Marine Sterols. Part 20.[1] Polyhydroxy Sterols of the Soft Corals of the Andaman and Nicobar Coasts. Part 4.[2] Andamansterol and Nicobarsterol, Novel Sterols with 3,9,11,21-Tetrahydroxylated, and 11,21-Epoxy-9,11-secosteroid Skeletons, from a *Sclerophytum* sp. of Soft Coral. X-Ray Molecular Structure of Andamansterol

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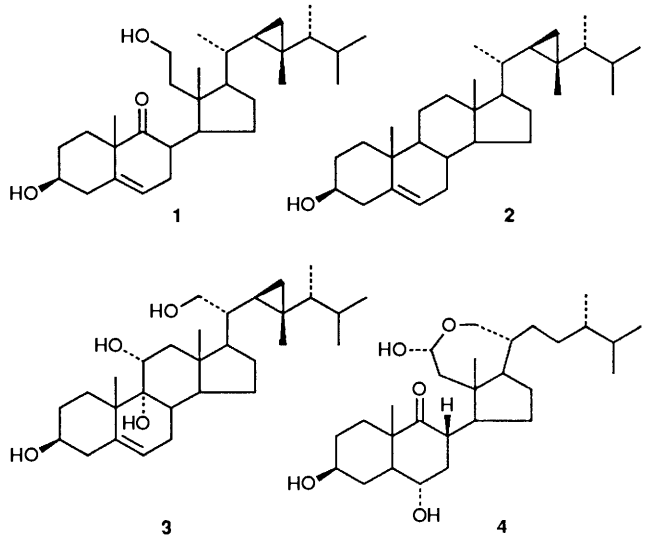
The lipid extract of a *Sclerophytum* sp. of soft coral, collected off the coast of the Andaman and Nicobar Islands, afforded two new polyhydroxy sterols, designated andamansterol **3** and nicobarsterol **4**. The structure of compounds **3** and **4** was shown to be gorgost-5-ene-3β,9α,11α,21-tetraol and (11*R*,24*S*)-3β,6α,11-trihydroxy-11,21-epoxy-9,11-secoergostan-9-one, respectively, by spectral analysis (^{1}H–^{1}H COSY, HMQC*, HMBC*). X-Ray crystallography of andamansterol **3** confirmed the proposed structure, including the configuration at C-20. Lead tetraacetate treatment of andamansterol **3** gave the 9,11-seco derivative **6** having the same seven-membered hemiacetal ring as nicobarsterol **4**

9,11-Secosterols are unique marine sterols, and up to now two principal types were known. One type (**1**), isolated from a gorgonian (Coelenterate) together with its 5α,6-epoxide, was reported in 1972,[3] shortly after the long-pending question of the unique side-chain structure of gorgosterol **2** was finally clarified.[4] The other type is a more recently discovered one, the polyhydroxycholestane derivative herbasterol obtained from a sponge,[5] having an A/B-*cis* ring fusion. During our investigation of the soft corals (Coelenterate) off the Andaman and Nicobar coasts, we obtained two novel sterols, which we have designated andamansterol **3**, and nicobarsterol **4**, the latter a new type of 9,11-secosterol, from material identified as a *Sclerophytum* sp. Four known compounds were simultaneously isolated; namely, lobosterol [(24*S*)-3β,4β,5β,25-tetrahydroxyergostan-6-one 25-monoacetate],[6] (24*S*)-3β,5α,6β,25-tetrahydroxyergostane[7a] and its 25-monoacetate,[7b] and (24*S*)-ergostane-3β,5α,6β,25ξ,26-pentaol;[8] these compounds were identified by direct comparison with authentic specimens. Both compounds **3** and **4** bear an oxygenated C-21, which is rare in the marine sterols except for those found in brittle stars (Echinoderms).[9] The C-11 of nicobarsterol **4** is at a carboxaldehyde oxidation level, unlike the situation in other known 9,11-secosterols, and forms a seven-membered hemiacetal ring with the C-21 hydroxy group. This type of structure is unprecedented in the previously known natural and synthetic steroids.

Andamansterol **3**, $C_{30}H_{50}O_4$, is a tetrahydroxygorgostane-type sterol and afforded a triacetate on acetylation. Owing to the polyhydroxylated structure, pyridine-induced deshielding[10] was prominent and the ^{1}H NMR pattern varied drastically when the spectrum was taken in [$^2H_5$]pyridine as compared with that taken in $CDCl_3$; the free sterol **3** was quite sparingly soluble in $CDCl_3$. The ^{1}H NMR (in [$^2H_5$]pyridine) spectrum indicated it to have one primary (δ_H 3.92 and 4.19, each dd, *J* 10.5, 2.5 Hz), and two secondary (δ_H 3.90, m, $w_{\frac{1}{2}}$ 20 Hz; 4.53, dd, *J* 11.5, 5.0 Hz) hydroxy groups. The ^{13}C NMR ([$^2H_5$]pyridine; Table 1) showed the presence of one tertiary hydroxy group (δ_C 75.9), and one trisubstituted double bond (δ_C 140.4, s; 121.5, d). The coupling pattern of the three cyclopropanoid protons (in $CDCl_3$; 22-H, δ_H 0.43, ddd, *J* 9.0, 9.0, 5.5 Hz; 29-H, 0.04, dd, *J* 5.5, 4.5 Hz; and 0.59, dd, *J* 9.0, 4.5 Hz), and that of 24-H (δ_H 0.32, dq, *J* 8.5, 7.0 Hz), which is known to be intensely shielded by an adjacent cyclopropane ring,[4a] are virtually identical with those of compound **2**, previously isolated from a soft coral *Sarcophyton glaucum*.[11] In contrast, their chemical shifts were significantly different from those of **2** (22-H, δ_H 0.16; 29-H, −0.14, 0.45; 24-H, 0.23).[11] The signals due to three secondary methyl groups in andamansterol **3** (in [$^2H_5$]pyridine; δ_H 0.85, 0.96 and 1.01) were assignable to those of 26, 27- and 28-H_3, considering their close similarity to the corresponding signals of compound **2** (δ_H 0.89, 1.00 and 1.03).[4a] In the ^{1}H NMR spectrum taken in [$^2H_5$]pyridine, the 22-H (δ_H 0.74) and one (δ_H 0.16, dd, *J* 5.5, 4.5 Hz) of the C-29 methylene protons were affected by pyridine-induced deshielding (22-H, Δδ +0.31 ppm; 29-H, +0.12 ppm),[10] which was caused by the C-21 hydroxy group (δ_C 64.9, t). The signals, assigned by HMQC[12] and HMBC[13] correlations, of the D-ring carbons occurred at normal positions, as found in cholesterol,[14] except that C-14 (δ_C 49.6) and C-17 (δ_C 51.6) are shifted *ca.* 6 ppm upfield. This is due



* HMBC = heteronuclear multiple bond correlation spectroscopy. HMQC = heteronuclear multiple quantum coherence.

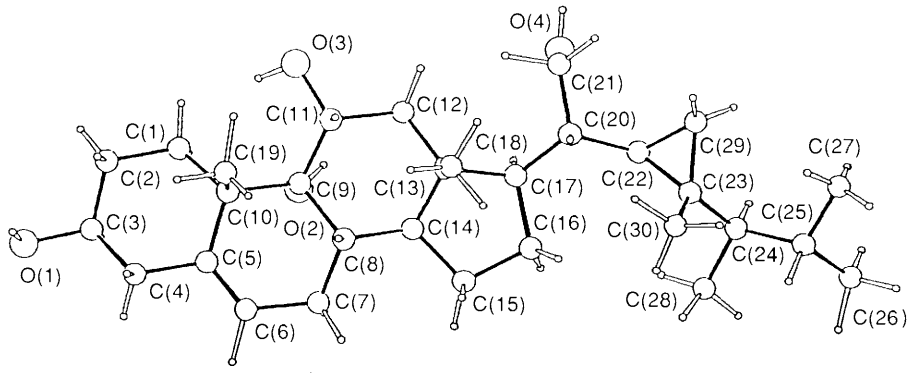


Fig. 1 Crystal structure of andamansterol **3**

Table 1 ^{13}C NMR data (δ_C) of compounds **3**, **4** and **6** and the calculated δ_C-values of compound **5**

Carbon	3	4	5*	6	Multiplicity
C-1	31.7	32.7	31.6	32.2[a]	t
C-2	32.7	31.5	31.0	32.1[a]	t
C-3	70.9	70.3	70.1	71.1	d
C-4	44.4	33.6	34.3	41.8	t
C-5	140.4	51.9	52.1	141.6	s (**4** and **5**, d)
C-6	121.5	68.1	72.0	121.0	d
C-7	27.6	41.9	40.7	31.7[a]	t
C-8	35.5	41.5	42.1	41.3[b]	d
C-9	75.9	214.9	215.0	215.3	s
C-10	43.9	47.1	47.4	48.4	s
C-11	69.7	94.5		94.2	d
C-12	46.5	45.8		45.7	t
C-13	43.2	44.7		45.0	s
C-14	49.6	45.3	16.3	45.0	d
C-15	24.5	22.4		23.5	t
C-16	28.6	26.5		26.9	t
C-17	51.6	58.1		59.8	d
C-18	13.0	12.8		12.7	q
C-19	22.2	17.2	17.2	22.9	q
C-20	42.4	41.8	(10-Me)	42.7[b]	d
C-21	64.9	65.8		66.9	t
C-22	27.9	31.7		26.0	d (**4**, t)
C-23	25.5	28.9		24.4	s (**4**, t)
C-24	51.0	39.3		50.8	d
C-25	32.3	31.6		32.2	d
C-26	21.6	17.7		21.6	q
C-27	22.4	20.5		22.2	q
C-28	15.6	15.4		15.9	q
C-29	21.1			21.4	t
C-30	14.4			14.0	q

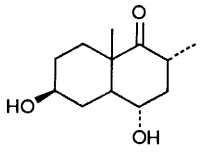
[a,b] Signals may be interchanged. * Numbering scheme follows that of the steroids 1–**4** and **6**, and does not coincide with the systematic name given in the text.

to the γ-hydroxy substituent effect caused by the C-21 hydroxy group (on C-17), and by the C-9 hydroxy group (*vide infra*) (on C-14). The chemical shifts of the carbons with regard to atoms C-3 to C-6 (δ_C 70.9, 44.4, 140.4 and 121.5 respectively) corresponded to those of the common 3β-hydroxy-Δ^5-steroids.[14] In the ^1H NMR spectrum, both 18-H (δ_H 0.91) and 19-H (δ_H 1.47) showed an NOE when one of the hydroxymethine protons (δ_H 4.53, 11β-H) was irradiated. This hydroxymethine proton was shown, by decoupling experiments, to be coupled with one of the C-12 methylene protons at δ_H 2.68 (dd, *J* 12.5, 5.0 Hz, 12β-H). This NOE, together with the coupling pattern of 11β-H (dd), indicates that the remaining tertiary hydroxy group is at C-9 (α). The assignment of the structure gorgost-5-ene-3β,9α,11α,21-tetraol for andamansterol **3** was fully supported by HMBC[13] correlations (4-H: C-2,-3,-5,-6,-10; 6-H: C-4,-7,-8; 12-H: C-9,-11,-13,-14,-18; 18-H: C-14,-17; 19-H: C-1,-9,-10; 21-H: C-17,-22), indicating that the proton and the carbons in each group are separated by two or three bonds. The identical coupling pattern of 22-H of compound **3** with that of compound **2** (*J* 9.0, 9.0, 5.5 Hz), suggested that their configurations at C-20 are identical. However, biogenetically, the C-21 hydroxylation process might have involved a precursor having a Δ^{20}-double bond, which could lead to both a conventional as well as the diastereoisomeric (at C-20) configuration. Compound **3** was, therefore, subjected to X-ray crystallography. The results, shown as a perspective drawing in Fig. 1, confirmed the proposed structure and the C-20 configuration of andamansterol **3** to be the same as in compound **2**, namely the conventional one. The occurrence of a 9,11-dihydroxy derivative of compound **2** in a gorgonian, with unidentified C-9 and C-11 configurations, has been referred to,[15] but a detailed report has not been published.

Nicobarsterol **4**, $C_{28}H_{48}O_5$, bears three secondary hydroxy groups, one oxymethylene (in [$^2H_5$]pyridine; δ_C 65.8, t; δ_H 3.79, dd, *J* 12.5, 2.5 Hz; 4.04, dd, *J* 12.5, 10.5 Hz), and one carbonyl group (δ_C 214.9). The extra oxygen atom was believed to be involved in an ethereal linkage. The ^1H and ^{13}C NMR spectra indicated the presence of an ergostane-type side-chain. The three secondary methyl signals (δ_H 0.776, 0.779, 0.850), taken in $CDCl_3$, corresponded better to those of the 26, 27- and 28-H_3 of (24*S*)-24-methylcholesterol (δ_H 0.775, 0.783, 0.852)[16] than to those of the (24*R*)-isomer (δ_H 0.773, 0.802, 0.850).[16] The same (24*S*) configuration of the polyhydroxy sterols, simultaneously isolated, has previously been confirmed by synthesis.[17] This indicated that C-21 of nicobarsterol **4** was oxygenated as in andamansterol **3**. The deshielded hydroxy methine signal (in [$^2H_5$]pyridine; δ_H 5.59, dd, *J* 8.5, 5.5 Hz) and the characteristic ^{13}C NMR signal (δ_C 94.5, d) indicated the presence of a hemiacetal moiety in structure **4**. The proton at δ_H 5.59 was coupled with a proton at δ_H 2.29 (dd, *J* 15.0, 5.5 Hz), which is assignable to one of the C-12 methylene protons. These signals and their coupling patterns indicated that nicobarsterol **4** is a secosteroid, cleaved at C-9 and C-11, and the C-11 carboxaldehyde was, in turn, linked to C-21, forming a seven-membered hemiacetal ring. The C-10 quarternary carbon is shifted significantly downfield (δ_C 47.1), as compared with that of 10-methyl-*trans*-decalin (δ_C 34.8),[18] indicating the presence of a carbonyl group at C-9. Of the remaining two secondary hydroxymethine protons, one (δ_H 3.90, br m, $w_{\frac{1}{2}}$ 20 Hz) was assigned to that of 3α-H of the biogenetically common 3β-hydroxy-A/B-*trans*-steroids. The other (δ_H 4.34, ddd, *J* 10.0, 10.0, 3.5 Hz) showed couplings with two anti periplanar and one *gauche* protons. An NOE (5.5%) was observed between this hydroxymethine proton and 19-H, so that only the presence of a 6α-hydroxy group would account for these facts. The 4α-H signal, assigned by the ^1H–^1H COSY spectrum, was shifted to lowfield (δ_H 2.98, br d, *J* 12.5 Hz), due to the pyridine-induced

deshielding effect [10] caused by the 1,3-synperiplanar 6α-hydroxy group. The presence of an NOE between 8-H (δ_H 3.26, ddd, *J* 13.5, 5.0, 3.5) and 19-H (8%) and between 8-H and 6-H (5%) indicated the normal 8β configuration; hence the bulky C-8 substituent is equatorially orientated. Application of the semiempirical calculation rule of ^{13}C NMR chemical shifts, described by Beierbeck *et al.*, [18] for the model compound 4α,6β-dihydroxy-2α,8aβ-dimethyl-1-oxo-*trans*-decalin **5** gave the predicted chemical shifts which show good agreement with those of the carbons in the A- and B-rings of nicobarsterol **4** (Table 1). The structure derived for compound **4** was fully supported by the HMBC correlation spectrum (4α-H: C-3, -10; 7-H: C-5, -6, -8, -9; 8-H: C-13; 11-H: C-21; 12-H: C-11, -13, -17; 18-H: C-17; 19-H: C-1, -5, -9, -10; 21-H: C-11, -17). The NOEs, observed between 8-H and 18-H (3%) and between 8-H and 12-H at δ_H 2.29 (5%), and the coupling constant between 8-H and 14-H (5.0 or 3.5 Hz) suggested that 8-H and 14-H are arranged in a *gauche*-like disposition, due to the conformational rotation about the C-8–C-14 bond. A weak NOE was observed between 11-H and 18-H (*ca.* 3%). A molecular model study of compound **4** indicated that only the (11*R*)-configuration was possible to account for this NOE.

The structure of compound **4** suggests, obviously, that it was derived from a precursor having a 9,11-glycolated steroid nucleus. Compound **3** has this functionality, albeit andamansterol **3** is a gorgostane and nicobarsterol **4** is an ergostane derivative. On a biogenetic basis, it can be supposed that the configuration at C-20 of compound **3** is identical with that of compound **4**. In order to confirm the proposed structure of compound **4**, compound **3** was converted into 9,11-seco derivative, since it was expected that the derived secoaldehyde would form the cyclic hemiacetatal **6**, and show chemical shifts



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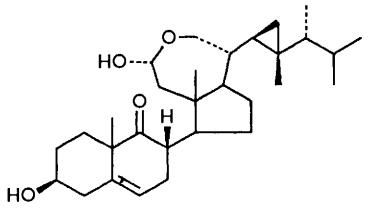

6

in common with those of compound **4**. Treatment of andamansterol **3** with lead tetraacetate (LTA) in $CHCl_3$ gave the secosteroid **6** in quantitative yield. The NMR chemical shifts of compound **6** indeed showed close similarity with those of compound **4**, regarding the structurally common carbons (C-9, C-11 to C-18, and C-21, Table 1) and protons (Experimental section). The 11-H coupling constants of compound **6** (8.5, 5.5 Hz) were identical with those of nicobarsterol **4**, indicating the same (11*R*) configuration.

Experimental

General Details.—M.p.s 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 JNM GX-270 spectrometer at 270 MHz (^1H) and on a JEOL JNM FX-90Q spectrometer at 22.5 MHz (^{13}C) with tetramethylsilane as internal standard *J*-values are given in Hz. Mass spectra were determined on a JEOL JMS D 300 mass spectrometer. Flash column chromatography [19] was performed on silica gel (Wako gel C-300, 200–300 mesh, Wako Pure Chemical industries).

Material.—The collection locations and the code numbers of the soft corals, and details of the individual polyoxy sterols and their general isolation process, have been reported previously.[20] The soft coral material, code name MF-CBR-38 (1.4 kg after extraction), gave the polyhydroxy sterol derivatives MF-CBR-38-01 (lobosterol, 150 mg), MF-CBR-38-02 [(24*S*)-ergostane-3β,5α,6β,25-tetraol 25-monoacetate, 230 mg], MF-CBR-38-03 (a mixture containing ergostane-3β,5α,6β-triol, 38 mg), MF-CBR-38-04 (compound **3**, 30 mg), MF-CBR-38-05 [mixture of nicobarsterol **4** and (24*S*)-ergostane-3β,5α,6β,25-tetraol, 45 mg], MF-CBR-38-06 [(24*S*)-ergostane-3β,5α,6β,25-tetraol, 14 mg], and MF-CBR-38-07 [(24*S*)-ergostane-3β,5α,6β,25ξ,26-pentaol, 42 mg]. MF-CBR-38-05 (35 mg) was subjected to column chromatography with 6% MeOH in $CHCl_3$ to afford compound **4** (18.4 mg).

Andamansterol **3**.—M.p. 265–266 °C, $[\alpha]_D^{22}$ −34° (*c* 1.00, pyridine); $\delta_H([^2H_5]$pyridine) 0.16 (1 H, dd, *J* 5.5, 4.5, 29-H), 0.27 (1 H, dq, *J* 8.5, 7.5, 24-H), 0.56 (1 H, dd, *J* 9.0, 4.5, 29-H), 0.74 (1 H, ddd, *J* 9.0, 9.0, 5.5, 22-H), 0.91 and 0.953 (each 3 H, s, 18- and 30-H_3), 1.47 (3 H, s, 19-H_3), 0.85, 0.955 and 1.01 (each 3 H, d, *J* 6.5, 26-, 27- and 28-H_3), 2.32 (1 H, dd, *J* 12.5, 11.5, 12α-H), 2.68 (1 H, dd, *J* 12.5, 5.0, 12β-H), 2.75 and 2.77 (each 1 H, br s, 4-H_2), 3.90 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 3α-H), 3.92 and 4.19 (each 1 H, dd, *J* 10.5, 21-H_2), 4.53 (1 H, dd, *J* 11.5, 5.0, 11β-H) and 5.61 (1 H, m, 6-H); $\delta_H(CDCl_3)$ 0.04 (1 H, dd, *J* 5.5, 4.5, 29-H), 0.32 (1 H, dq, *J* 8.5, 7.0, 24-H), 0.43 (1 H, ddd, *J* 9.0, 9.0, 5.5, 22-H), 0.59 (1 H, dd, *J* 9.0, 4.5, 29-H), 0.71 (3 H, s, 18-H_3), 0.91 (3 H, s, 30-H_3), 1.23 (3 H, s, 19-H_3), 0.88, 0.96 and 0.97 (each 3 H, d, *J* 6.5, 26-, 27- and 28-H_3), 1.99 (1 H, dd, *J* 12.0, 5.0, 12β-H), 3.48 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 3α-H), 3.61 and 3.86 (each 1 H, dd, *J* 10.5, 2.0, 21-H_2), 4.12 (1 H, dd, *J* 11.5, 5.0, 11β-H) and 5.45 (1 H, m, 6-H); *m/z* 456 ($M^+ - H_2O$), 438, 420, 407 (438 − CH_2OH), 349 (M^+ − C-22–C-30) and 305 (M^+ − side-chain) [Found: ($M^+ - H_2O$), 456.3602. $C_{30}H_{48}O_3$ ($M^+ - H_2O$) requires *m/z* 456.3604].

Andamansterol 3,11,21-*Triacetate*.—Compound **3** (2 mg) was acetylated in the usual way with Ac_2O-pyridine at room temperature overnight. Chromatography of the crude product with Et_2O–$CHCl_3$ (1:19) gave the triacetate (1.8 mg) as needles from MeOH, m.p. 142–145 °C/164–165 °C, $[\alpha]_D^{26}$ −52° (*c* 0.36, $CHCl_3$); $\delta_H(CDCl_3)$ 0.01 (1 H, dd, *J* 5.5, 4.5, 29-H), 0.29 (1 H, dq, *J* 8.5, 7.0, 24-H), 0.36 (1 H, ddd, *J* 9.0, 9.0, 5.5, 22-H), 0.53 (1 H, dd, *J* 9.0, 4.5, 29-H), 0.79 (3 H, s, 18-H_3), 0.90 (3 H, s, 30-H_3), 1.18 (3 H, s, 19-H_3), 0.86 (3 H, d, *J* 6.5), 0.94 (6 H, d, *J* 7.0), 2.03, 2.04 and 2.05 (each 3 H, s, OAc), 4.07 and 4.16 (each 1 H, dd, *J* 11.0, 3.5, 21-H_2), 4.59 (1 H, m, 3α-H), 5.39 (1 H, dd, *J* 11.5, 5.0, 11β-H) and 5.49 (1 H, m, 6-H); *m/z* 600 (M^+), 540, 522, 498, 480, 462, 420, 402, 387 and 120 (Found: M^+, 600.3978. $C_{36}H_{56}O_7$ requires M, 600.4026).

Crystallographic Analysis of Andamansterol **3**.—Crystal data, $C_{30}H_{50}O_4$, M = 474.37, orthorhombic, *a* = 13.154(3), *b* = 31.910(7), *c* = 6.432(2) Å, *V* = 2700(1) Å^3, *Z* = 4, D_c = 1.168 g cm^{-3}, *F*(000) = 1048, space group $P2_12_12_1$. A crystal of approximate dimensions 0.31 × 0.22 × 0.09 mm was mounted on an Enraf-Nonius CAD4 diffractometer and intensity data were measured using graphite-monochromatized Mo-*K*α radiation, λ = 0.710 73 Å, in the ω-scan mode within 2θ < 55°. 2164 Independent reflections were considered as observed [$|F_o| > 4\sigma(|F_o|)$]. The structure was solved by direct methods with MULTAN 78 and refined using the block-diagonal least-squares method to give a final *R*-factor of 0.072 (R_w 0.069). The refined fractional atomic co-ordinates are shown in Table 2, bond lengths in Table 3, and bond angles in Table 4, and the resulting molecular structure is illustrated in Fig. 1.*

* *Supplementary data* (see section 5.6.3 of Instructions for Authors, January issue). Tables of thermal parameters are available from the Cambridge Crystallographic Data Centre.

Table 2 Fractional atomic co-ordinates (× 10^4) for compound **3**, with estimated deviations in parenthesis

	x	*y*	*z*
O(1)	−613(3)	2 852(1)	5 131(9)
O(2)	3 903(3)	3 044(1)	5 139(8)
O(3)	4 117(3)	2 588(1)	1 133(8)
O(4)	8 211(4)	2 998(1)	1 504(9)
C(1)	2 106(5)	2 708(2)	3 283(14)
C(2)	941(5)	2 641(2)	3 300(13)
C(3)	479(5)	2 915(2)	4 956(12)
C(4)	706(5)	3 375(2)	4 481(12)
C(5)	1 841(5)	3 458(2)	4 300(11)
C(6)	2 248(5)	3 771(2)	5 348(11)
C(7)	3 364(5)	3 888(2)	5 253(12)
C(8)	3 904(4)	3 696(2)	3 365(11)
C(9)	3 626(4)	3 223(2)	3 168(11)
C(10)	2 433(5)	3 166(2)	2 814(11)
C(11)	4 266(4)	3 037(2)	1 392(11)
C(12)	5 432(5)	3 109(2)	1 607(12)
C(13)	5 669(4)	3 580(2)	1 753(10)
C(14)	5 040(5)	3 741(2)	3 631(11)
C(15)	5 470(5)	4 185(2)	3 995(13)
C(16)	6 624(5)	4 140(2)	3 529(13)
C(17)	6 778(5)	3 699(2)	2 501(11)
C(18)	5 421(5)	3 807(2)	−317(12)
C(19)	2 157(5)	3 274(2)	528(12)
C(20)	7 610(5)	3 708(2)	790(11)
C(21)	7 829(5)	3 271(2)	−97(13)
C(22)	8 620(5)	3 892(2)	1 571(12)
C(23)	9 014(5)	4 333(2)	1 206(11)
C(24)	9 718(5)	4 502(2)	2 903(12)
C(25)	10 462(5)	4 845(2)	2 133(16)
C(26)	11 195(7)	4 985(3)	3 881(20)
C(27)	11 096(7)	4 705(3)	212(21)
C(28)	9 101(7)	4 661(3)	4 749(16)
C(29)	9 430(5)	3 971(2)	36(14)
C(30)	8 364(5)	4 663(2)	90(14)

Table 3 Bond lengths (Å) for compound **3**, with estimated deviations in parenthesis

C(1)–C(2)	1.547(9)	C(1)–C(10)	1.554(9)
C(2)–C(3)	1.506(11)	C(3)–C(4)	1.530(9)
C(3)–O(1)	1.455(8)	C(4)–C(5)	1.520(9)
C(5)–C(6)	1.320(9)	C(5)–C(10)	1.544(9)
C(6)–C(7)	1.517(9)	C(7)–C(8)	1.535(10)
C(8)–C(9)	1.560(8)	C(8)–C(14)	1.511(8)
C(9)–C(10)	1.597(8)	C(9)–C(11)	1.538(9)
C(9)–O(2)	1.437(8)	C(10)–C(19)	1.553(10)
C(11)–C(12)	1.557(8)	C(11)–O(3)	1.454(7)
C(12)–C(13)	1.536(8)	C(13)–C(14)	1.552(9)
C(13)–C(17)	1.583(8)	C(13)–C(18)	1.551(10)
C(14)–C(15)	1.543(8)	C(15)–C(16)	1.553(10)
C(16)–C(17)	1.567(10)	C(17)–C(20)	1.553(9)
C(20)–C(21)	1.534(9)	C(20)–C(22)	1.538(9)
C(21)–O(4)	1.440(9)	C(22)–C(23)	1.518(8)
C(22)–C(29)	1.505(11)	C(23)–C(24)	1.529(10)
C(23)–C(29)	1.508(10)	C(23)–C(30)	1.535(10)
C(24)–C(25)	1.549(10)	C(24)–C(28)	1.526(12)
C(25)–C(26)	1.547(14)	C(25)–C(27)	1.556(16)

Nicobarsterol **4**.—M.p. 193–194 °C, $[\alpha]_D^{29}$ −43° (*c* 1.36, pyridine); δ_H([$^2H_5$]pyridine) 0.76, 0.77 and 0.83 (each 3 H, d, *J* 6.5, 26-, 27- and 28-H_3), 1.06 (3 H, s, 18-H_3), 1.25 (3 H, s, 19-H_3), 2.29 (1 H, dd, *J* 15.0, 5.5, 12-H), 2.60–2.80 (2 H, m), 2.98 (1 H, m, 4α-H), 3.26 (1 H, ddd, *J* 13.5, 5.0, 3.5, 8β-H), 3.79 (1 H, dd, *J* 12.5, 2.5, 21-H), 3.90 (1 H, m, 3α-H), 4.04 (1 H, dd, *J* 12.5, 10.0, 21-H), 4.34 (1 H, ddd, *J* 10.0, 10.0, 3.5, 6β-H) and 5.59 (1 H, dd, *J* 8.5, 5.5, 11-H); δ_H($CDCl_3$) 0.773, 0.776 and 0.847 (each 3 H, d, *J* 7.0, 26-, 27- and 28-H_3), 0.83 (3 H, s, 18-H_3), 1.19 (3 H, s, 19-H_3), 1.77 (1 H, dd, *J* 14.5, 5.5, 12-H), 2.90 (1 H, ddd, *J* 13.5, 5.0, 3.5, 8β-H), 3.54 (1 H, dd, *J* 13.0, 2.5, 21-H), 3.55 (1 H, m, 3α-H), 3.69 (1 H, dd, *J* 13.0, 9.5, 21-H), 3.95 (1 H, ddd, *J* 10.0, 10.0, 4.5, 6β-H) and 5.11 (1 H, dd, *J* 8.5, 5.5, 11-H); *m/z* 464 (M^+), 446, 418, 321, 305, 281, 263, 251, 248, 208 and 199 (Found: M^+, 464.3477. $C_{28}H_{48}O_5$ requires M, 464.3502).

Table 4 Bond angles (°) for compound **3**, with estimated deviations in parenthesis

C(2)–C(1)–C(10)	113.9(0.5)	C(1)–C(2)–C(3)	108.9(0.6)
O(1)–C(3)–C(2)	111.9(0.6)	O(1)–C(3)–C(4)	109.9(0.5)
C(2)–C(3)–C(4)	109.7(0.6)	C(3)–C(4)–C(5)	111.9(0.5)
C(4)–C(5)–C(6)	119.3(0.6)	C(4)–C(5)–C(10)	116.0(0.5)
C(6)–C(5)–C(10)	124.7(0.6)	C(5)–C(6)–C(7)	124.0(0.6)
C(6)–C(7)–C(8)	112.4(0.6)	C(7)–C(8)–C(9)	110.1(0.5)
C(7)–C(8)–C(14)	109.3(0.5)	C(9)–C(8)–C(14)	109.5(0.5)
O(2)–C(9)–C(8)	104.7(0.5)	O(2)–C(9)–C(10)	109.2(0.5)
O(2)–C(9)–C(11)	111.3(0.5)	C(8)–C(9)–C(10)	110.6(0.5)
C(8)–C(9)–C(11)	107.8(0.5)	C(10)–C(9)–C(11)	112.9(0.5)
C(1)–C(10)–C(5)	107.9(0.5)	C(1)–C(10)–C(9)	110.5(0.5)
C(1)–C(10)–C(19)	109.2(0.6)	C(5)–C(10)–C(9)	109.8(0.5)
C(5)–C(10)–C(19)	109.5(0.5)	C(9)–C(10)–C(19)	109.8(0.5)
O(3)–C(11)–C(9)	113.1(0.5)	O(3)–C(11)–C(12)	106.8(0.4)
C(9)–C(11)–C(12)	114.6(0.5)	C(11)–C(12)–C(13)	110.5(0.5)
C(12)–C(13)–C(14)	105.3(0.5)	C(12)–C(13)–C(17)	116.2(0.5)
C(12)–C(13)–C(18)	111.2(0.5)	C(14)–C(13)–C(17)	100.0(0.5)
C(14)–C(13)–C(18)	113.6(0.5)	C(17)–C(13)–C(18)	110.0(0.5)
C(8)–C(14)–C(13)	114.0(0.5)	C(8)–C(14)–C(15)	117.8(0.5)
C(13)–C(14)–C(15)	103.2(0.5)	C(14)–C(15)–C(16)	104.1(0.5)
C(15)–C(16)–C(17)	106.9(0.5)	C(13)–C(17)–C(16)	103.1(0.5)
C(13)–C(17)–C(20)	116.0(0.6)	C(16)–C(17)–C(20)	112.0(0.5)
C(17)–C(20)–C(21)	112.4(0.5)	C(17)–C(20)–C(22)	112.6(0.6)
C(21)–C(20)–C(22)	107.9(0.5)	O(4)–C(21)–C(20)	110.5(0.6)
C(20)–C(22)–C(23)	126.8(0.6)	C(20)–C(22)–C(29)	116.8(0.6)
C(23)–C(22)–C(29)	59.8(0.4)	C(22)–C(23)–C(24)	115.0(0.6)
C(22)–C(23)–C(29)	59.7(0.5)	C(22)–C(23)–C(30)	125.2(0.5)
C(24)–C(23)–C(29)	115.3(0.5)	C(24)–C(23)–C(30)	115.5(0.5)
C(29)–C(23)–C(30)	118.7(0.6)	C(23)–C(24)–C(25)	113.8(0.6)
C(23)–C(24)–C(28)	110.5(0.6)	C(25)–C(24)–C(28)	110.5(0.6)
C(24)–C(25)–C(26)	111.4(0.8)	C(24)–C(25)–C(27)	112.9(0.7)
C(26)–C(25)–C(27)	109.0(0.7)	C(22)–C(29)–C(23)	60.5(0.5)

$Pb(OAc)_4$ *Treatment of compound* **3**.—$Pb(OAc)_4$ (95 mg) was added, in portions, to a stirred solution of andamansterol **3** (15 mg) in $CHCl_3$ (15 cm^3) during 2.5 h at room temperature. The mixture was filtered and the filtrate was washed successively with water, 5% aq. K_2CO_3, water, and saturated aq. NaCl. Evaporation of the solvent gave a residue (14.5 mg), which was crystallized from MeOH, m.p. 198–200 °C; $[\alpha]_D^{25}$ −46° (*c* 0.31, pyridine); δ_H([$^2H_5$]pyridine) 0.86, 0.93 and 0.99 (each 3 H, d, *J* 7.0, 26-, 27- and 28-H_3), 0.90 (3 H, s, 30-H_3), 1.06 (3 H, s, 18-H_3), 1.34 (3 H, s, 19-H_3), 2.34 (1 H, dd, *J* 15.0, 6.0, 12-H), 3.19 (1 H, dt, *J* 12.0, 6.0, 8-H), 3.83 (1 H, m, 3α-H), 3.86 (1 H, dd, *J* 12.5, 3.5, 21-H), 4.22 (1 H, dd, *J* 12.5, 10.5, 21-H), 5.50 (1 H, m, 6-H) and 5.63 (1 H, dd, *J* 8.5, 5.5, 11-H); *m/z* 472 (M^+), 454, 442, 383, 371, 303 and 120 (Found: M^+, 472.3576. $C_{30}H_{48}O_4$ requires M, 472.3552).

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