Six Novel Eudesmane-Like Sesquiterpenes from *Illicium spathulatum*

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The four diastereoisomeric gorgonane sesquiterpenes **1**–**4** and the two diastereoisomeric forfugane sesquiterpenes **6** and **7**, which all have the same molecular formula $C_{15}H_{28}O_3$ and belong to the same eudesmane-like sesquiterpenes, were isolated from the leaves and twigs of *Illicium spathulatum*. Their structures were elucidated by spectroscopic methods, including 1D- and 2D-NMR spectroscopy.

Introduction. – The genus *Illicium* is the only member of the family Illiciaceae and is an evergreen toxic shrub or tree. About 35 species have been found disjunctively in North America and eastern Asia, among which 25 species are indigenous to southern China [1]. Although the *Illicium* family is a rich source of sesquiterpenes [2] and known to be characterized by secoprezizaane sesquiterpenes [3], there is only one previous report concerning the chemistry of *I. spathulatum* which has described the isolation of sesqui-neolignans [4]. For the purpose of finding sesquiterpene compounds, we carried out systematic studies on the chemical constituents of *I. spathulatum*. Here, we report the isolation and structure elucidation of the four new gorgonane sesquiterpenes **1**–**4**[1]) [5] and two new forfugane sesquiterpenes, **6**[1]) and **7** [6] (gorgonane = 4a,8a-*trans*-decahydro-1,4a-dimethyl-6-(1-methylethyl)naphthalene; forfugane = 4a,8a-*cis*-decahydro-1,5-dimethyl-3-(1-methylethyl)naphthalene), together with one known compound, *trans*-eudesmane-4,11-diol (**5**) [7] (*Fig. 1*).

Results and Discussion. – *Structure Elucidation.* Compound **1** was obtained as a white powder and possessed the molecular formula $C_{15}H_{28}O_3$ (two degrees of unsaturation) as revealed by its HR-ESI-MS (*m/z* 279.1934 ($[M+Na]^+$). In the NMR spectra (*Tables 1* and *2*), the assignments were guided by DEPT, HMQC, ^{1}H,^{1}H-COSY, HMBC, and HSQC-TOCSY experiments. The ^{13}C-NMR data (*Table 2*) showed the presence of 15 C-atoms which were attributed by DEPT analysis to 4 Me (δ(C) 13.7, 28.5, 30.9 and 30.1), 5 CH_2 (δ(C) 27.1, 40.4, 50.3, 32.5 and 38.5), and 3 CH groups (δ(C) 79.2, 58.4, and 31.1), and to 3 quaternary C-atoms (δ(C) 71.3, 71.2, and 46.5). The MS and NMR data suggested the presence of a sesquiterpenoid skeleton. The structure must be bicyclic to account for the two degrees of unsaturation required by the molecular formula which was constructed further by interpretation of the 2D-NMR

[1]) Trivial atom numbering; for systematic names, see *Exper. Part.*

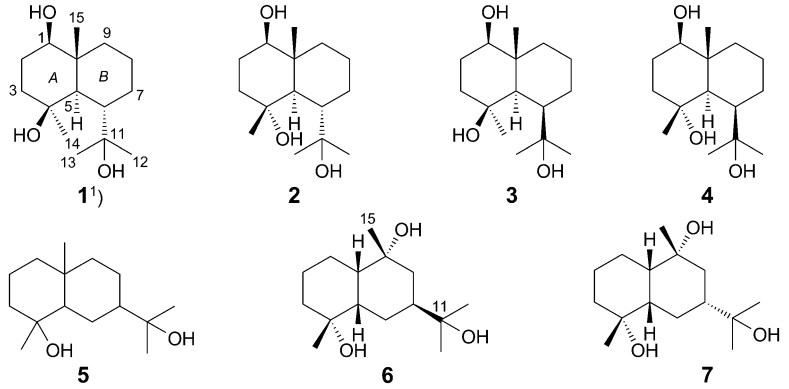


Fig. 1. *Compounds* **1**–**7** *isolated from* I. spathulatum

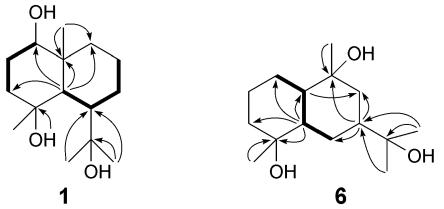
Table 1. *^{1}H-NMR Data* ($CDCl_3$/MeOH; 400 MHz) *of* **1**–**4**[1]). δ in ppm, J in Hz.

H-Atom	**1**	**2**	**3**	**4**
H–C(1)	3.15 (*dd*, *J* = 4.1, 11.5)	3.27 (*dd*, *J* = 4.3, 11.1)	3.11 (*dd*, *J* = 3.7, 10.7)	3.06 (*dd*, *J* = 4.3, 11.1)
H_a–C(2)	1.40–1.50 (*m*)	1.50–1.69 (*m*)	1.47–1.51 (*m*)	1.40–1.55 (*m*)
H_b–C(2)	1.60–1.75 (*m*)	1.50–1.69 (*m*)	1.70–1.78 (*m*)	1.40–1.55 (*m*)
H_a–C(3)	1.20–1.32 (*m*)	1.50–1.69 (*m*)	1.54–1.58 (*m*)	1.52–1.60 (*m*)
H_b–C(3)	1.47–1.50 (*m*)	1.76–1.79 (*m*)	1.54–1.58 (*m*)	1.52–1.60 (*m*)
H–C(5)	0.76 (*d*, *J* = 10.8)	1.57–1.65 (overlap)	1.41–1.45 (*m*)	1.01 (*d*, *J* = 5.6)
H–C(6)	2.00–2.10 (*m*)	1.48–1.50 (*m*)	1.41–1.45 (*m*)	1.05–1.18 (*m*)
H_a–C(7)	1.15–1.20 (*m*)	1.48–1.69 (*m*)	1.36–1.40 (*m*)	1.68–1.73 (*m*)
H_b–C(7)	1.80–2.00 (*m*)	1.76–1.79 (*m*)	1.41–1.45 (*m*)	1.68–1.73 (*m*)
H_a–C(8)	1.15–1.20 (*m*)	1.48–1.50 (*m*)	1.17–1..23 (*m*)	1.38–1.48 (*m*)
H_b–C(8)	1.80–2.00 (*m*)	2.03 (*d*, *J* = 14.2)	1.41–1.45 (*m*)	1.38–1.48 (*m*)
H_a–C(9)	0.96–1.10 (*m*)	1.48–1.55 (*m*)	1.28 (*dd*, *J* = 3.0, 13.0)	1.68 (*d*, *J* = 13.5)
H_b–C(9)	1.40–1.49 (*m*)	1.48–1.55 (*m*)	1.47–1.51 (*m*)	0.88–0.93 (*m*)
Me(12)	1.06 (*s*)	1.26 (*s*)	0.81 (*s*)	0.98 (*s*)
Me(13)	1.06 (*s*)	1.27 (*s*)	0.79 (*s*)	1.00 (*s*)
Me(14)	1.09 (*s*)	1.09 (*s*)	0.98 (*s*)	0.91 (*s*)
Me(15)	0.84 (*s*)	0.90 (*s*)	0.82 (*s*)	0.66 (*s*)

data. The fragments $CH(1)CH_2(2)CH_2(3)$ and $CH(5)CH(6)CH_2(7)$ were deduced from COSY cross-peaks (*Fig. 2*). The HMBC cross-peaks from H–C(5)/C(4), C(3), C(10), and C(1) confirmed the six-membered ring *A*. The HSQC-TOCSY cross-peaks H–C(6)/C(5), C(7), C(8) and C(9) further confirmed the fragment $CH(5)CH(6)CH_2(7)CH_2(8)CH_2(9)$, and the HMBC cross-peaks H–C(5)/C(9) and C(10) established the six-membered ring *B* and also confirmed the *A*/*B* ring fusion, which was that of a decahydronaphthalene ring. The ^{1}H-NMR displayed signals of 25 H-atom, so the remaining 3 H-atoms in the molecular formula came from 3 OH groups which must be attached to C(1) (δ(C) 71.2), C(4) (δ(C) 71.3), and C(11) (δ(C) 79.2). The IR spectrum showed an absorption band for OH functions at 3358 cm^{-1}. Compound **1** displayed 4*s* of 4 Me groups at δ(H) 1.09, 0.84, 1.06, and 1.06. The

Table 2. *^{13}C-NMR Data* (in $CDCl_3$/MeOH; 100 MHz) *of* **1**–**4**[1]). δ in ppm.

C-Atom	**1**	**2**	**3**	**4**
C(1)	79.2	79.4	78.9	78.8
C(2)	27.1	28.1	26.1	27.9
C(3)	40.4	40.8	39.2	40.3
C(4)	71.3	71.9	71.0	71.3
C(5)	58.4	46.8	44.5	52.4
C(6)	31.1	41.0	38.9	49.2
C(7)	50.3	20.2	28.1	20.8
C(8)	32.5	20.8	28.8	22.1
C(9)	38.5	37.3	34.2	40.3
C(10)	46.5	38.6	38.5	38.6
C(11)	71.2	74.4	73.6	72.4
C(12)	28.5	28.8	16.4	25.4
C(13)	30.1	29.1	16.6	26.8
C(14)	30.9	21.3	29.0	21.7
C(15)	13.7	12.9	11.1	12.7



1 **6**

Fig. 2. *Selected HMBC* (arrows) *and COSY* (bold line) *features of* **1** *and* **6**

latter two Me groups showed HMBCs with the quaternary C-atom at δ(C) 71.2, which beared an OH group. Thus the partial structure $C(OH)Me_2$, a substituted i-Pr group, was assembled. HMBCs from these two Me groups to C(6) showed that this fragment was located at C(6). The ^{1}H-NMR signal at δ(H) 0.84 and the ^{13}C-NMR signal at δ(C) 13.7 (C(15)) must be assigned to a Me group at the ring-fusion site. Further interpretation of the HMBC spectra showed that Me(14) was attached to C(4), thus forming the 4,10-dimethyl-6-isopropyl-decalin structure [8], a rare sesquiterpene gorgonane skeleton which was previously known from the literature [9]. *Ando* and *co-workers* [7] reported that the ring fusion of decahydronaphthalene structure can be determined to be a *cis* or *trans* by the δ(C) values of the angular Me group, the angular Me group of *trans*-decahydronaphthalenes appearing around δ(C) 18.5. and that of the *cis*-isomers around δ(C) 28–31. The δ(C) 13.7 (C(15)) implied a *trans*-decahydronaphthalene ring in **1**. The relative configuration of **1** was determined by analysis of vicinal coupling constants and the ROESY data (*Fig. 3*). The coupling constants for H_α–C(1)/H_α–C(2) ($J = 11.5$ Hz) suggested that the OH group at C(1) was in quasi-equatorial β-position which was also confirmed by the ROESY correlation H_α–C(1) and H_α–C(5). The large vicinal coupling of H_α–C(5)/H_β–C(6) ($J = 10.8$ Hz) confirmed that H–C(6) was in β-position, which was also supported by a ROESY correlation H–C(6)/Me(15). The ROESY correlation H–C(5)/Me(14) established the β-position

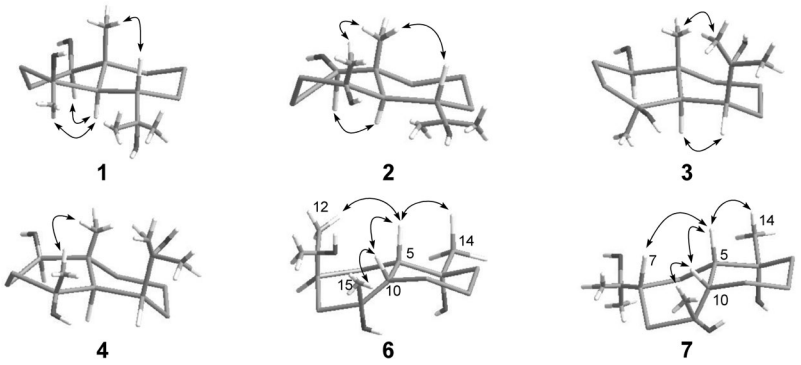


Fig. 3. *Key NOESY correlations of* **1**–**4**, **6**, *and* **7**

of OH–C(4) and α-position of Me(14). Thus, compound **1** was identified as (1β,4β,6α)-gorgonane-1,4,11-triol.

Compounds **2**–**4** had the same molecular formula $C_{15}H_{28}O_3$ as **1**,established by HR-ESI-MS. Their ^{1}H-NMR spectra (*Table 1*) all displayed signals of 25 H-atoms, the remaining 3 H-atoms in the molecular formula coming from 3 OH groups. Their IR spectrum also showed OH absorption bands. According to their ^{13}C-NMR data (*Table 2*), **2**–**4** all had 15 C-atom signals: 4 Me, 5 CH_2, 3 CH groups, and 3 quaternary C-atoms, which were very similar to those of **1**. Three of the 15 ^{13}C-NMR signals appeared at lower field and were assigned to the oxygenated C-atoms C(1), C(4), and C(11), which where attached to the OH groups. The HMBC spectrum confirmed the presence of a substituted i-Pr group located at C(6). These data suggested that **2**–**4** have the same gorgonane skeleton [9] as **1**. The ^{13}C-NMR signal of their angular Me group C(15), appearing around δ(C) 18.5 indicated that they also had a *trans*-fused decahydronaphthalene structure. Further NMR studies including HMQC, HMBC, ^{1}H,^{1}H-COSY, and HSQC-TOCSY experiments showed that compounds **2**–**4** were diastereoisomers of **1**. The relative configuration of compounds **2**–**4** was determined in the same manner as described for **1**. Their large vicinal coupling constant J(H_α–C(1), H_α–C(2)) (*Table 1*) established the quasi-equatorial β-position of OH–C(1). The ROESY correlations Me(14)/Me(15) and Me(14)/Me(6) of 2 indicated that OH–C(4) and H–C(6) were α- and β-oriented, respectively (*Fig. 3*). Therefore, **2** was identified as (1β,4α,6α)-gorgonane-1,4,11-triol. The ROESY correlations H–C(5)/Me(14) and H–C(5)/H–C(6) of **3** indicated that OH–C(4) and H–C(6) were in β- and α-position, respectively (*Fig. 3*). Therefore, **3** was identified as (1β,4β,6β)-gorgonane-1,4,11-triol. In compound **4**, H_α–C(5) was placed in axial and H–C(6) in α-position on the basis of the small vicinal coupling of H_α–C(5) and H_α–C(6) ($J = 5.6$ Hz). The ROESY correlations Me(14)/Me(15) indicated that OH–C(4) was in α-position (*Fig. 3*). Thus **4** was identified as (1β,4α,6β)-gorgonane-1,4,11-triol.

The C-atom skeleton of compounds **1**–**4** is a gorgonane structure which is simlar to the eudesmane skeleton, except that the isopropyl side chain is at C(6) instead of C(7) [10]. Meanwhile, we also obtained another eudesmane-like sesquiterpenoid from *I. spathulatum*, farfugin A [11] which is a 15(10 → 9)-*abeo*-eudesmane derivative, the Me

group at C(10) having migrated to C(9). The reported farfugane skeleton of farfugin A has an aromatic ring *B* [12]. However, the here isolated 15(10 → 9)-*abeo*-eudesmane derivative **6** and **7** have an aliphatic ring *B*.

The molecular formula of **6** was $C_{15}H_{28}O_3$ as deduced from its HR-ESI-MS (*m/z* 279.1933 ($[M+Na]^+$), indicating two degrees of unsaturation. The IR spectrum showed the presence of an OH group (3479 cm^{-1}). The EI-MS of **6** displayed peaks at *m/z* 238 ($[M - H_2O]^+$), 220 ($[M-2\ H_2O]^+$), and 202 ($[M-3\ H_2O]^+$), disclosing the presence of three OH groups. The ^{13}C-NMR and DEPT spectra of **6** (*Table 3*) exhibited 15 signals due to 4 Me (δ(C) 24.3, 26.9, 27.3, and 31.6), 5 CH_2 (δ(C) 23.6, 25.2, 27.0, 34.3, and 37.1), 3 CH groups (δ(C) 44.9, 48.8, and 51.6), and three oxygenated quaternary sp^3 C-atoms (δ(C) 73.6, 74.1, and 83.2) where the three OH groups were attached. Accordingly, the ^{1}H- and ^{13}C-NMR data of **6** were assigned, and confirmed by 2D-NMR experiments (HMBC, HSQC, NOESY, and HSQC-TOCSY), suggesting the structure of a bicyclic sesquiterpenoid. The connectivity CH_2(1)CH(10)-CH(5)CH(6) was deduced by COSY cross-peaks (*Fig. 2*). Another fragment, CH_2(6)CH(7)CH_2(8)C(9), was revealed by the HMBC cross-peaks H–C(7)/C(6), C(8), and C(9). The HMBC H–C(10)/C(8) linked two fragments in ring *B*, and the HMBC H–C(5)/C(4), C(3), C(10), and C(1) confirmed the connectivity CH_2(1)CH(10)CH(5)C(4)CH_2(3). The HMBC H–C(10)/C(2) and C(1) confirmed the connectivity CH_2(2)CH_2(1)CH(10). HSQC-TOCSY Cross-peaks from the methine H-atom at δ(H) 0.78 (H–C(5)) to C(3) allowed the complete assignment of ring *A*. The HMBCs H–C(5)/C(10) and H–C(10)/C(5) confirmed the *A*/*B* ring fusion. The ^{1}H- and ^{13}C-NMR spectra of **6** exhibited signals due to a substituted i-Pr group (δ(H) 1.19 (*s*) and 1.22 (*s*); δ(C) 26.9 (Me), 27.3 (Me), and 73.6 (C)). The position of the substituted i-Pr group C(7) of ring *B* was determined by the HMBC spectrum (*Fig. 2*). Further interpretation of the HMBC spectra showed that Me(14) and Me(15) were attached to

Table 3. *The ^{1}H- and ^{13}C-NMR Data* (in $CDCl_3$/MeOH; 400 and 100 MHz, resp.) *of* **6** *and* **7**. δ in ppm, *J* in Hz.

Position	**6**		**7**	
	δ(H)	δ(C)	δ(H)	δ(C)
CH_2(1)	1.81–1.90, 1.47–1.60 (2*m*)	25.2	0.80–0.92, 1.75–1.90 (2*m*)	26.0
CH_2(2)	1.65–1.84 1.65–1.84 (2*m*)	23.6	0.88–0.92 1.39–1.50 (2*m*)	25.1
CH_2(3)	1.63–1.75 (*m*)	37.1	1.68–1.71 (*m*)	38.5
C(4)	–	83.2	–	81.6
H–C5)	2.15 (*dd*, *J* = 4.4, 7.3)	48.8	1.78–1.88 (*m*)	53.5
CH_2(6)	1.63–1.75, 1.47–1.60 (2*m*)	27.0	1.75–1.90, 0.88–0.92 (2*m*)	25.5
H–C7)	1.47–1.60 (*m*)	44.9	1.40–1.52 (*m*)	49.3
CH_2(8)	1.81–1.90, 1.47–1.60 (2*m*)	34.3	1.48–1.52, 1.81–1.85 (2*m*)	37.3
C(9)	–	74.1	–	74.5
H–C10)	2.71(*dd*, *J* = 9.8, 6.9)	51.6	2.53 (*m*)	51.5
C(11)	–	73.6	–	73.7
Me(12)	1.22 (*s*)	26.9	1.77 (*s*)	24.4
Me(13)	1.19 (*s*)	27.3	1.20 (*s*)	27.4
Me(14)	1.19 (*s*)	31.6	1.22 (*s*)	28.4
Me(15)	1.34 (*s*)	24.3	1.24 (*s*)	23.9

C(4) and C(9), respectively, to form a farfugane sesquiterpenoid skeleton. The relative configuration of **6** was determined by the NOESY correlation H–C(5)/H–C(10) (*Fig. 3*), which indicated a *cis*-fused decahydronaphthalene skeleton. Furthermore, the NOESY correlations H–C(5)/Me(12), Me(14)/H–C(5), and Me(15)/H–C(10) were observed. On the basis of above data, H–C(7), OH–C(4), and OH–C(9) should be in α-configuration. Thus, the structure of **6** was established as (4α,7β,9α)-farfugane-4,9,11-triol.

Compounds **7** had the same molecular formula $C_{15}H_{28}O_3$ as **6**, as established by HR-ESI-MS (*m*/*z* 279.1943 ($[M+Na]^+$). The NMR data of **7** (*Table 3*) were very similar to those of **6**. Analysis of its 2D-NMR spectra (HMBC, HSQC, NOESY, and HSQC-TOCSY) suggested the same farfugane sesquiterpenoid skeleton as that found for **6**. Further, a detailed comparison of the ^{13}C-NMR data of **7** and **6** revealed that the signals of C(5) and C(7) of **7** were downfield-shifted by $\Delta\delta$ *ca.* 4.7 and 4.4, respectively, largely due to the absence of the γ-gauche effects from the substituted i-Pr group in the quasi-axial orientation. This implied that H–C(7) of **7** was in β-position instead of α-position in compound **6**, which was further confirmed by a NOESY correlation H–C(5)/H–C(7). The NOESY correlation H–C(5)/H–C(10) established a *cis*-fused *A*/*B* ring junction. The OH–C(4) and OH–C(9) were in α-position on the basis of the NOESY correlations Me(15)/H–C(10) and Me(14)/H–C(5). Thus, the structure of **7** was established as (4α,7α,9α)-farfugane-4,9,11-triol.

Financial support from the *Natural Science Foundation of China* (No.31100256) and the *Fundamental Research Funds for the Central Universities* (GK201002045) is gratefully acknowledged.

Experimental Part

General. TLC: precoated silica-gel GF_{254} plates (*Qingdao Haiyang Chemical Co.*). Column chromatography (CC): silica gel (SiO_2; 200–300 mesh) (*Qingdao Haiyang Chemical Co.*), *RP-*C_{18} silica gel (40–75 μm; *Pharmacia Chemical Co.*), and *Sephadex-LH-20* gel (*Pharmacia*). Optical rotations: *Horiba-SEAP-300* spectropolarimeter. IR Spectra: *Bio-Rad-FtS-135* spectrometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker AM-400* and *DXR-500* spectrometers; δ in ppm, *J* in Hz. ESI-MS: *VG-Autospec-3000* mass spectrometer; in *m*/*z*. HR-ESI-MS: *API-Qstar-Pulsar* LC/TOF instrument; in *m*/*z*.

Plant Material. The leaves and twigs of *Illicium spathulatum* were collected from Wenshan County, Yunnan Province, P. R. China, in September 2004, and identified by Dr. *En-De Liu*. A voucher specimen (No. 200409D) was deposited with the Herbarium of the Department of Taxonomy, Key Laboratory of Medicinal Resource and Natural Pharmaceutical Chemistry of Ministry of Education, Shaanxi Normal University.

Extraction and Isolation. Dried, powdered *I. spathulatum* (10 kg) was extracted with MeOH at r.t. The MeOH extract was concentrated and the resulting extract (1200 g) suspended in H_2O and extracted first with petroleum ether and then AcOEt. The AcOEt extract (90 g) was subjected to CC (SiO_2, $CHCl_3$/acetone 4:1, 3:1, and 2:1, then $CHCl_3$/MeOH 5:1): *Fractions I–X* (monitoring by TLC). *Fr. II* (30.1 g) was further separated by CC (*Sephadex LH-20*, MeOH) and repeated CC (SiO_2; $CHCl_3$/MeOH 30:1): **5** (30 mg) and **4** (12 mg). *Fr. III* (20.6 g) was further separated by CC (*Sephadex LH-20*, MeOH) and purified by CC (SiO_2, $CHCl_3$/*i*-PrOH 10:1): **1** (26 mg) and **6** (4 mg). *Fr. IV* (30.1 g) was further separated by CC (*Sephadex LH-20*, MeOH) and repeated CC (*RP-*C_{18} silica gel, 60% aq. MeOH): **3** (56 mg), **2** (10 mg), and **7** (20 mg).

(1β,4β,6α)-Gorgonane-1,4,11-triol (= rel-*(1*R,*4*S,*4a*S,*8*R,*8a*S*)-Decahydro-8-(1-hydroxy-1-methylethyl)-1,4a-dimethylnaphthalene-1,4-diol*; **1**): White amorphous powder. $[\alpha]_D^{26.7} = +47.25$ ($c = 1.01$, $CHCl_3$).

IR (KBr): 3358, 2969, 2950, 2862. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS: 279 ($[M+Na]^+$). HR-ESI-MS: 279.1934 ($[M+Na]^+$, $C_{15}H_{28}NaO_3^+$; calc. 279.1936).

(1β,4α,6α)-Gorgonane-1,4,11-triol (= rel-*(1*R*,4*R*,4a*R*,8*S*,8a*R*)-Decahydro-8-(1-hydroxy-1-methylethyl)-1,4a-dimethylnaphthalene-1,4-diol*; **2**): White amorphous powder. $[\alpha]_D^{26.6} = +40.3$ ($c = 1.01$, $CHCl_3$). IR (KBr): 3414, 2968, 2939, 2870. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS: 279 ($[M+Na]^+$). HR-ESI-MS: 279.1939 ($[M+Na]^+$, $C_{15}H_{28}NaO_3^+$; calc. 279.1936).

(1β,4β,6β)-Gorgonane-1,4,11-triol (= rel-*(1*R*,4*S*,4a*S*,8*S*,8a*S*)-Decahydro-8-(1-hydroxy-1-methylethyl)-1,4a-dimethylnaphthalene-1,4-diol*; **3**): White amorphous powder. $[\alpha]_D^{25.4} = -20.7$ ($c = 0.99$, $CHCl_3$). IR (KBr): 3468, 2977, 2962, 2952, 2854. ^{1}H- and ^{13}C-NMR: *Tables 1 and 2.* ESI-MS: 279 ($[M+Na]^+$). HR-ESI-MS: 279.1937($[M+Na]^+$, $C_{15}H_{28}NaO_3^+$; calc. 279.1936)

(1β,4α,6β)-Gorgonane-1β,4α,11-triol (= rel-*(1*R*,4*R*,4a*R*,8*R*,8a*R*)-Decahydro-8-(1-hydroxy-1-methylethyl)-1,4a-dimethylnaphthalene-1,4-diol*; **4**): White amorphous powder. $[\alpha]_D^{25.2} = -10.0$ ($c = 1.12$, $CHCl_3$). IR (KBr): 3417, 2972, 2936, 2865. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS: 279 ($[M+Na]^+$). HR-ESI-MS: 279.1932 ($[M+Na]^+$, $C_{15}H_{28}NaO_3^+$; calc. 279.1936).

(4α,7β,9α)-Farfugane-4,9,11-triol (= rel-*(1*R*,3*S*,4a*S*,5*R*,8a*S*)-Decahydro-3-(1-hydroxy-1-methylethyl)-1,5-dimethylnaphthalene-1,5-diol*; **6**): White amorphous powder. $[\alpha]_D^{26.4} = +25.4$ ($c = 0.55$, $CHCl_3$). IR (KBr): 3385, 3280, 2961, 2874. ^{1}H- and ^{13}C-NMR: *Table 3*. ESI-MS: 279 ($[M+Na]^+$). HR-ESI-MS: 279.1933 ($[M+Na]^+$, $C_{15}H_{28}NaO_3^+$; calc. 279.1936).

(4α,7α,9α)-Farfugane-4,9,11-triol (= rel-*(1*R*,3*R*,4a*S*,5*R*,8a*S*)-Decahydro-3-(1-hydroxy-1-methylethyl)-1,5-dimethylnaphthalene-1,5-diol*; **7**): White amorphous powder. $[\alpha]_D^{24.6} = -19.6$ ($c = 0.67$, acetone). IR (KBr): 3422, 2958, 2925, 2855. ^{1}H- and ^{13}C-NMR: *Table 3*. ESI-MS: 279 ($[M+Na]^+$). HR-ESI-MS: 279.1943 ($[M+Na]^+$, $C_{15}H_{28}NaO_3^+$; calc. 279.1936).

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Received April 11, 2012