spectra were recorded on a Shimadzu UV 240 spectrometer, IR spectra on a Perkin-Elmer 781 spectrometer, ^1H and ^{13}C NMR and 2D NMR spectra were recorded on a GE-500 or 300 MHz NMR spectrometer, mass spectra on a VG micromass 70-70H spectrometer and optical rotations were measured on an Autopol III automatic polarimeter. Separation and

purifications were performed by column chromatography over Acme silica gel (Finer than 200 mesh or 100–200 mesh).

Collection of the Soft Coral

Specimens of the soft coral *Lobophytum denticulatum* were collected from Mandapam (9°16′N, 79°12′E) coast during March 1995 and *Lobophytum strictum* from Car Nicobar Islands of the Indian Ocean during April 1991. The specimens were authenticated as *Lobophytum denticulatum* Tixier-Durivault, 1957 by Dr. V. Jayasree, National Institute of Oceanography, Goa and *Lobophytum strictum* Tixier-Durivault, 1957 by Dr. Phil Alderslade, National Territory Museum of Arts and Sciences, Darwin, Australia. Voucher specimens are on deposit at NIO, Goa; NTM, Darwin, Australia and at the Departments of Chemistry, Sri Venkateswara University, Tirupati and Andhra University, Visakhapatnam, India.

Extraction and Isolation

Specimens of the soft corals were cut into thin slices and soaked in ethanol (95%) at the site of collection. After a month, the ethanol solution was decanted and the material was reextracted six times more with methanol; solvent was removed under reduced pressure and the combined residue was repeatedly partitioned with ethyl acetate. Removal of the solvent from the ethyl acetate extract of *Lobophytum denticulatum* gave dark coloured gummy residue (22 g) whereas, the ethyl acetate extract of *Lobophytum strictum* yielded green residue (35 g).

Ethyl acetate extracts of *Lobophytum denticulatum* (22 g) and *Lobophytum strictum* (35 g) were chromatographed, independently, over silica gel column using solvents of increasing polarity from n-hexane through ethyl acetate. Rechromatography of selected fractions of *Lobophytum denticulatum* over silica gel column yielded **1** (80 mg), **2** (10 mg), **3** (90 mg), **4** (200 mg) and a mixture of **5** and **6** (30 mg); whereas, the chromatography of selected fractions of *Lobophytum strictum* over silica gel column resulted in the isolation of **3** (60 mg), **7** (110 mg) and a polyhydroxysterol fraction which on acetylation followed by chromatography over silica gel column gave **8** (3 mg) and **10** (2 mg).

(7E,11E,1R,2S,3R,4R,14S)-14-Acetoxy-3,4-epoxycembra-7,11,15-triene-17,2-olide (**1**) Pale yellow needles from methanol, 80 mg, mp. 145–46°C (Ref. [17] m.p. 146°C), $[\alpha]_D^{25}$ −254 (C 0.35, $CHCl_3$); UV (MeOH)

λ_{max} 226 nm; IR (KBr) ν_{max} 1769, 1731 and 1661 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (1H, m, H_a-5), 1.30 (3H, s, H-18), 1.65 (3H, s, H-19), 1.68 (3H, s, H-20), 1.95 (1H, m, H_a-9), 2.00 (3H, s, acetoxylmethyl), 2.10 (1H, m, H_b-5), 2.11 (1H, m, H_b-9), 2.05–2.35 (4H, m, H-6 and H-10), 2.38 (1H, dd, $J = 14.4, 2.3$ Hz, H_a-13), 2.24 (1H, m, H_b-13), 2.73 (1H, d, $J = 9.0$ Hz, H-3), 3.42 (1H, m, H-1), 4.12 (1H, dd, $J = 8.8, 2.6$ Hz, H-2), 4.96 (1H, brd, $J =$ 7.8 Hz, H-7), 5.11 (1H, dt, $J = 11.2, 2.8$ Hz, H-14), 5.18 (1H, brt, $J = 7.7$ Hz, H-11); 5.80 (1H, d, $J = 1.9$ Hz, H_a-16); 6.50 (1H, d, $J = 1.9$ Hz, H_b-16); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 41.6 (C-1), 80.6 (C-2), 65.5 (C-3), 59.9 (C-4), 37.2 (C-5), 24.3 (C-6), 123.6 (C-7), 136.2 (C-8), 39.6 (C-9), 24.7 (C-10), 129.1 (C-11), 130.4 (C-12), 39.6 (C-13), 72.8 (C-14), 133.5 (C-15), 125.4 (C-16), 169.6 (C-17), 16.7 (C-18), 15.6 (C-19), 17.0 (C-20), 170.6, 20.9 (acetyl); EIMS *m/z* [M^+ – AcOH] 314(8), 147(42), 119(73), 109(98), 81(100), 69(68), 55(48).

(24S)-Ergost-5-en-3β,25-diol (**2**) Colourless needles from hexane–EtOAc (9 : 1), 20 mg, m.p. 193–94°C (Ref. [15] m.p. 192–94°C), $[\alpha]_D^{25}$ −50.9 (C 0.1, $CHCl_3$); IR (KBr) ν_{max} 3330, 2966, 1464, 1062 and 951 cm^{-1}. EIMS *m/z* $[M]^+$ 416(19), [$M^+ - H_2O$] 398(100), [$M^+ - H_2O - CH_3$] 383(38), [$M^+ - 2H_2O$] 380(13), 314(19), 273(40), 255(27), 145(15), 59(48).

(24S)-Ergostane-3β,5α,6β,25-tetrol 25-monoacetate (**3**) Colourless solid from hexane–EtOAc (9 : 1), 90 mg, m.p. 236–37°C (Ref. [10] m.p. 235–38°C), $[\alpha]_D^{25}$ −19.6 (C 1.5, MeOH); IR (KBr) ν_{max} 3394, 1725, and 1254 cm^{-1}; EIMS *m/z* [M^+ – AcOH] 432(23), [M^+ – AcOH – H_2O] 414(71), 381(31), 348(9), 305(48), 247(54), 229(40), 161(25), 123(43), 95(73), 69(100).

Batyl alcohol (**4**) Amorphus powder from methanol, 200 mg m.p. 70–72° (Ref. [16] m.p. 69–71°C); IR (KBr) ν_{max} 3292, 2919, 1471, 1119, 1062 and 718 cm^{-1}. EIMS *m/z*: [$M^+ - CH_2OH$] 313(4), 283(28), 253(22), 125(14), 97(38), 71(77), 57(100).

(24S)-Ergostane-1β,3β,5α,6β-tetraol (**5**) *and cholestane-1β,3β,5α,6β-tetraol* (**6**) Colourless solid from hexane–EtOAc (8 : 2), 30 mg, IR (KBr) ν_{max} 3382, 1376, 947 cm^{-1}; ^1H NMR (d_5-pyridine, 400 MHz): δ 0.78 (3H, s, 18-Me), 0.80 (6H, d, $J = 6.4$ Hz, 26-Me and 28-Me of ergostane), 0.86 (3H, d, $J = 6.6$ Hz, 27-Me of ergostane), 0.85 (6H, d, $J = 6.8$ Hz, 26-Me and 27-Me of cholestane), 0.94 (3H, d, $J = 6.4$ Hz, 21-Me), 1.93 (3H, s, 19-Me), 3.10 (1H, brt, $J = 12.1$ Hz, H-4β), 4.20 (1H, brs, H-6α), 4.90–4.94 (2H, m, H-1α and H-3α), 5.53 (1H, d, $J = 6.6$ Hz, 1β-OH), 5.40 (1H, s, 5α-OH), 6.12 (1H, d, $J = 5.1$ Hz, 3β-OH), 6.24 (1H, d, $J = 4.2$ Hz, 6β-OH); ^{13}C NMR (d_5-pyridine, 100 MHz); chemical shifts of the nucleus of **5** and **6**: δ 73.8 (C-1), 44.1 (C-2), 65.4 (C-3), 43.2 (C-4), 76.9 (C-5), 77.1 (C-6), 35.7 (C-7), 31.7 (C-8), 47.1 (C-9), 44.9 (C-10), 25.0 (C-11), 41.4 (C-12), 42.6 (C-13),

56.7 (C-14), 24.9 (C-15), 28.5 (C-16), 56.8 (C-17), 12.5 (C-18), 10.7 (C-19). Chemical shifts of the side chain of **5**: 34.0 (C-20), 19.0 (C-21), 36.6 (C-22), 31.0 (C-23), 39.3 (C-24), 31.9 (C-25), 17.7 (C-26), 20.7 (C-27), 15.7 (C-28); Chemical shifts of the side chain of **6**: 36.2 (C-20), 18.9 (C-21), 36.5 (C-22), 24.2 (C-23), 39.7 (C-24), 28.0 (C-25), 22.7 (C-26), 22.9 (C-27). Mass spectral (EIMS) fragmentation of **5**: *m/z* [$M^+ - H_2O$] 432(3), [$M^+ - 2H_2O$] 414(9); **6**: [$M^+ - 2H_2O$] 400(2), [$M^+ - 3H_2O$] 382(4).

(24S)-Ergostane-3β,5α,6β,25-tetraol (**7**) Colourless solid from hexane–EtOAc (7:3), 110 mg, m.p. 256–58° (Ref. [10] m.p. 255–58°C) $[\alpha]_D^{25}$ −20 (C 0.3, MeOH); IR (KBr) ν_{max} 3310, 1457 and 1382 cm^{-1}; ^{1}H NMR (d_5-pyridine, 300 MHz): δ 0.72 (3H, s, H-18), 1.03 (3H, d, J = 7.2 Hz, H-21), 1.11 (3H, d, J = 7.2 Hz, H-28) 1.62 (3H, s, H-19), 1.35 (6H, s, H-26 and 27), 2.89 (1H, brt, J = 11.5 Hz, H-4β), 4.11 (1H, brs, H-6α), 4.70–5.20 (1H, m, H-3α); ^{13}C NMR (d_5-pyridine, 22.5 MHz) δ 32.4 (C-1), 33.3 (C-2), 67.4 (C-3), 42.8 (C-4), 75.9 (C-5), 76.3 (C-6), 35.5 (C-7), 31.2 (C-8), 45.9 (C-9), 39.1 (C-10), 21.8 (C-11), 40.7 (C-12), 43.1 (C-13), 56.5 (C-14), 24.6 (C-15), 28.5 (C-16), 56.5 (C-17), 12.4 (C-18), 17.2 (C-19), 35.7 (C-20), 19.3 (C-21), 36.8 (C-22), 28.5 (C-23), 46.0 (C-24), 72.3 (C-25), 26.6 (C-26), 28.0 (C-27), 15.4 (C-28); EIMS *m/z* [M^+] 450(11), [$M^+ - H_2O$] 432(12), 413(24), 350(12), 322(26), 286(11), 150(18), 69(100), 55(94).

Andamansterol triacetate (Gorgost-5-en-3β,9α,11α,21-tetraol 3,11,21-triacetate) (**8**) Semi solid, 3 mg; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.00 (1H, t, J = 5.0, H-29), 0.23–0.40 (2H, m, H-22 and 24), 0.53 (1H, dd, J = 9.0, 4.5 Hz, H-29), 0.78 (3H, s, H-18), 0.85 (3H, d, J = 6.6 Hz, H-28), 0.89 (3H, s, H-30), 0.94 (6H, d, J = 6.6 Hz, H-26 and H-27), 1.18 (3H, s, H-19), 2.02, 2.03, 2.04 (each 3H, s, 3 × OAc), 4.07 and 4.15 (each 1H, dd, J = 10.8, 3.0 Hz, H-21), 4.58 (1H, m, H-3α), 5.38 (1H, dd, J = 11.4, 5.1 Hz, H-11β), 5.49 (1H, brs, H-6); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.4 (C-1), 27.9 (C-2), 72.8 (C-3), 38.7 (C-4), 137.4 (C-5), 122.6 (C-6), 26.9 (C-7), 34.8 (C-8), 75.2 (C-9), 43.2 (C-10), 72.6 (C-11), 42.5 (C-12), 41.0 (C-13), 49.1 (C-14), 23.7 (C-15), 27.6 (C-16), 51.8 (C-17), 12.4 (C-18), 21.0 (C-19), 38.9 (C-20), 68.0 (C-21), 26.6 (C-22), 25.5 (C-23), 50.6 (C-24), 32.1 (C-25), 22.1 (C-26), 21.4 (C-27), 15.4 (C-28), 21.0 (C-29), 14.1 (C-30), 171.2, 170.5, 169.5, 21.4, 21.6 and 21.9 (3 × OAc); EIMS *m/z* [$M^+ - 2$AcOH] 480(15), [$M^+ - 3$AcOH] 420(14), 161(30), 133(15), 95(43), 81(31), 43(100).

Gorgst-5-en-3,7α,9α,11α,21-pentaol 3,7,11,21-tetraacetate (**10**) Semi-solid, 2 mg, ^{1}H NMR, ^{13}C NMR and HMBC spectral data see Table 1. FABMS *m/z* [$M^+ - $AcOH + Na] 621(10), [$M^+ - 2$AcOH + H] 539(13), [$M^+ - 3$AcOH + H] 479(14), [$M^+ - 4$AcOH + H] 419(7), 391(20), 257(14), 154(85), 137(100), 123(45).

Acknowledgements

The authors thank Dr. Phil Alderslade, Northern Territory Museum of Arts and Sciences, Darwin, Australia and Dr.V. Jayasree, National Institute of Oceanography, Goa for the identification of the soft corals; Prof. R.E. Moore, University of Hawaii, USA for some of the spectral data. This research was partly funded by the Department of Ocean Development, Ministry of Science and Technology, Government of India to CBR.

References

[1] D.J. Faulkner, *Nat. Prod. Rep.* 1998, 113–158 and earlier parts of the same series.
[2] A.S.R. Anjaneyulu and G.V. Rao, *Nat. Prod. Sci.* 1995, **1**, 70–85.
[3] P.S. Parameswaran, C.G. Naik, B. Das and S.Y. Kamat, *Indian J. Chem.* 1989, **28B**, 1089–1090.
[4] P.S. Parameswaran, C.G. Naik, B. Das and S.Y. Kamat, *Indian J. Chem.* 1991, **30B**, 449.
[5] M. Kobayashi, M.M. Krishna and V. Anjaneyulu, *J. Chem. Res(s).* 1993, 112–113.
[6] M.E. Rani, G.V. Subbaraju, B.L. Raju, C.B. Rao and D.V. Rao, *Indian J. Nat. Prod.* 1994, **10**, 3–8.
[7] A.S.R. Anjaneyulu, G.V. Rao and C.V.S. Prakash, *Indian J. Chem.* 1994, **33B**, 1165–1169.
[8] Y. Uchio, S. Eguchi, J. Kuramoto, M. Nakayama and T. Hase, *Tetrahedron Lett.* 1985, **26**, 4487–4490.
[9] Y. Uchio, S. Eguchi, Y. Fukazawa and M. Kodama, *Bull. Chem. Soc. Jpn.* 1992, **65**, 1182–1184.
[10] B.L. Raju, G.V. Subbaraju, M.C. Reddy, D.V. Rao, C.B. Rao and V.S. Raju, *J. Nat. Prod.* 1992, **55**, 904–911.
[11] B.L. Raju, G.V. Subbaraju, C.B. Rao and G. Trimurtulu, *J. Nat. Prod.* 1993, **56**, 961–966.
[12] B.L. Raju, G.V. Subbaraju and C.B. Rao, *Indian J. Chem.* 1995, **34B**, 221–226.
[13] B.L. Raju, G.V. Subbaraju, K.V. Reddy and C.B. Rao, *Indian J. Chem.* 1994, **33B**, 1033–1037.
[14] M. Vanisree, G.V. Subbaraju and C.B. Rao, *Indian J. Chem.* 1999, **38B**, 394–396.
[15] V. Anjaneyulu and B. Haribabu, *Indian J. Chem.* 1992, **31B**, 708–710.
[16] D.V. Rao, T.S. Rao and C.B. Rao, *Indian J. Chem.* 1990, **29B**, 683–684.
[17] B.F. Bowden, J.C. Coll, M.S.L. de Costa, M.F. Mackay, M. Mahendran, E.D. de silva and R.H. Willis, *Aust. J. Chem.* 1984, **37**, 545–552.
[18] A.S.R. Anjaneyulu and G.V. Rao, *Indian J. Chem.* 1996, **35B**, 826–831.
[19] S.J. Coval, R.W. Patton, J.M. Petrin, L. James, M.L. Ruthofsky, S.L. Lin, M. Patel, J.K. Reed, A.T. Mc Phail and W.R. Bishop, *Bioorg. Med. Chem. Lett.* 1996, **6**, 909–912.
[20] K.E. Cooper, Analytical Microbiology, In: Kavanagh, F. (Ed.), Academic press, New York, 1972, Vol. 2, p. 13.
[21] M. Kobayashi, T. Hayashi, F. Nakajima and H. Mitsuhashi, *Steroids* 1979, **34**, 285–293.
[22] M. Kobayashi, K. Kobayashi, K.V. Ramana, C.V.L. Rao, D.V. Rao and C.B. Rao, *J. Chem. Soc. Perkin Trans. 1*, 1991, 493–497.
[23] M. Kobayashi, F. Kanda, S.R. Damarla, D.V. Rao and C.B. Rao, *Chem. Pharm. Bull.* 1990, **38**, 2400–2403.