Juncins G and H: new briarane diterpenoids of the Indian Ocean gorgonian *Junceella juncea* Pallas

Ammanamanchi S. R. Anjaneyulu* and Nidasanametla S. Kameswara Rao

School of Chemistry, Andhra University, Visakhapatnam-533 003, India

Chemical examination of the Indian Ocean gorgonian, *Junceella juncea* furnishes two new diterpenoids of the briarane skeleton, juncin G, 1 and juncin H, 3 along with the antipodal derivatives of known gemmacolides A, 4 and B, 2. The structures of juncin H and G are shown to be (1*S*,2*S*,6*S*,8*R*,9*S*,10*S*,11*R*,12*R*,14*R*,17*R*)-6-chloro-11,20-epoxy-14-(3-methylbutanoyl)-2,9,12-triacetoxy-8-hydroxybriar-5(16)-en-18,7-olide and (1*S*,2*S*,6*S*,9*S*,10*S*,12*R*,13*R*,14*R*)-6-chloro-13-(3-methylbutanoyl)-2,9,12,14-tetraacetoxybriaran-4,8(17)-dien-18,7-olide, respectively, by a comparative study of their spectral data. For the first time, three polyhydroxy sterols 6–8 are also isolated from this species.

Introduction

The briaranes are a group of highly oxygenated diterpenoids having a modified cembranoid carbocyclic system. A large number of briaranes have been reported from gorgonians, soft corals and sea pens.[1] So far, four species of the gorgonians of *Junceella* genus have been chemically examined and reported to contain these briarane derivatives.[2] *J. juncea* Pallas[3] (Gorgonaceae) collected from the sites in the entrances to the Gulf of Eilat and Gulf of Suez, Red Sea has been reported to yield six new briaranes Juncins A–F. Recently 10 new briarane diterpenoids have been reported from the common Caribbean gorgonian *Briareum asbestinum*.[4]

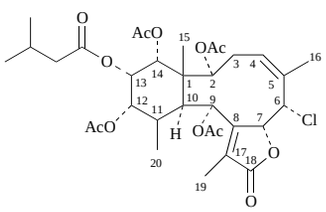
Results

In our continuing interest[5] on the bioactive secondary metabolites of marine organisms of the Indian Ocean, we have undertaken the chemical examination of *J. juncea* collected from the Mandapam coast (9° 16′ N, 79° 12′ E) and report herein the isolation of four briarane diterpenoids A–D in addition to three polyhydroxy steroids E–G. While two of the diterpenoids have been found to be new, all the four, surprisingly, are related to gemmacolides isolated from *J. gemmacea*[6] rather than to the juncins reported from *J. juncea*.[3]

The residue from the initial methanolic extract of the organism was re-extracted into ethyl acetate and the residue from it was chromatographed over a column of silica gel to furnish the following seven compounds. Compound A an oil (9 mg), compound B as colourless granules (58 mg), compound C as colourless cubes (70 mg), compound D as colourless needles (30 mg), compound E as colourless needles (125 mg), compound F as colourless needles (75 mg) and compound G as colourless needles (80 mg).

Discussion

Compound B, $C_{33}H_{45}ClO_{14}$, mp 298–300 °C, $[\alpha]_D^{25}$ +5.3† (*c* 0.44 in $CHCl_3$) and compound D, $C_{30}H_{39}ClO_{14}$, mp 273–75 °C, $[\alpha]_D^{25}$ +2.4 (*c* 0.20 in $CHCl_3$) were recognized as briarane diterpenoids from their spectral characteristics (Table 1 and 2) which were found to be exactly identical with those of gemmacolide B[6] and gemmacolide A[6], respectively, confirming their identity. However, they differed in their physical state and sign of specific rotation. Compound B and compound D could be obtained as crystalline solids with antipodal specific rotation to gem-



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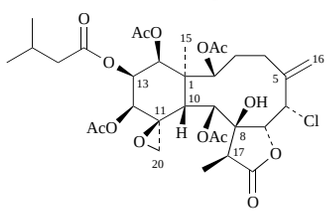

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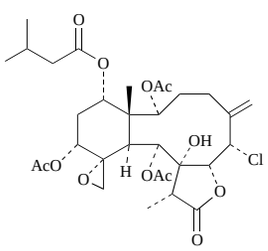

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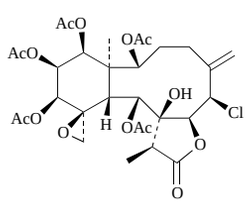

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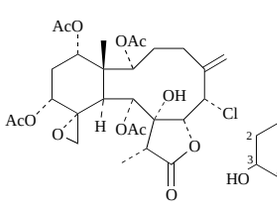

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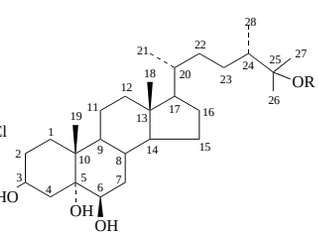
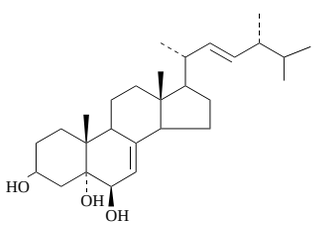


6 R = Ac
7 R = H



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† [*α*] Values in units of 10^{-1} deg cm^2 g^{-1}.

Table 1 ^{1}H NMR data of compounds A **1**, B **2**, C **3**, D **4** and **5** in $CDCl_3$, TMS as reference at 400 MHz, chemical shift (δ), J in brackets in Hz

Assignment	A	B	C	D	**5**
2-H	5.80 (br d, 10)	5.90 (br d, 8.2)	5.92 (br d, 8.3)	5.91 (br d, 8.3)	5.97 (br d, 8.3)
16-H	—	5.80 (br s)	5.82 (br s)	5.80 (br s)	5.82 (br s)
9-H	5.60 (d, 13)	5.70 (br s)	5.78 (br s)	5.71 (br s)	5.76 (br s)
16-H	—	5.50 (br s)	5.62 (br s)	5.51 (br s)	5.58 (br s)
13-H	5.25 (d, 6)	5.24 (br s)	2.20 (2 H, m)	5.22 (br s)	2.24 (m, 2 H)
14-H	5.25 (d, 6)	5.24 (br s)	4.96 (br s)	5.24 (br s)	4.91 (br s)
12-H	4.87 (br, s)	4.84 (br s)	4.60 (br s)	4.84 (br s)	4.55 (dd, 2.9, 1.8)
6-H	4.78 (br d, 5.5)	4.61 (br d, 2.9)	4.65 (br s)	4.61 (br s)	4.62 (brd, 3.2)
7-H	4.70 (d, 5.6)	4.45 (br s)	4.45 (br s)	4.44 (br s)	4.45 (br s)
10-H	3.30 (d, 6.6)	3.67 (br s)	3.66 (br s)	3.67 (br s)	3.70 (br s)
8-OH	—	3.48 (s)	3.45 (s)	3.48 (s)	3.44 (s)
17-H	—	2.95 (q, 6.8)	2.96 (m)	2.96 (m)	2.96 (q, 6.8)
20-H	—	2.93 (d, 3.7)	2.85 (d, 3.2)	2.94 (br s)	2.83 (d, 3.2)
3-H	2.75 (m)	2.70 (m)	2.74 (m)	2.70 (m)	2.72 (m)
11-H	2.49 (q)	—	—	—	—
4-H	5.05 (br s)	2.45 (2 H, m)	2.48 (2 H, m)	2.45 (2 H, m)	2.45 (2 H, m)
20-H	1.15 (3.6)	2.38 (d, 3.6)	2.36 (d, 3.2)	2.38 (d, 3.6)	2.36 (d, 3.2)
OAc	2.23 (s)	2.22 (s)	2.23 (s)	2.23 (s)	2.23 (s)
OAc	2.22 (s)	2.02 (s)	2.01 (s)	2.07 (s)	2.01 (s)
2′-H_2	2.20 (m)	2.06 (m)	2.1 (m)	—	—
OAc	2.00 (s)	2.01 (s)	2.02 (s)	2.02 (6 H, s)	2.01 (s)
OAc	1.99 (s)	2.00 (s)	—	1.95 (s)	1.96 (s)
3′-H	2.18 (m)	1.99 (m)	2.08 (m)	—	—
3-H	—	1.63 (m)	1.63 (m)	1.64 (m)	1.61 (m)
19-H_3	1.60 (s)	1.26 (d, 6.8)	1.26 (d, 6.8)	1.26 (d, 6.8)	1.27 (d, 6.8)
16-H_3	1.60 (s)	—	—	—	—
15-H_3	1.15 (s)	1.25 (s)	1.20 (s)	1.25 (s)	1.16 (s)
4′ and 5′-H_3	0.92 (d, 6.5)	0.92 (d, 6.5)	0.95 (d, 6.5)	—	—

Table 2 ^{13}C NMR data of compounds B **2**, C **3**, D **4** and **5** in $CDCl_3$ at 22.5 MHz

Carbon no.	B	C	D	**5**
1	47.4 (s)	47.9 (s)	47.2 (s)	47.8 (s)
2	72.7 (d)*	73.3 (d)*	72.7 (d)*	73.1 (d)
3	28.3 (t)	28.3 (t)	28.2 (t)	28.2 (t)
4	33.5 (t)	33.6 (t)	33.4 (t)	33.6 (t)
5	146.8 (s)	146.9 (s)	146.6 (s)	146.9 (s)
6	53.6 (d)	53.9 (d)	53.7 (d)	53.9 (d)
7	71.9 (d)	71.8 (d)	71.3 (d)	71.8 (d)
8	81.3 (s)	81.6 (s)	81.1 (s)	81.2 (s)
9	81.5 (d)	81.3 (d)	81.4 (d)	81.1 (d)
10	51.4 (d)	51.4 (d)	51.4 (d)	51.5 (d)
11	56.9 (s)	57.8 (s)	56.8 (d)	57.5 (s)
12	73.7 (d)*	73.5 (d)*	73.6 (d)*	73.5 (d)
13	66.6 (d)	29.6 (t)	66.8 (d)	29.1 (t)
14	73.2 (d)*	72.9 (d)*	73.0 (d)*	73.3 (d)
15	14.2 (q)	14.1 (q)	14.2 (q)	14.0 (q)
16	121.1 (t)	120.8 (t)	121.1 (t)	121.2 (t)
17	35.4 (d)	35.7 (d)	35.3 (d)	35.5 (d)
18	174.4 (s)	174.7 (s)	174.3 (s)	174.6 (s)
19	5.9 (q)	5.9 (q)	6.0 (q)	5.9 (q)
20	50.4 (t)	50.7 (t)	50.4 (t)	50.3 (t)
OAc	171.3 (s)*	170.8 (s)	171.3 (s)	171.0 (s)
	170.0 (s)	169.5 (s)	170.2 (s)	170.4 (s)
	169.3 (2s)	169.4 (s)	169.7 (3s)	169.5 (2s)
	21.6 (q)	21.3 (q)	21.6 (q)	21.1 (2q)
	21.2 (q)	21.2 (q)	21.2 (2q)	20.9 (2q)
	20.7 (2q)	20.9 (q)	20.6 (2q)	
1′	171.7 (s)*	172.3 (s)		
2′	42.7 (t)	43.2 (t)		
3′	25.0 (d)	24.7 (d)		
4′ and 5′	22.3 (2q)	22.5 (q)		

Multiplicities are assigned by the DEPT spectrum. * Close δ_C values may be interchangeable.

macolide B and gemmacolide A which were obtained as clear oils. A similar behaviour between antipodal substances was earlier observed in cembranoid derivatives.[7] The structures of compound B and compound D could then be regarded as (+)-gemmacolide B, **2** and (+)-gemmacolide A, **4** respectively.

Compound C, $C_{31}H_{43}ClO_{12}$, mp 250–252 °C $[\alpha]_D^{25}$ +9.8 (*c* 0.53 in $CHCl_3$), $[MH]^+$ 643 was recognized as a new briarane diterpenoid having close structural similarity to gemmacolide B **2** and gemmacolide C **5** which differed in themselves, the former having an additional isovalerate group at C-13 while both are tetraacetates. It was designated as juncin H.

The ^{1}H and ^{13}C NMR spectra (Table 1 and 2) of juncin H supported the presence of three secondary acetates and an isovalerate group besides the other common functionalities such as an exocyclic methylene, a γ-lactone *etc*. as found in gemmacolide B[6] **2** and gemmacolide C[6] **5**. A careful examination of its ^{1}H and ^{13}C NMR as well as its 2D NMR (^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY and NOESY, Table 3) data and comparison of the same with those of gemmacolide B and gemmacolide C established its structure. The chemical shifts of the geminal protons over the ester groups in juncin H were found to be nearly identical with those reported for gemmacolide C **5**. In particular, the two protons at C-13 in between C-12 and C-14 appeared at higher field in support of the absence of an ester group at C-13 which was further supported by the observation of the ^{1}H-^{1}H COSY connectivity of both 12-H and 14-H with 13-H_2 and NOESY coupling between 12-H and 14-H (Table 3 and Figs. 1 and 2).

The main problem was to locate the isovalerate group at one of the positions C-2, C-9, C-12 or C-14 and the three acetates, consequently, at the remaining three positions. The ^{1}H chemical shifts of H-2 and H-9 and the ^{13}C chemical shifts of C-2 and C-9 remained identical with the corresponding carbons in gemmacolide C enabling us to locate two of the acetates at these places. The remaining problem was to locate the third acetate at C-12 and isovalerate at C-14 or *vice-versa*. The chemical shifts of the carbons were found to be more or less similar irrespective of the type of ester group attached making their location difficult.[6] However, Faulkner and He[6] noticed a small difference of 0.3 ppm on the carbon with an isovalerate group appearing at higher field compared to that of an acetate group. A similar upfield shift (0.4 ppm) was, in fact, observed in the value of C-14 of juncin H compared to that in gemmacolide C while the C-12 appeared at the same place in both. From this, the isova-

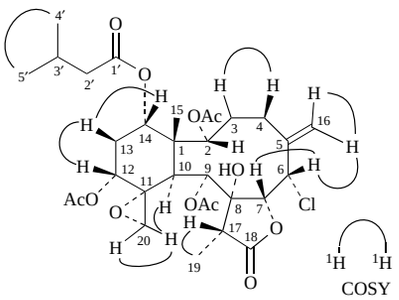

Fig. 1

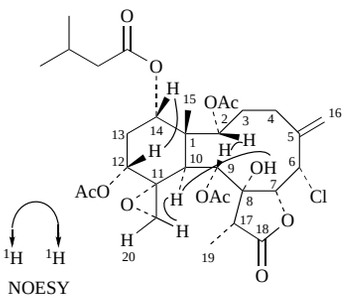

Fig. 2

lerate group could be located at C-14 in compound C. Thus, juncin H is related to gemmacolide C in having an isovalerate group at C-14 in place of an acetate at the same place in the latter. Juncin H and gemmacolide C had more or less identical ^{1}H, ^{13}C and 2D NMR data so allowing the structure and relative stereochemistry of the former to be assigned as **3**.

Compound A was obtained as a colourless oil, $C_{33}H_{45}ClO_{12}$, $[\alpha]_D^{25}$ +55.2 (*c* 0.27 in $CHCl_3$), in very small quantity giving access only to limited spectral data (UV, IR, ^{1}H and FABMS) to result in assignment of a tentative structure for the molecule. It could also be recognized as a new briarane diterpenoid from its ^{1}H NMR spectral results and allowed us to designate it as juncin G. As in gemmacolide B, it exhibited four acetate groups and an isovalerate group, but without an exocyclic methylene at C-5 and the epoxide at C-11. In the place of these, it showed a methyl on a trisubstituted double bond (possibly rearranged from the exocyclic methylene) and a secondary methyl. Juncin G also showed the absence of a tertiary hydroxy group at C-8 which by possible dehydration gave a methyl on the double bond at C-17. The presence of an α,β-unsaturated five-membered lactone was also supported from its UV absorption at 240 nm. A comparative study of the ^{1}H NMR spectral data of juncin G and gemmacolide B revealed that the former might have been derived from the latter with which it is co-occurring, by the elimination of a hydroxy group and rearrangement of the exocyclic methylene.

Compounds E–G were found to be polyhydroxy steroids. Compound E, $C_{30}H_{52}O_5$, mp 240–242 °C, $[\alpha]_D^{25}$ −17.9 (*c* 1.5 in MeOH); compound F, $C_{28}H_{50}O_4$, mp 260–262 °C, $[\alpha]_D^{25}$ −21.3 (*c* 0.3 in MeOH) and compound G, $C_{28}H_{46}O_3$, mp 221–224 °C, $[\alpha]_D^{25}$ −64.8 (*c* 1.44 in pyridine) could be characterized as 24-methylcholestane-3β,5α,6β,25-tetrol 25-monoacetate[8] **5**; 24-methylcholestane-3β,5α,6β,25-tetrol[8] **6** and (22*E*,24*R*)-24-methylcholesta-7,22-diene-3β,5α,6β-triol[9] **7** respectively by a comparative study of their physical and spectral data with those reported in the literature.

Gorgonians are known to elaborate polyhydroxy steroids[10] but so far no polyhydroxy steroid has been reported from the genus *Junceella*. Thus, this forms the first report of the occurrence of polyhydroxy steroids E–G from *J. juncea*.

Experimental

Mps were determined on a VEB Analytik Dresden HMK hot-stage apparatus and are uncorrected. Optical rotations were determined on a JASCO DIP-370 digital polarimeter. Elemental analyses were determined on a Carlo Erba-1108 instrument. IR spectra were recorded on a JASCO FT IR-5300 instrument, UV spectra were obtained with a Milton Roy Spectronic 1201 Spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker spectrometer using $SiMe_4$ as internal standard. ^{13}C NMR were recorded on a JEOL JNM EX-90 spectrometer at 22.5 MHz and Fast Atom Bambardment Mass Spectroscopy (FABMS) was carried out with JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol as matrix at an accelarating voltage of 10 kV. Column chromatography was performed on silica gel of 100–200 mesh.

Table 3 2D NMR (^{1}H-^{1}H COSY at 300 MHz and ^{1}H-^{13}C COSY & NOESY at 90 MHz) correlation data* of compound C (juncin H, **3**) in $CDCl_3$

^{1}H-^{1}H COSY	^{1}H-^{13}C COSY	NOESY
2 H, 3 H	2 H-C_2	2 H, 9 H
16 H, 16 H	16 H_a-C_{16}	12 H, 14 H
16 H, 6 H	9 H-C_9	10-H, 8-OH
6 H, 7 H	16 H_b-C_{16}	20-H, 10-H
13 H, 14 H	14 H-C_{14}	
12 H, 13 H	6 H-C_6	
10 H, 20 H	12 H-C_{12}	
20 H, 20 H	7 H-C_7	
17 H, 19 H_3	10 H-C_{10}	
4′ H_3, 5′ H_3	17 H-C_{17}	
3 H, 4 H	4 H_2-C_4	
	20 H-C_{20}	
	13 H_2-C_{13}	
	2′ H_2-$C_{2'}$	
	15 H_3-C_{15}	
	19 H_3-C_{19}	
	4′ H_3-$C_{4'}$	
	5′ H_3-$C_{5'}$	

* ^{1}H-^{1}H COSY and NOESY correlations of juncin H are represented diagrammatically in Fig. 1 and Fig. 2, respectively.

Extraction and isolation

The gorgonian *Junceella juncea* was collected from Mandapam coast in April 1993. The freshly collected species were washed thoroughly with fresh water and shade dried. The organism was sliced and treated several times with methanol in a Soxhlet apparatus. The combined alcoholic extract (8 l) was distilled under reduced pressure. The residue from the combined alcoholic extract was fractionated with ethyl acetate. The ethyl acetate extract (30 g) was dried ($MgSO_4$) and chromatographed over a silica gel (100–200 mesh; 300 g) column using solvents of increasing polarity from hexane through benzene to ethyl acetate. The selected fractions were further purified by passage through a silica gel column or by recrystallization to yield seven pure compounds.

Compound A, juncin G 1. Colourless oil (9 mg); $[\alpha]_D^{25}$ +55.2 (*c* 0.27 in $CHCl_3$) (Found: C, 59.2; H, 6.79. $C_{33}H_{45}ClO_{12}$ requires C, 59.28; H, 6.74%); $\lambda_{max}(CHCl_3)$/nm 242; $\nu_{max}(CHCl_3)$/cm^{-1} 1760–1745 (OAc), 1730 (α,β-unsaturated 1-γ-lactone); δ_H: see Table 1; FABMS (+ve): *m/z* 669 $[MH]^+$, 609, 549, 489, 507, 447, 565, 505, 445 and 409.

Compound B, (+)-gemmacolide B 2. Colourless granules (58 mg), mp 298–300 °C (hexane–chloroform), $[\alpha]_D^{25}$ +5.3 (*c* 0.44 in $CHCl_3$) (Found: C, 56.41; H, 6.50. Calc. for $C_{33}H_{45}ClO_{14}$: C, 56.57; H, 6.43%); $\lambda_{max}(CHCl_3)$/nm: no absorption above 200 nm; ν_{max}/cm^{-1}($CHCl_3$): 3456 (OH), 1800 (lactone), 1745 and 1226 (OAc). δ_H, δ_C: see Tables 1 and 2. FABMS (+ve): *m/z* $[MH]^+$ 701, 641, 581, 521, 539, 479, 497, 437, 419, 377 and 341.

Compound C, juncin H 3. Colourless cubes (70 mg), mp 250–252 °C (hexane–chloroform), $[\alpha]_D^{25}$ +9.8 (*c* 0.83 in $CHCl_3$) (Found: C, 57.90; H, 6.72. Calc. for $C_{31}H_{43}ClO_{12}$: C, 57.94; H, 6.69%); $\lambda_{max}(CHCl_3)$/nm: no absorption above 200 nm;

$\nu_{max}(CHCl_3)/cm^{-1}$ 3452 (OH), 1797 (lactone) and 1750 and 1238 (OAc); δ_H, δ_C and 2D NMR data: see Tables 1–3; FABMS(+ve): *m/z* $[MH]^+$ 643, 583, 523, 463, 419 and 406.

Compound D, (+)-gemmacolide A 4. Colourless flakes (30 mg); mp 273–275 °C (hexane–acetone); $[\alpha]_D^{25}$ +2.4 (*c* 0.20 in $CHCl_3$) (Found: C, 54.21; H, 5.82. Calc. for $C_{30}H_{39}ClO_{14}$: C, 54.71; H, 5.93%), $\lambda_{max}(CHCl_3)$/nm: no absorption above 200 nm; $\nu_{max}(CHCl_3)/cm^{-1}$ 3460, 1800, 1745, 1635 and 1200; δ_H, δ_C: see Tables 1 and 2; FABMS (+ve): *m/z* 659 $[MH]^+$, 641, 599, 539, 479, 419, 359 and 443.

Compound E, (24*S*)-24-methylcholestane-3β,5α,6β,25-tetrol 25-mono-acetate 6. Colourless needles (125 mg); mp 240–242 °C (chloroform–methanol); $[\alpha]_D^{25}$ −17.9 (*c* 1.5 in MeOH): *m/z* 474 ($C_{30}H_{52}O_5$, $M^+ - H_2O$); $\lambda_{max}(CHCl_3)$/nm: no absorption above 200 nm; $\nu_{max}(KBr)/cm^{-1}$ 3560–3450, 1728 and 1260; $\delta_H([^2H_5]$pyridine) 0.72 (3 H, s, 18-CH_3), 0.92 (3 H, d, *J* 7, 28-CH_3), 1.00 (3 H, d, *J* 6.5, 21-H_3), 1.48 and 1.49 (each 3H, s, 26 and 27-CH_3), 1.66 (3 H, s, 19-CH_3), 2.95 (1 H, t, *J* 13, 4β-H), 4.17 (1 H, br s, 6α-H), 4.88 (1 H, m, 3α-H) and 2.00 (3 H, s, OAc). These data are in good agreement with those reported for (24*S*)-24-methylcholestane-3β,5α,6β,25-tetrol 25-monoacetate.[8]

Compound F, (24*S*)-24-methylcholestane-3β,5α,6β,25-tetrol 7. Colourless needles (75 mg); mp 260–262 °C (chloroform–methanol); $[\alpha]_D^{25}$ −21.3 (*c* 0.3 in MeOH); *m/z* 432 ($C_{28}H_{50}O_4$, $M^+ - H_2O$); λ_{max}(MeOH)/nm: no absorption above 200 nm; $\nu_{max}(KBr)/cm^{-1}$ 3500, 2980, 1425, 1060 and 925; $\delta_H([^2H_5]$pyridine) 0.71 (3 H, s,18-CH_3), 1.07 (3 H, d, *J* 6, 28-CH_3), 1.00 (3 H, d, *J* 7, 21-H_3), 1.35 and 1.36 (each 3 H, s, 26 and 27-CH_3), 1.65 (3 H, s, 19-CH_3), 2.96 (1 H, t, *J* 12.5, 4β-H), 4.15 (1 H, br s, 6α-H) and 4.85 (1 H, m, 3α-H). Based on the above data the compound was identified as (24*S*)-24-methylcholestane-3β,5α,6β,25-tetrol.[8]

Compound G, (24*R*)-24-methylcholesta-7,22-diene-3β,5α,6β-triol 8. Colourless needles (80 mg); mp 221–224 °C (chloroform–methanol); $[\alpha]_D^{25}$ −64.8 (*c* 1.44 in pyridine); $\nu_{max}(KBr)/cm^{-1}$ 3460; $\delta_H([^2H_5]$pyridine) 5.20 (2 H, m, 22-H and 23-H), 5.08 (1 H, br s, 7-H), 4.80 (1 H, m, 3-H), 4.29 (1 H, br s, 6-H), 3.0 (1 H, dd, *J* 13, 4-H), 0.65 (3 H, s, 18-CH_3), 0.95 (3 H, d, *J* 7, 28-CH_3), 1.06 (3 H, d, *J* 7, 21-H_3), 1.35 and 1.86 (6 H, d, *J* 7, 26 and 27-CH_3) and 1.50 (3 H, s, 19-CH_3); based on the above data, the compound was identified as (24*R*)-24-methylcholesta-7,22-diene-3β,5α,6β-triol.[9]

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