JOURNAL OF NATURAL PRODUCTS

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J. Nat. Prod., **1991**, 54 (2), 364-371• DOI: 10.1021/np50074a002 • Publication Date (Web): 01 July 2004

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Journal of Natural Products
Vol. 54, No. 2, pp. 364-371, Mar-Apr 1991

METABOLITES OF PORIFERA, PART III.[1] NEW 24-METHYLSCALARANES FROM *PHYLLOSPONGIA DENDYI* OF THE INDIAN OCEAN

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ABSTRACT.—Three new scalaranes, 12β,16β,22-trihydroxy-24-methylscalaran-25,24-olide [**2**], 12β,16β-dihydroxy-24-methylscalaran-25,24-olide [**3**], and 12β,16β,22-trihydroxy-24-methyl-24-oxo-25-norscalarane [**4**], as well as the known 16β,22-dihydroxy-24-methyl-24-oxoscalaran-25,12β-olide [**1**], are reported from the sponge *Phyllospongia dendyi* collected on the coasts of the Andaman and Nicobar Islands in the Indian Ocean. Structural elucidation of these compounds is based on spectral data and chemical conversions.

The occurrence of sesterterpenes in nature is somewhat uncommon, but for the last two decades an increasing number of examples have been reported. Interestingly, many of the recent additions have been isolated from marine sponges of the order Dictyoceratida (3,4). These metabolites may be listed in two main groups: (1) linear sesterterpene molecules terminated by a furan ring at one end and by a tetranoic acid or lactone ring at the other end and (2) tetra- or pentacyclic sesterterpenes, analogues of the scalarane skeleton. Sponges of the genus *Phyllospongia* are known to produce scalarane-type sesterterpenes (6–8). A C_{22}-furanoterpene, furodendin, and two scalarane derivatives are reported from two *Phyllospongia* spp. *Phyllospongia dendyi* Lendenfeld provided 24-methyl-24,25-dioxoscalar-16-en-12β-yl-3-hydroxybutanoate and 12α-acetoxy-24-methyl-24-oxoscalar-16-en-25-al (5,6). The former scalarane derivative was found to be responsible for the biological activity of the crude extract, which showed antifungal and anti-inflammatory properties. Foliaspongin, an anti-inflammatory bishomosesterterpene possessing a 4α-ethyl group, was isolated from *Phyllospongia foliascens* (7,8).

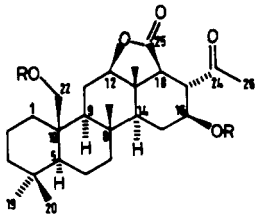
In a continuing investigation on the metabolites of the Porifera from the Indian Ocean (1,2), we have reported from *P. dendyi* three C_{21} furanoterpenes (2), and we report in this paper the structural elucidation of four scalarane derivatives isolated from the same source.

RESULTS AND DISCUSSION

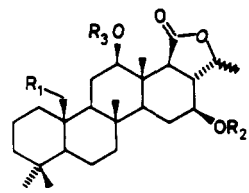
The sponge *P. dendyi* was collected at Andaman and Nicobar Islands of the Indian Ocean during December 1986 and extracted with 95% aqueous EtOH. The EtOAc-soluble material from the EtOH extract was chromatographed over Si gel using solvents of increasing polarity from petroleum ether through C_6H_6 to EtOAc to obtain four sesterterpenes **1–4** in addition to three C-21 furanoterpenes already reported (2).

Compound **1** was obtained as colorless crystals from MeOH, mp 280–282°, analyzed for $C_{26}H_{40}O_5$ (*m/z* 432 $[M]^+$), $[\alpha]^{25}D$ +45° (*c* = 1 in MeOH). It possesses two hydroxylated carbons indicated by ir 3510 (br) cm^{-1} and the corresponding carbon resonances at δ 74.3 and 60.7; a γ-lactone moiety indicated by ir at 1770 cm^{-1} and carbon resonances at δ 175.3 and 89.6; an acetyl function indicated by ^1H resonance at

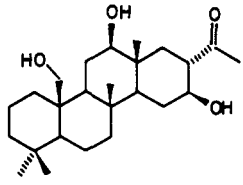
[1]For Part I, see Kalidindi *et al.* (1); for Part II, see Rao *et al.* (2).



1 R=H
5 R=Ac



2 R_1=OH, R_2=R_3=H
6 R_1=OAc, R_2=R_3=H
8 R_1=OH, R_2=Ac, R_3=H
7 R_1=OAc, R_2=Ac, R_3=H
9 R_1=OAc, R_2=R_3=Ac
3 R_1=R_2=R_3=H



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δ 2.22 (3H, s); carbonyl carbon resonance at δ 209.6 with an ir band at 1710 cm^{-1}; and four tertiary methyl proton signals at δ 0.77, 0.85, 0.86, and 1.06. The presence of a *gem*-dimethyl unit was also revealed by the ir absorption at 1385, 1390, 1185, and 1220 cm^{-1}. The ^1H nmr showed four single proton signals at δ 3.61 (bs), 3.81 (d, 12 Hz), 3.68 (d, 12 Hz), and 3.80 (m). It gave a diacetate (mp 194–196°) on treatment with pyridine/Ac_2O. The spectral data of compound **1** and its diacetate corresponded very well with those recorded for 16β,22-dihydroxy-24-methyl-24-oxoscalaran-25,12β-olide [**1**] and its diacetate **5** (9).

Compound **2** appeared as colorless crystals from MeOH: mp 313–316°, analyzed for $C_{26}H_{42}O_5$ (*m/z* 434 $[M]^+$), $[\alpha]^{25}D$ +15.8° (*c* = 0.91, pyridine). Its ir spectrum showed bands at 3620, 3340, 3270 (hydroxyls), and 1715 cm^{-1} (lactone carbonyl which is involved in intramolecular hydrogen bonding). The ^1H-nmr spectrum exhibited four tertiary methyls (δ 0.77, 0.85, 0.87, and 0.92, each s), a secondary methyl (δ 1.44, d, 6 Hz), a hydroxymethyl [δ 3.77 (1H, d, 12 Hz), 3.64 (1H, d, 12 Hz)], and a lactone methine [δ 4.37 (1H, dq, *J* = 10, 6 Hz)]. The ^{13}C-nmr spectrum showed four oxygenated carbons at δ 81.5, 78.9, 70.5, and 60.1 and a lactone carbonyl at δ 178.6. The data suggest that compound **2** is also a 24-methylscalarane derivative. The absence of an acetyl group and presence of lactone methine and secondary methyl on an oxygenated carbon in compound **2** strongly indicate a lactone involving C-24 and C-25.

On acetylation with pyridine/Ac_2O at room temperature, compound **2** gave a mixture of two monoacetates and a diacetatae. The spectral data of one of the acetates are found to be identical with those recorded for 22-acetoxy-12β,16β-dihydroxy-24-methylscalaran-25,24-olide [**6**] isolated from *Lendenfeldia* species (9). The diacetate has been found to be identical with 16β,22-diacetoxy-12β-hydroxy-24-methylscalaran-25,24-olide [**7**] prepared from **6** (9). The other monoacetate was, however, described as 16β-acetoxy-12β,22-dihydroxy-24-methylscalaran-25,24-olide [**8**] based on its nmr studies, and it was not reported in literature.

However, when acetylation of compound **2** was performed under reflux using Ac_2O/pyridine, a mixture of the diacetate **7** and triacetate **9** (ca. 3:1) was obtained. In the triacetate **9** the C-12 and C-25 resonances were shifted upfield by about 1.3 and 5.5 ppm, respectively, upon acetylation of the C-12 hydroxyl, and the ir absorption of the

lactone carbonyl was shifted to 1775 cm^{-1}. This can be accounted for by the presence of intramolecular hydrogen bonding between the lactone carbonyl and 12-OH in compound **2**; this bonding was not there in compound **9**. Compound **2** may now be described as 12β,16β,22-trihydroxy-24-methylscalaran-25,24-olide [**2**]. The stereochemistry at carbons 17 and 18 in compound **2** is based on the multiplicities and coupling constants of H-17 (δ 2.27, ddd, J = 10, 10, 14 Hz) and H-18 (δ 2.36, d, 14 Hz).

Compound **3** was obtained as colorless crystals from petroleum ether/$CHCl_3$, mp 282–285°, analyzed for $C_{26}H_{42}O_4$ (*m/z* 418 $[M]^+$), $[\alpha]^{25}D$ +11.0° (*c* = 0.13 in $CHCl_3$). Its ir spectrum contained bands at 3540 and 3420 (hydroxyls) and 1720 cm^{-1} (lactone carbonyl, which is involved in intramolecular hydrogen bonding). The ^{1}H-nmr spectrum exhibited five tertiary methyls [δ 0.80 (3H), 0.85 (9H), 1.00 (3H), each s], a secondary methyl (δ 1.6, d, 6 Hz), and a lactone methine at δ 4.35 (1H, dq, J = 10, 6 Hz). The conspicuous absence of hydroxy methylene protons and an oxygen-bearing carbon around 61.0 ppm and presence of an additional tertiary methyl in compound **3** lead to the structure **3** and account for all the data given above. Hence compound **3** could be described as 12β,16β-dihydroxy-24-methylscalaran-25,24-olide [**3**]. This compound is a new 24-methylscalarane derivative.

Compound **4** appeared as colorless crystals from MeOH, mp 288–291°, and analyzed for $C_{25}H_{42}O_4$ (*m/z* 406 $[M]^+$). It possesses hydroxyls indicated by ir bands at 3520, 3400 (br) cm^{-1} and a carbonyl function at 1690 cm^{-1}. The ^{1}H-nmr spectrum exhibited four tertiary methyl protons as three proton singlets at δ 0.78, 0.85, 0.86, and 0.91 in addition to resonances of an acetyl methyl singlet at δ 2.09, two α-methines of secondary hydroxyl functions at δ 2.84 (1H, ddd, J = 12, 4, 4 Hz) and 3.51 (1H, dddd, J = 10, 10, 5, 5 Hz), and a hydroxymethyl function at δ 3.76, 3.62 (each dd, J = 10, 4 Hz). Its ^{13}C-nmr data contain resonances of a carbonyl carbon at δ 211.7 and three oxygenated carbons at δ 80.2, 71.6, and 60.1.

A perusal of the above data in comparison with those of compound **1** suggest that compound **4** is also a scalarane with an acetyl function and three oxygenated carbons but has one carbon less than the former. The lack of a lactone function is evident from the absence of carbon resonances at δ 175 in the ^{13}C-nmr spectrum and an ir band at 1770 cm^{-1}. While the ^{1}H nmr and ^{13}C nmr of compounds **4** and **1** are in general agreement, there are the following additional differences: One of the oxygenated carbons appeared at δ 89.6. It is interpreted that the C-12 carbon in compound **4** lacks paramagnetic influence of C-25 lactone carbonyl and appeared at higher field by 9.4 ppm. Similarly, H-12 appeared at δ 2.84, nearly 1 ppm farther upfield than the corresponding methine of compound **1**.

The acetyl function could be assigned to C-17. The H-17 which couples to methylene protons of C-18 and the methine proton of C-16 appeared at δ 2.43 (1H, ddd, J = 12, 10, 4 Hz). In this context, this proton signal was compared with the H-17β of 12α,16β-diacetoxy-20,24-dimethyl-24-oxo-25-norscalarane (**10**) that appeared at δ 2.84 (1H, ddd, J = 11, 10, 3). In view of the identical multiplicity and coupling constants of H-17 in these two compounds, the stereochemistry of the acetyl on C-17 is the α orientation.

From the above, the structure of compound **4** may be described as 12β,16β,22-trihydroxy-24-methyl-24-oxo-25-norscalarane [**4**]. Compound **4**, like furoscalarol and scalarobutenolide, cannot strictly be considered as a scalarane (11,12), although with respect to their biogenesis, it may be argued that 24-methyl-25-norscalaranes might have been generated by the alternate cyclization in the ring D of geranyl-farnesol (12). It may be noted that this is the first report of the isolation of 24-methyl-25-norscalarane from a *Phyllospongia* sponge and may have some taxonomic significance.

The ^{1}H- and ^{13}C-nmr assignments have been gathered in Tables 1 and 2.

TABLE 1. Selected ^{1}H nmr Data of Compounds **1–9**.[a]

Proton	Compound								
	1	**5**	**2**	**6**	**8**	**7**	**9**	**3**	**4**
Me-19	0.77[b] s	0.84[b] s	0.77[b] s	0.83[b] s	0.77[b] s	0.82[b] s	0.82[b] s	0.80[b] s	0.78[b] s
Me-20	0.85[b] s	0.89[b] s	0.85[b] s	0.87[b] s	0.84[b] s	0.86[b] s	0.87[b] s	0.85[b] s	0.85[b] s
Me-21	0.86[b] s	0.97[b] s	0.87[b] s	0.89[b] s	1.00[b] s	0.90[b] s	0.91[b] s	0.85[b] s	0.86[b] s
Me-22								0.85[b] s	
Me-23	1.06[b] s	1.02[b] s	0.92[b] s	1.02[b] s	1.04[b] s	1.04[b] s	1.14[b] s	1.00[b] s	0.91[b] s
Me-26	2.22 s	2.38 s	1.44 d,6	1.55 d,6	1.50 d,6	1.40 d,6	1.34 d,6	1.60 d,6	2.09 s
H-12	3.80 m	3.72 dd,11,3.5	3.24 dd,10,4.5	3.45 dd,10,4.5	3.45 dd,10,4.5	3.41 dd,10.7,4.2	4.75 m	3.53 dd,10.5,4.5	2.84[c] ddd,12,4,4
H-16	3.61 bs	4.97 ddd,11,11,6	3.46 bs,$w_{1/2}$ = 25	3.67 ddd,10,10,5	4.85 ddd,10,10,5	4.72 ddd,10,10,5	4.75 m	3.61 ddd,10,10,5	3.51[c] dddd,10,10,5,5
H-22A	3.81 d,12	4.64 d,12	3.77 d,12	4.63 d,12	4.08 d,12	4.56 d,12	4.56 d,12		3.76[c] dd,10,4
H-22B	3.68 d,12	4.12 d,12	3.64 d,12	4.20 d,12	3.91 d,12	4.10 d,12	4.12 d,12		3.62[c] dd,10,4
H-24			4.37 dq,10,6	4.40 dq,10,6	4.40 dq,10,6	4.30 dq,10,6	4.11 m	4.35 dq,10,6	
H-17	2.76 dd,12,10	3.08 t,11	2.27 ddd,10,10,14						2.43 ddd,12,10,4
H-18	2.33 d,12	2.36 d,12	2.36 d,14					2.08 d,14	2.25 bd,12.5

TABLE 1. Continued.

Proton	Compound								
	1	**5**	**2**	**6**	**8**	**7**	**9**	**3**	**4**
Acetoxyl methyls . .		2.01 s 2.08 s		2.05 s	2.07 s	2.08 s 2.08 s	2.07 s 2.08 s 2.12 s		
Hydroxyl protons . .			5.24 s 4.73 bs 3.88 bs	5.65 s	5.67 s	5.66 s		5.73 s	4.45 d,5 4.02 d,4 3.82 t,4

[a]Spectra of **1**, **2**, **4** in DMSO-d_6 at 70° on 360 MHz instrument, **3** in $CDCl_3$ on 500 MHz instrument, **6** and **8** in $CDCl_3$ on 400 MHz instrument, **5** and **9** in $CDCl_3$ on 300 MHz instrument, and **7** in $CDCl_3$ on 200 MHz instrument.

[b]Methyl signal assigments may be interchanged within a column.

[c]12, 16, and 22 hydroxyl protons are coupled to adjacent methine and methylene protons respectively, due to chelation with solvent, DMSO-d_6.

TABLE 2. ^{13}C-nmr Data of Compounds **1–4**, **7** and **9**.[a]

Carbon	Compound					
	1	**2**	**7**[b]	**9**	**3**[b]	**4**
C-1	34.4	34.1	34.8	34.6	39.9	34.2
C-2	17.2	17.8	18.1	18.1	18.4	17.7
C-3	41.4	41.6	41.6	41.5	41.8	41.7
C-4	32.8	32.6	32.9	32.9	33.4	32.7
C-5	55.4[c]	55.3[c]	56.5[c]	56.5[c]	56.5[c]	54.1[c]
C-6	18.2	18.4	18.4	18.2	18.6	18.4
C-7	42.8	42.0	42.0	42.2	42.1	41.9
C-8	37.5	36.8	37.5	37.5	37.4	37.0
C-9	57.1[c]	56.9[c]	58.4[c]	56.6[c]	58.4[c]	56.5[c]
C-10	41.0	41.2	40.6	40.5	37.5	39.0
C-11	29.8	28.5	28.3	27.1	25.9	29.5
C-12	89.6	81.5	80.6	78.7	81.9	80.2
C-13	42.3	41.6	42.2	41.1	42.1	41.6
C-14	51.4[c]	51.2[c]	49.0[c]	49.3[c]	51.6[c]	53.9[c]
C-15	32.4	30.1	26.7	26.4	31.0	29.6
C-16	74.3	70.5	73.5	73.6	72.7	71.6
C-17	60.3[c]	58.4[c]	58.5[c]	58.3[c]	58.6[c]	59.1[c]
C-18	51.0[c]	56.4[c]	57.0[c]	56.6[c]	56.7[c]	29.6[c]
C-19	33.8	33.7	33.7	33.6	33.3	33.8
C-20	21.6	21.6	21.8	21.7	21.3	21.6
C-21	17.2	15.9	16.2	16.3	16.8	16.3
C-22	60.7	60.1	64.5	64.5	16.1	60.1
C-23	13.7	11.9	12.3	12.3	12.7	14.7
C-24	209.6	78.9	79.3	77.6	78.9	211.7
C-25	175.3	178.6	177.1	171.6	177.6	
C-26	23.9	19.8	19.6	19.7	20.1	29.5
(-OCOMe)			171.3	171.3		
			170.4	170.8		
				170.2		
(-OCOCH$_3$)			21.1	21.7		
			21.0	21.2		

[a]Spectra of **1**, **2**, and **4** are recorded in DMSO-d_6, those of **3**, **7**, and **9** in $CDCl_3$, at operating frequencies of 90.8 and 50.4, respectively.

[b]Assignments of compounds **3** and **7** are confirmed by INEPT experiment.

[c]Assignments in the same column may be interchanged.

EXPERIMENTAL

COLLECTION, EXTRACTION, AND PURIFICATION.—Specimens of the sponge *P. dendyi* (dry wt ca. 500 g) were collected on the coasts of Little Andaman (10°38′N,92°22′E) of the Indian Ocean during December 1986. A voucher specimen (MS/CBR/10) is on deposit at the School of Chemistry, Andhra University, Visakhapatnam. The animals were repeatedly extracted with EtOH at room temperature. The 95% aqueous EtOH extract was concentrated under reduced pressure, redissolved in EtOAc, and dried over anhydrous $MgSO_4$. Evaporation of the solvent yielded a dark greenish gum (30 g) that was chromatographed over Si gel using solvent mixtures of increasing polarity from petroleum ether (bp 60–80°) through C_6H_6 to EtOAc. Repeated chromatography of selected fractions from suitable solvents yielded three furanoterpenes (2), and crystallization of other fractions gave the following scalarane derivatives: 16β,22-dihydroxy-24-methyl-24-oxoscalaran-25,12β-olide [**1**] (50 mg), 12β,16β,22-trihydroxy-24-methylscalaran-25,24-olide [**2**] (1000 mg), 12β,16β-dihydroxy-24-methylscalaran-25,24-olide [**3**] (60 mg), and 12β,16β,22-trihydroxy-24-methyl-24-oxo-25-norscalarane [**4**] (50 mg).

16β,22-DIHYDROXY-24-METHYL-24-OXOSCALARAN-25,12β-OLIDE [**1**].—White solid, mp 280–282°. Found C 72.4, H 9.5; $C_{26}H_{40}O_5$ requires C 72.2, H 9.3%. $[\alpha]^{25}D$ +45° (c = 1, MeOH); ir (KBr) 3510 (br), 1770, 1710, 1390, 1385, 1185, 1220, 920 cm^{-1}; ^{1}H nmr see Table 1; ^{13}C nmr see

Table 2; eims *m/z* (%) 432 (21), 404 (15), 403 (21), 401 (20), 285 (19), 317 (20), 289 (13), 203 (16), 177 (64), 109 (54), 95 (59), 81 (60), 69 (56), 55 (48), 43 (100).

16β,22-DIACETOXY-24-METHYL-24-OXOSCALARAN-25,12β-OLIDE [**5**].—A solution of **1** (10 mg) in Ac_2O (200 μl) and pyridine (200 μl) was kept at room temperature overnight. Si gel chromatography of the reaction mixture after usual workup yielded the diacetate **5** (9 mg): crystalline solid; mp 194–196°. Found C 69.9, H 8.7; $C_{30}H_{44}O_7$ requires C 69.7, H 8.6%. Ir ($CHCl_3$) 1785, 1735 (br), 1375, 1025, 965, 940 cm^{-1}; ^1H nmr see Table 1.

12β,16β,22-TRIHYDROXY-24-METHYLSCALARAN-25,24-OLIDE [**2**].—Crystalline solid: mp 313–316°. Found C 72.0, H 9.8; $C_{26}H_{42}O_5$ requires C 71.9, H 9.7%. $[\alpha]^{25}D$ +15.8°; ir (KBr) 3620, 3340, 3270, 1715, 1200, 1025 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (%) 434 (8), 433 (6), 404 (28), 403 (92), 386 (31), 385 (100), 367 (9), 239 (24), 109 (32), 95 (36), 81 (31), 69 (34), 55 (28), 43 (26).

ACETYLATION OF **2**.—A mixture of **2** (20 mg), Ac_2O (500 μl), and pyridine (500 μl) was kept at room temperature for two min and worked up. The reaction mixture on chromatography over Si gel gave acetate **6** (8 mg), acetate **8** (8 mg), and diacetate **7** (1 mg).

The reaction mixture was kept at room temperature for 24 h and worked up when only diacetate **7** was obtained. A mixture of **2** (20 mg), pyridine (300 μl), and Ac_2O (300 μl) was heated on a steam bath for 120 min, and usual workup followed by chromatography gave a mixture of diacetate **7** (15 mg) and triacetate **9** (5 mg).

22-ACETOXY-12β,16β-DIHYDROXY-24-METHYLSCALARAN-25,24-OLIDE [**6**].—Crystalline solid: mp 270°. Found C 70.8, H 9.4; $C_{28}H_{44}O_6$ requires C 70.6, H 9.3%. Ir ($CHCl_3$) 3440, 1740 (br), 1390 cm^{-1}; ^1H nmr see Table 1.

16β-ACETOXY-12β,22-DIHYDROXY-24-METHYLSCALARAN-25,24-OLIDE [**8**].—Crystalline solid: mp 266–268°. Found C 70.7, H 9.4; $C_{28}H_{44}O_6$ requires C 70.6, H 9.3%. $[\alpha]^{25}D$ +11.0° (c = 0.06, $CHCl_3$); ir ($CHCl_3$) 3300, 1730 (br), 1350, 1020 cm^{-1}; ^1H nmr see Table 1.

16β,22-DIACETOXY-12β-HYDROXY-24-METHYLSCALARAN-25,24-OLIDE [**7**].—Crystalline solid: mp 207°. Found C 69.7, H 9.2; $C_{30}H_{46}O_7$ requires C 69.5, H 8.9%. Ir ($CHCl_3$) 3420, 1740 (br), 1375, 1220 (br), 1030, 985, 910 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Table 2.

12β,16β,22-TRIACETOXY-24-METHYLSCALARAN-25,24-OLIDE [**9**].—Crystalline solid: mp 154°. Found C 68.8, H 8.8; $C_{32}H_{48}O_8$ requires C 68.5, H 8.6%. Ir ($CHCl_3$) 1775, 1725, 1390, 1210 (br), 1020 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Table 2.

12β,16β-DIHYDROXY-24-METHYLSCALARAN-25,24-OLIDE [**3**].—Colorless needles: mp 282–285°. Found C 74.8, H 10.3; $C_{26}H_{42}O_4$ requires C 74.6, H 10.1%. $[\alpha]^{25}D$ +11.0 (c = 0.13, $CHCl_3$). Ir (Nujol) 3540, 3420, 1720, 1470, 1390, 1060 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (%) 418 (100), 417 (27), 403 (24), 386 (16), 213 (14), 208 (13), 191 (24), 95 (28), 81 (33), 69 (38), 55 (33), 43 (21).

12β,16β,22-TRIHYDROXY-24-METHYL-24-OXO-25-NORSCALARANE [**4**].—Colorless solid: mp 288–291°. Found C 74.0, H 10.7; $C_{25}H_{42}O_4$ requires C 73.8, H 10.4%. $[\alpha]^{25}D$ +6.1 (c = 0.46, pyridine); ir (KBr) 3520, 3400 (br), 1690, 1350, 1085, 1015 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (%) 406 (10), 389 (20), 358 (28), 357 (93), 340 (34), 339 (100), 304 (17), 215 (19), 95 (41), 43 (66).

ACKNOWLEDGMENTS

The authors thank Dr. P.A. Thomas, The Central Marine Fisheries Research Institute, Trivandrum, India for identifying the sponge; Dr. G.S. Reddy, DuPont Laboratories, Wilmington, Delaware, for some of the nmr spectra; RSIC, Lucknow for mass spectra; and Council of Scientific and Industrial Research and Department of Science and Technology, New Delhi for financial support to CBR.

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Received 6 December 1989

ERRATUM

For the paper by Migliuolo *et al.* entitled "Steroidal Ketones from the Sponge *Geodia cydonium*," *J. Nat. Prod.*, **53**, 1262 (1990), the printer left out a line of type as follows: Page 1262 after line 3:

. . . family Geodidae). This sponge also contains the 4-ene-3-keto-steroids **5–8** that are . . .