Marine Sterols. XXV.[1] Isolation of 23-Demethylgorgost-7-ene-3β,5α,6β-triol and (24*S*)-Ergostane-3β,5α,6β,7β,15β-pentol from Soft Corals of the Andaman and Nicobar Coasts

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Two new marine polyhydroxysterols, 23-demethylgorgost-7-ene-3β,5α,6β-triol (4a) and (24*S*)-ergostane-3β,5α,6β,7β,15β-pentol (6), were isolated from soft corals (Sinularia sp. and *Lobophytum crassum*, respectively) collected off the Andaman and Nicobar Islands, Indian Ocean. (24*S*)-Ergost-5-ene-3β,7α-diol (1), a known synthetic compound, was isolated from *Sclerophytum* sp. soft coral of the same region. The structures of 4a and 6 were derived by comparison of the ^{1}H- and ^{13}C-NMR data with those of reference compounds having the same partial structures. The previous assignments of C-1 and C-2 of 3β,5α,6β-trihydroxysterol were reversed.

Keywords (24*S*)-ergostane-3β,5α,6β,7β,15β-pentol; *Lobophytum crassum*; soft coral; 23-demethylgorgost-7-ene-3β,5α,6β-triol; *Sinularia* sp.; *Sclerophytum* sp.

Soft corals (Coelenterate) contain diverse mono- and polyhydroxysterols, most of which are derivatives of (24*S*)-ergostane-type C_{28} sterols.[2-4] The predominant component of the 3β-monohydroxysterol mixture of soft corals is, in most cases, (24*S*)-ergost-5-en-3β-ol (22,23-dihydrobrassicasterol). This is in contrast to sponges, which often contain the compound as the C-24 isomeric pair. Examination of three soft coral materials, collected off the coasts of the Andaman and Nicobar Islands, Indian Ocean, resulted in the isolation of six polyhydroxysterols, **1** and **2a** (from *Sclerophytum* sp.), **2a**, **3** and **4a** (*Sinularia* sp.), and **2a**, **5** and **6** (*Lobophytum crassum*), of which two (**4a** and **6**) are hitherto unknown compounds. The present paper describes the structure elucidation of **4a**, the first polyhydroxylated derivative of demethylgorgosterol (**7**) to be isolated from soft coral, and **6**, the first 15β-hydroxy derivative.

Compound **1** was a monounsaturated C_{28} diol. It immediately showed a deep green color on a thin-layer chromatography (TLC) plate, when sprayed with anisaldehyde–phosphomolybdic acid reagent,[5] suggesting it to be the 7-hydroxy derivative of the conventional 3β-hydroxy Δ^5 sterol. Comparison of the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra indicated

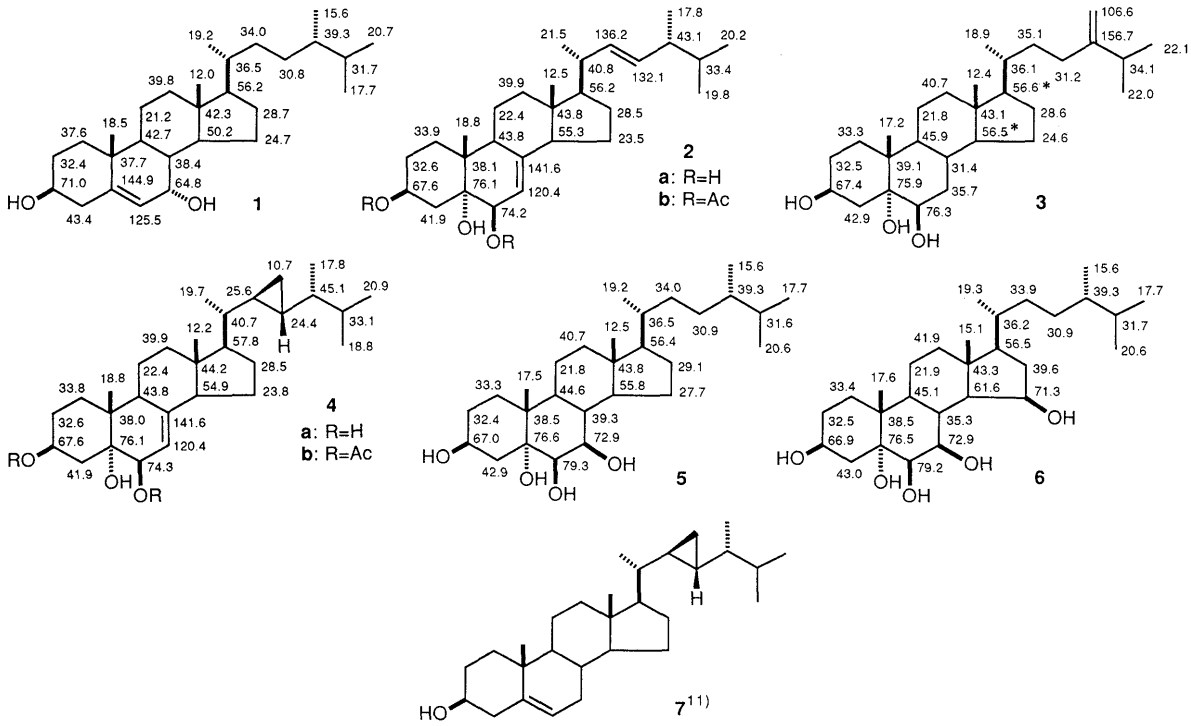


Chart 1. Structures and ^{13}C-NMR Signals (δ, in Pyridine-d_5) of **1** to **7**

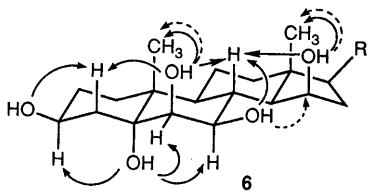
* Exchangeable.

that **1** is identical with synthetic 7α-hydroxycholesterol, as regards the steroid ring. The chemical shift of 27-H_3 (δ 0.781, 3H, d, J=7.0 Hz) was of (24*S*)-ergostane-type (lit., δ 0.783) and was different from that of the C-24 isomer (δ 0.802).[6] Compound **1** has been synthesized,[7] but its isolation from natural sources has not previously been reported. Compound **2a** was identical with (24*R*)-ergosta-7,22-diene-3β,5α,6β-triol, previously obtained from a *Sinularia* sp. soft coral.[1] Compound **3** was identified as ergost-24(28)-ene-3β,5α,6β-triol, from the identity of ^{1}H- and ^{13}C-NMR signals of the steroid ring and side chain with those of (24*S*)-ergostane-3β,5α,6β,25-tetrol 25-monoacetate and ergosta-5,24(28)-dien-3β-ol,[4a,8] respectively. This compound has been isolated from the soft coral *Sinularia dissecta* by Bortolotto *et al.*[9]

The new compound **4a** was isolated as a *ca.* 3 : 1 mixture with **2a**. The separation was accomplished as the diacetates, taking advantage of their slightly different affinity for Ag ion on 15% $AgNO_3$-impregnated preparative silica gel TLC. The major compound **4a**, which was less polar on this chromatography than **2a**, was found to be a C_{29} sterol having the steroid ring in common with **2a**. The structure of the side chain was identical with that of 23-demethylgorgosterol (**7**), showing four secondary methyl signals (in $CDCl_3$, δ 0.862, 0.892, 0.920, 0.934, each 3H, d, J= 7.0 Hz), and five protons (δ 0.13, 2H, m, 29-H_2; 0.31, 1H, m, 22-H; 0.55, 2H, m, 23,24-H) which are strongly shielded by the cyclopropane ring. These chemical shifts agreed well with those of the natural (22*R*,23*R*)-isomer **7** and differred from those of four isomeric synthetic compounds.[10] The side chain carbon signals also showed good agreement with those of the demethylgorgosterol derivative stoloniferone-d.[11] The heteronuclear multiple bond correlation spectroscopy (HMBC) spectrum showed the necessary correlation peaks (21-H_3 (C-17, 22), 28-H_3 (C-23), 29-H_2 (C-22, 23, 24)). The diastereoisomeric side chain structure should, mainly due to the change of the *gauche* γ-effects, cause significant discrepancies in the carbon signals. It seems unusual that such a derivative of **7**, instead of that of gorgosterol, was obtained since **7** is usually a minor component of a soft coral's 3β-monohydroxysterol mixture (*e.g.* 1% in *Sarcophyton glaucum*) compared with gorgosterol (23%).[12]

Compounds **5** and **6** were tetra- and pentahydroxy C_{28} sterols with a (24*S*)-ergostane-type side chain, as in **1** (Experimental). Their ^{1}H-NMR spectra (in pyridine-d_5) indicated the presence of a 3β,5α,6β-trihydroxyl grouping, from the prominent pyridine-induced deshielding of the 4β-H (δ 2.94, dd, J=12.5, 12.0 Hz) and 19-H_3 (δ 1.61, 3H, s) signals.[1,4a] The broad hydroxymethine singlet observed in **3** (δ 4.16), due to 6α-H, was converted to a sharp doublet (J=4.5 Hz) in **5** (δ 4.14) and **6** (4.18). This shows that 6α-H is coupled to a *gauche* hydroxymethine at C-7 which is axially oriented (δ 4.45, dd, J=9.5, 4.5 Hz). The C-15 signal appeared at δ 27.7, at *ca.* 4 ppm lower field than that of cholestane. This is due to the δ_1 hydroxy substituent effect[13] of the 7β-equatorial hydroxyl group, which takes a 1,3-*syn* periplanar arrangement with respect to the C-14, 15 bond (Chart 2). Compound **5** has previously been isolated from the soft corals *Anthelia glauca*[14a] and a *Xenia* sp.[14b]

The new compound **6** is a monohydroxy derivative of **5** and showed common ^{1}H- and ^{13}C-NMR signals regarding



6

Chart 2. Pyridine-Induced Deshieldings (→) and δ_1 Hydroxy Substituent Effects (⇢) in **6**

the A- and B-rings, C-11 to C-13, and the side chain. The extra secondary hydroxyl group, on the D-ring, caused a γ-substituent effect (−4.0 ppm) at C-8 (δ 35.3) and a δ_1-hydroxy substituent effect (+2.6 ppm) at C-18 (δ 15.1), as compared with **5** (C-8, δ 39.3; C-18, 12.5). The 18-H_3 signal, which appears at δ 0.79 (pyridine-d_5) in **5**, was shifted to δ 1.29 in **6**. The pyridine-induced deshielding ($\Delta\delta$: $\delta_{\text{pyridine-}d_5} - \delta_{CDCl_3}$)[15] at 18-$H_3$, due to the parallel 15β-OH, was +0.46 ppm whereas that at 8β-H, due to 6β- and 15β-OH, and *gauche* 7β-OH, was +0.71 ppm (Chart 2). These results indicate unambiguously that compound **6** is (24*S*)-ergostane-3β,5α,6β,7β,15β-pentol. The HMBC spectrum of **6** confirmed this, showing the necessary correlations (Experimental).

In the two reports of **5**,[14] the ^{13}C-NMR assignments reported were δ 32.3 for C-1 and 33.2 for C-2. However, the HMBC spectrum of **6** revealed the three-bond correlation of 4α-H with C-2 (δ 32.5), and 19-H_3 with C-1 (δ 33.4), so that the assignments in ref. 14 should be reversed. Similarly, there were clear correlations between 4α-H and C-2 (δ 32.6), and 19-H_3 and C-1 (33.8) in **4a**. These results indicate that, in 3β,5α,6β-trihydroxysteroid derivatives, the C-1 resonates at *ca.* 1 ppm lower field than C-2, thus requiring the revision of earlier assignments, *e.g.* cholestane-3β,5α,6β-triol,[16] and our[4] and other assignments,[17] for sterols of this type.

Experimental

Melting points were determined on a Kofler hot stage and are uncorrected. Optical rotations were determined on a JASCO DIP-370 digital polarimeter. NMR spectra were determined on a JEOL JMN GX-400 spectrometer at 400 MHz (^{1}H) and on a JEOL JMN FX-90Q spectrometer at 22.5 MHz (^{13}C) with $CHCl_3$ (^{1}H, δ 7.260) and pyridine-d_5 (^{13}C, center peak δ 135.5) as internal standards. Mass spectra (MS) were determined on a JEOL JMS D300 mass spectrometer.

Isolation of Compounds 1 to 6 (a) The *Sclerophytum* sp. soft coral, code name MFVA-10 (dry weight 0.8 kg), was collected in April 1991 off the coasts of the Andaman and Nicobar Islands (Chiriatapu, 11°41′N, 92°43′E). The organism was washed with fresh water, cut into slices and preserved in EtOH. The extraction was carried out using EtOH by percolation every 2 d (7 times). The EtOH extract was reextracted with ethyl acetate several times. The extract (30 g) was chromatographed over silica gel using solvent mixtures of petroleum ether (A) and ethyl acetate (B). Elution with A–B (2 : 1) and A–B (1 : 1) gave fraction I, which contained **1**, and fraction II which contained **2a**. Repeated chromatography followed by recrystallization from MeOH–$CHCl_3$ gave **1** (20 mg) and **2a** (15 mg).

(b) The *Sinularia* sp. soft coral, code name MF-VA-9 (dry weight 1.2 kg), was collected at Maya Bunder (12°40′N, 92°53′E) and identified as a new species. The specimen was deposited at the Northern Territory Museum of Arts and Science, Australia, with the registration No. NTM C 11196. The organism was treated as described in (a) and the extract (20 g) was chromatographed as follows: elution with A gave a mixture of diterpenoids, which are under investigation; elution with A–B (19 : 1) gave a monohydroxysterol mixture (2.5 g); elution with A–B (1 : 1) gave **3** (80 mg); elution with A–B (2 : 3) and A–B (3 : 7) gave fractions I (35 mg) and II (30 mg), respectively. Repeated chromatography followed by recrystallization from $CHCl_3$–MeOH gave a mixture of **4a** and **2a** (*ca.* 3 : 1, 18 mg)

from fraction I, and **2a** (15 mg) from fraction II. The mixture of **4a** and **2a** was acetylated under usual conditions (Ac_2O–pyridine, room temperature, overnight). The acetate mixture was subjected to 15% $AgNO_3$-impregnated preparative silica gel TLC according to Idler's method.[18] Development with 3% Et_2O in $CHCl_3$ 3 times gave sufficient separation of two broad bands. Elution with ethyl acetate gave **4b** (13.1 mg) from the less polar band, and **2b** (4.2 mg) from the more polar band. Brief treatment of each diacetate with refluxing 7.5% NaOH in MeOH followed by usual work-up gave **4a** (7.3 mg) and **2a** (3.5 mg), respectively.

(c) The soft coral (dry weight 1.2 kg), code name MFVA-11, collected at Rangat (12°27′N, 92°55′E) and identified as *Lobophytum crassum*, was treated as described in (a). The extract (30 g), on chromatography with A–B (2:3), A–B (1:4), and B, gave fractions which contained **2a**, **5**, and **6**, respectively. Repeated chromatography of each fraction followed by recrystallization from $CHCl_3$–MeOH gave **2a** (25 mg), **5** (150 mg) and **6** (12 mg), respectively.

(24*S*)-Ergost-5-ene-3β,7α-diol (1) Colorless needles, mp 210—212 °C, $[\alpha]_D$ −75° (*c* = 0.38, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.68 (3H, s, 18-H_3), 0.781, 0.775, 0.853 (each 3H, d, *J* = 7.0 Hz), 0.929 (3H, d, *J* = 6.5 Hz, 21-H_3), 1.00 (3H, s, 19-H_3), 2.28 (1H, br dd, *J* = 13.0, 11.0 Hz, 4β-H), 2.34 (1H, ddd, *J* = 13.0, 5.5, 2.0 Hz, 4α-H), 3.59 (1H, m, 3α-H), 3.86 (1H, br s, 7β-H), 5.61 (1H, br d, *J* = 5.0 Hz, 6-H). MS *m/z*: 416 (M^+), 398. HIgh-resolution MS *m/z*: Calcd for $C_{28}H_{46}O_2$ (M^+): 416.3655. Found: 416.3659.

(24*R*)-Ergosta-7,22-diene-3β,5α,6β-triol (2a) Colorless needles, mp 251—252 °C, $[\alpha]_D$ −36° (*c* = 1.06, pyridine). The identification was made by comparison of the ^{1}H-NMR data with those reported in the literature,[17] and those in the preceding report.[1]

Ergost-24(28)-ene-3β,5α,6β-triol (3) Colorless needles, mp 241—242 °C, $[\alpha]_D$ −4° (*c* = 0.26, pyridine). ^{1}H-NMR (pyridine-d_5) δ: 0.73 (3H, s, 18-H_3), 0.99 (3H, d, *J* = 7.0 Hz, 21-H_3), 1.05, 1.06 (each 3H, d, *J* = 7.0 Hz, 26,27-H_3), 1.66 (3H, s, 19-H_3), 2.96 (1H, dd, *J* = 12.0, 11.5 Hz, 4β-H), 4.16 (1H, br s, 6α-H), 4.84, 4.85 (each 1H, br s, 28-H_2), 4.86 (1H, m, 3α-H). MS *m/z*: 432 (M^+), 417, 414, 399, 381, 363, 348, 330, 312, 305.

23-Demethylgorgost-7-ene-3β,5α,6β-triol (4a) Colorless needles, mp 229—232 °C, $[\alpha]_D$ −45° (*c* = 2.18, pyridine). ^{1}H-NMR (pyridine-d_5) δ: 0.16 (2H, m, 29-H_2), 0.30 (1H, m, 22-H), 0.53 (2H, m, 23,24-H), 0.64 (3H, s, 18-H_3), 0.89, 0.91, 0.94, 0.99 (each 3H, d, *J* = 7.0 Hz), 1.53 (3H, s, 19-H_3), 2.51 (1H, ddd, *J* = 13.0, 5.0, 1.5 Hz, 4α-H), 2.57 (1H, br dd, *J* = 11.5, 7.0 Hz, 9α-H), 3.01 (1H, dd, *J* = 13.0, 12.0 Hz, 4β-H), 4.31 (1H, br s, 6α-H), 4.82 (1H, m, 3α-H), 5.77 (1H, m, 7-H). ($CDCl_3$): 0.13 (2H, m, 29-H_2), 0.31 (1H, m, 22-H), 0.55 (3H, s, 18-H_3), 0.55 (2H, m, 23,24-H), 0.934, 0.920, 0.892, 0.862 (each 3H, d, *J* = 7.0 Hz), 1.08 (3H, s, 19-H_3), 3.63 (1H, br s, 6α-H), 4.08 (1H, m, 3α-H), 5.37 (1H, m, 7-H). HMBC correlation (in pyridine-d_5): 4β-H (C-3, 5), 4α-H (C-2, 10, 3, 5), 6α-H (C-8, 7, 5), 7-H (C-9, 5, 14), 9α-H (C-8), 19-H (C-1, 10, 9, 5), 21-H (C-22, 17), 28-H (C-23, 24), 29-H (C-22, 23, 24). MS *m/z*: 444 (M^+), 426, 408, 393. High-resolution MS *m/z*: Calcd for $C_{29}H_{48}O_3$ (M^+): 444.3603. Found: 444.3593.

23-Demethylgorgost-7-ene-3β,5α,6β-triol 3,6-Diacetate (4b) Colorless oil, $[\alpha]_D$ −64° (*c* = 3.92, $CHCl_3$). ^{1}H-NMR ($CDCl_3$), 0.13 (2H, m, 29-H_2), 0.30 (1H, m, 22-H), 0.54 (2H, m, 23,24-H), 0.55 (3H, s, 18-H_3), 0.859, 0.889, 0.915, 0.928 (each 3H, d, *J* = 7.0 Hz), 1.05 (3H, s, 19-H_3), 2.03, 2.06 (each 3H, s), 4.83 (1H, br d, *J* = 4.0 Hz, 6α-H), 5.13 (1H, m, 3α-H), 5.26 (1H, m, 7-H). MS *m/z*: 468 (M^+ − AcOH), 450, 408, 390, 378, 306, 292, 251. High-resolution MS *m/z*: Calcd for $C_{31}H_{48}O_3$ (M^+ − AcOH): 468.3604. Found: 468.3588.

(24*S*)-Ergostane-3β,5α,6β,7β-tetrol (5) Colorless needles, mp 212—215 °C, $[\alpha]_D$ +16° (*c* = 0.50, pyridine). ^{1}H-NMR ($CDCl_3$): identical with reported data.[14a] (pyridine-d_5) δ: 0.79 (3H, s, 18-H_3), 0.810, 0.815, 0.870 (each 3H, d, *J* = 7.0 Hz), 1.01 (3H, d, *J* = 6.5 Hz, 21-H_3), 1.61 (3H, s, 19-H_3), 2.94 (1H, dd, *J* = 12.5, 12.0 Hz, 4β-H), 4.14 (1H, d, *J* = 4.5 Hz, 6α-H), 4.45 (1H, dd, *J* = 9.5, 4.5 Hz, 7α-H), 4.85 (1H, m, 3α-H). MS *m/z*: 450 (M^+), 432, 414, 396, 381, 321, 304, 287.

(24*S*)-Ergostane-3β,5α,6β,7β,15β-pentol (6) Colorless needles, mp 285—289 °C, $[\alpha]_D$ −14° (*c* = 0.34, pyridine). ^{1}H-NMR (pyridine-d_5) δ: 0.805 (6H, d, *J* = 7.0 Hz), 0.862 (3H, d, *J* = 7.0 Hz), 1.035 (3H, d, *J* = 6.5 Hz, 21-H_3), 1.29 (3H, s, 18-H_3), 1.62 (3H, s, 19-H_3), 1.78 (1H, m, 16α-H), 2.29 (1H, m, 2-H), 2.39 (1H, br dd, *J* = 13.0, 5.5 Hz, 4α-H), 2.51 (1H, dt, *J* = 14.0, 8.5 Hz, 16β-H), 2.58 (1H, br q, *J* = 11.0 Hz, 8β-H), 2.96 (1H, dd, *J* = 13.0, 11.5 Hz, 4β-H), 4.18 (1H, d, *J* = 4.0 Hz, 6α-H), 4.66 (1H, dd, *J* = 10.0, 4.0 Hz, 7α-H), 4.74 (1H, ddd, *J* = 8.5, 5.5, 2.5 Hz, 15α-H), 4.84 (1H, m, 3α-H). ($CDCl_3$) 0.780, 0.782, 0.856, 0.934 (each 3H, d, *J* = 7.0 Hz), 0.97 (3H, s, 18-H_3), 1.19 (19-H_3) (due to the low solubility, only methyl signals were recognizable). (CD_3OD : $CDCl_3$ = 1 : 9) 0.633, 0.667, 0.740, 0.813 (each 3H, d, *J* = 7.0 Hz), 0.83 (3H, s, 18-H_3), 1.03 (3H, s, 19-H_3), 1.87 (1H, br q, *J* = 10.5 Hz, 8β-H), 1.96 (1H, dd, *J* = 13.5, 12.0 Hz, 4β-H), 2.25 (1H, dt, *J* = 14.5, 8.5 Hz, 16β-H), 3.29 (1H, d, *J* = 4.5 Hz, 6α-H), 3.82 (1H, dd, *J* = 10.0, 4.5 Hz, 7α-H), 3.88 (1H, m, 3α-H), 4.16 (1H, ddd, *J* = 8.0, 5.5, 2.5 Hz, 15α-H). HMBC correlation (in pyridine-d_5): 4β-H (C-3, 5), 4α-H (C-2, 10, 3, 5, 6), 6α-H (C-8, 10, 4, 7, 5), 7α-H (C-14), 8β-H (C-9, 14, 7), 15α-H (C-13, 17), 16α-H (C-20, 17, 15), 16β-H (C-13), 18-H_3 (12, 13, 17, 14), 19-H_3 (C-1, 10, 9, 5), 21-H_3 (C-22, 20, 17). MS *m/z*: 448 ($M^+ - H_2O$), 430, 412, 397, 379, 322, 303, 285, 267. High-resolution MS *m/z*: Calcd for $C_{28}H_{48}O_4$ ($M^+ - H_2O$): 448.3552. Found: 448.3555.

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