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## TWO NEW OXYGENATED LOBANES FROM A SOFT CORAL OF *LOBOPHYTUM* SPECIES OF THE ANDAMAN AND NICOBAR COASTS

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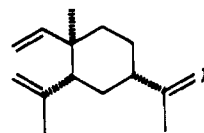
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**ABSTRACT.**—Isolation and structural elucidation of two new lobanes, 17,18-epoxyloba-8,10,13(15)-trien-16-ol [**4**] and loba-8,10,13(15)-triene-16,17,18-triol [**7**], in addition to a known norsesquiterpenoid, 15-nor-13-keto- $\beta$ -elemene [**1**], from a soft coral of *Lobophytum* species of the Andaman and Nicobar coasts are reported. Structural elucidation of the compounds is based on interpretation of 2D nmr spectral data and chemical conversions.

Alcyonarians are a rich storehouse of novel and bioactive secondary metabolites such as prostanoids, terpenoids, and polyhydroxysterols (1–3). The terpenoid content of soft corals varies considerably based on geographical location (4,5) and is particularly striking in the genus *Lobophytum* (5–10). In a continuing study of these animals from the Andaman and Nicobar Islands (11), we have examined the chemical constituents of a new *Lobophytum* species (family Alcyonidae) and the results are presented in this paper.

Specimens of a new *Lobophytum* species were collected on the coasts of the Andaman and Nicobar Islands. The animals (wet wt ca. 15 kg) were cut into thin slices and soaked in 95% EtOH at the site of the collection. The residue obtained by concentration of the EtOH extract under reduced pressure was digested in EtOAc, and the EtOAc-soluble portion, after removal of the solvent, was extracted with CHCl<sub>3</sub> and EtOAc. The CHCl<sub>3</sub>-soluble fraction was concentrated under reduced pressure, and the gummy residue was chromatographed over Si gel columns to give three pure terpenoids.

Terpenoid **1** was isolated as an oil, [ $\alpha$ ]<sub>D</sub> +16° ( $c$ =0.5, CHCl<sub>3</sub>), which analyzed for C<sub>14</sub>H<sub>22</sub>O, cims (positive, CH<sub>4</sub>+NH<sub>4</sub>Cl, 180°) [M+NH<sub>4</sub>]<sup>+</sup> 224. A study of its ir and <sup>1</sup>H-nmr spectral data



- 1** X=O
- 2** X=CH<sub>2</sub>
- 3** X=Me, OH

led to the identification of terpenoid **1** as 15-nor-13-keto- $\beta$ -elemene [**1**]. The compound had been isolated previously from a gorgonian, *Eunicea fusca*, in the Caribbean Sea (12) and from a soft coral of *Sclerophytum* sp. found on the Andaman and Nicobar coasts (13). [The coral was subsequently reidentified as part of a variable *Lobophytum pauciflorum* complex (Dr. Phil Alderslade, personal communication)]. The identity of **1** was rigorously confirmed by direct comparison with an authentic sample (13). <sup>13</sup>C-nmr data of **1** are reported for the first time (Table 1).

Terpenoid **2** was obtained as an oil, [ $\alpha$ ]<sub>D</sub> +10.7° ( $c$ =1.4, CHCl<sub>3</sub>), which analyzed for C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>, cims (positive, CH<sub>4</sub>, 180°) [M-H<sub>2</sub>O]<sup>+</sup> 286. Its ir spectrum showed bands at 3425 (hydroxyl) 1638, 1439, 1003, and 904 cm<sup>-1</sup> (vinyl and unsaturation). The <sup>1</sup>H-nmr (500 MHz) spectrum indicated the presence of a vinyl group ( $\delta$  4.88, 1H, d,  $J$ =10.5; 4.89, 1H, d,  $J$ =17.5 and 5.79, 1H, dd,  $J$ =17.5, 10.5), an isopropylidene group ( $\delta$  4.57,

TABLE 1.  $^{13}\text{C}$ -nmr Data of Compounds 1-3.<sup>a</sup>

Carbon	Compound		
	1	2 <sup>b</sup>	3 <sup>b</sup>
C-1 .....	39.1	40.0	39.8
C-2 .....	52.0	52.8	52.7
C-3 .....	29.3	33.0	28.4
C-4 .....	51.6	45.8	49.3
C-5 .....	23.7	27.0	22.4
C-6 .....	39.6	40.0	39.6
C-7 .....	16.5	16.7	16.6
C-8 .....	149.6	150.2	150.0
C-9 .....	110.3	109.8	109.8
C-10 .....	146.9	147.6	147.6
C-11 .....	112.6	112.1	111.9
C-12 .....	24.7	24.8	24.7
C-13 .....	211.5	150.2	72.4
C-14 .....	28.1	21.1	27.0
C-15 .....		108.2	27.0

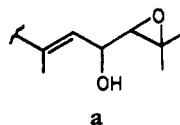
<sup>a</sup>Solvent  $\text{CDCl}_3$ ;  $\delta$  values from TMS.

<sup>b</sup>Data taken from Dunlop and Wells (14) and reinterpreted.

1H, br s; 4.80, 1H, br s; 1.69, 3H, s), a methyl group on a trisubstituted double bond ( $\delta$  1.69, 3H, d,  $J=1.5$  and 5.13, 1H, d,  $J=8.0$ ) and a *gem*-dimethyl deshielded by an oxygen ( $\delta$  1.29, 3H, s and 1.31, 3H, s) characteristic of lobane (prenylated elemane) type diterpenoids (14).

The  $^1\text{H}$ -nmr spectrum also exhibited a carbinol methine proton signal at  $\delta$  4.22 (1H, t,  $J=8.0$ ), and the compound formed a monoacetate **5** with pyridine/ $\text{Ac}_2\text{O}$ . However, its  $^{13}\text{C}$ -nmr data showed the presence of three oxygenated carbons. The other oxygen present is assigned as an epoxide oxygen between carbons 17 and 18, based on the carbon chemical shifts of  $\delta$  67.5 (C-17) and 59.7 (C-18). This assignment was further supported by a high field proton signal at  $\delta$  2.80 (1H, d,  $J=8.0$ ). The proposed epoxide ring also accounted for the deshielded *gem*-dimethyl unit at C-18. The interrelationship between the epoxide moiety, the carbinol group, and the methyl substituted ethylene unit was established by decoupling experiments; irradiation of the signal at  $\delta$  4.22 (16-CHOH) caused the collapse of the two doublets at  $\delta$  5.34 (H-

15) and 2.84 (H-17) into singlets. Hence, the side chain had to have the structure shown in **a**.



COLOC experiments (2D, parameters optimized to 10 Hz) added support for the connectivity of various carbons in the side chain. For example, the protons on C-14 showed coupling to C-4, C-13, and C-15, and the protons on C-19 showed couplings to C-17, C-18, and C-20; other connectivities are presented in Table 2. Based on the above data, the structure of terpenoid **2** is concluded to be 17,18-epoxyloba-8,10,13(15)-trien-16-ol [**4**]. The present COLOC data for **4** require the reassignment of some of the  $^{13}\text{C}$ -nmr data reported earlier (14) for lobane type diterpenoids (see Table 3). The  $^{13}\text{C}$ -nmr assignments for **4** correlate better with assignments made for related prenylated elemanes, the fuscoides (15). The stereochemistry of C-1, C-2, and C-4 is de-

TABLE 2. 1D and 2D nmr Data of Compound 4.<sup>a</sup>

Carbon	<sup>1</sup> H	<sup>1</sup> H- <sup>1</sup> H COSY	<sup>13</sup> C (XHCORR)	COLOC <sup>b</sup>
C-1 .....			39.7 (s)	
C-2 .....	1.99, 1H, dd (3.5, 13.0 Hz)		52.8 (d)	
C-3 .....	1.50, 2H, m		32.7 (t)	C-4,C-2
C-4 .....	1.95, 1H, m	H-5, H-3, H-14	47.6 (d)	
C-5 .....	1.62-1.54, 2H, m		26.5 (t)	C-3
C-6 .....	1.45, 2H, m		39.8 (t)	C-1
C-7 .....	0.98, 3H, s		16.7 (q)	C-8,C-1,C-2
C-8 .....	5.79, 1H, dd (17.5, 10.5 Hz)	H-9	150.1 (d)	
C-9 .....	4.89, 1H, d (17.5 Hz)	H-8	110.0 (t)	C-1
	4.88, 1H, d (10.5 Hz)			
C-10 .....			147.5 (s)	
C-11 .....	4.80, 1H, br s	HB-11	112.2 (t)	C-2,C-12
	4.57, 1H, br s	HA-11		
C-12 .....	1.68, 3H, s		24.7 (q)	C-2,C-10,C-11
C-13 .....			145.4 (s)	
C-14 .....	1.69, 3H, d (1.5 Hz)		15.4 (q)	C-4,C-13,C-15
C-15 .....	5.31, 1H, d (8.0 Hz)	H-16, H-14	121.1 (d)	C-14
C-16 .....	4.22, 1H, t (8.0 HZ)	H-17, H-15	67.8 (d)	
C-17 .....	2.80, 1H, d (8.0 Hz)		67.5 (d)	
C-18 .....			59.7 (s)	
C-19 .....	1.31, 3H, s		24.9 (q)	C-17,C-18,C-20
C-20 .....	1.29, 3H, s		19.5 (q)	C-18

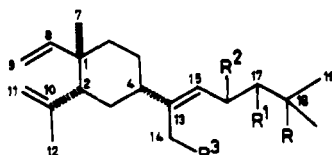
<sup>a</sup>Solvent CDCl<sub>3</sub>; 500 MHz/125 MHz data; δ values from TMS.

<sup>b</sup>Long range correlation experiments, parameters optimized to 10 Hz.

duced as 1*R*, 2*R*, and 4*R* based on comparison of <sup>13</sup>C-nmr data of terpenoid 2 and those of fuscil [6] (15), whose stereochemistry was recently established by synthesis (16). The stereochemistry at C-16 and C-17 could not be determined and is left unassigned.

Terpenoid 3, which was isolated as colorless crystals, mp 73-75°, [α]<sub>D</sub> -14.1° (c=1.0, CHCl<sub>3</sub>), was found to have the molecular formula C<sub>20</sub>H<sub>34</sub>O<sub>3</sub>, cims(positive, NH<sub>4</sub>Cl+CH<sub>4</sub>, 160°)[M]<sup>+</sup> 322. Its ir spectrum showed bands at 3559, 3418 (hydroxyl), 1543, 1418, 1119, 1028, 931, and 647 cm<sup>-1</sup>

(unsaturation). The <sup>1</sup>H-nmr spectrum displayed an ABX pattern of signals (δ 4.89, 2H, m, and 5.81, 1H, dd, *J*=10.5, 17.7) characteristic of a vinyl group and other signals for an isopropylidene group (δ 4.57, 1H, br s; 4.81, 1H, br s; and 1.73, 3H, s), a methyl substituted ethylene unit (δ 1.73, 3H, s; 5.48, 1H, d, *J*=8.4) and a *gem*-dimethyl deshielded by an oxygen (δ 1.27, 6H, s). The <sup>13</sup>C-nmr data of terpenoid 3 exhibited peaks for six olefinic carbons (δ 109.9, 112.1, 123.3, 144.0, 147.4, and 150.0) and three oxygenated carbons (δ 66.1, 73.5, and 78.5). A comparison of the data above with



- 4 R,R<sup>1</sup>=O; R<sup>2</sup>=OH; R<sup>3</sup>=H  
 5 R,R<sup>1</sup>=O; R<sup>2</sup>=OAc; R<sup>3</sup>=H  
 6 R=OH; R<sup>1</sup>,R<sup>2</sup>=double bond; R<sup>3</sup>=H  
 7 R=R<sup>1</sup>=R<sup>2</sup>=OH, R<sup>3</sup>=H  
 8 R=OH, R<sup>1</sup>=R<sup>2</sup>=OAc, R<sup>3</sup>=H

- 9 R=R<sup>1</sup>=R<sup>2</sup>=OAc, R<sup>3</sup>=H  
 10 R,R<sup>1</sup>=O; R<sup>2</sup>=R<sup>3</sup>=H  
 11 R=R<sup>1</sup>=OH, R<sup>2</sup>=R<sup>3</sup>=H  
 12 R=OH; R<sup>2</sup>=H; R<sup>1</sup>,R<sup>3</sup>=O  
 13 R=R<sup>1</sup>=OH, R<sup>2</sup>=H, R<sup>3</sup>=OAc

TABLE 3.  $^{13}\text{C}$ -nmr Data of Lobanes **7** and **10-13**.<sup>a</sup>

Carbon	Compound				
	<b>7</b>	<b>10<sup>b</sup></b>	<b>11<sup>b</sup></b>	<b>12<sup>b</sup></b>	<b>13<sup>b</sup></b>
C-1 .....	39.8	39.9	39.5	39.9	39.5
C-2 .....	52.8	52.8	52.6	52.8	52.6
C-3 .....	32.6	32.9	32.7	32.9	33.1
C-4 .....	47.5	47.6	47.4	41.7	43.6
C-5 .....	26.5	27.9	24.6	24.8	24.5
C-6 .....	39.7	39.9	39.7	39.9	39.5
C-7 .....	16.7	16.6	16.5	16.6	16.4
C-8 .....	150.0	150.1	149.9	150.0	149.7
C-9 .....	109.9	109.7	109.6	110.0	109.7
C-10 .....	147.4	147.6	147.2	147.4	147.0
C-11 .....	112.1	112.0	111.8	112.3	111.9
C-12 .....	24.6	24.8	23.4	23.8	23.6
C-13 .....	144.0	142.1	142.1	141.1	139.8
C-14 .....	15.1	24.8	23.4	68.1	61.3
C-15 .....	123.3	117.3	119.2	116.4	126.9
C-16 .....	66.1	29.6	30.2	27.0	30.0
C-17 .....	78.5	64.0	77.9	80.4	77.6
C-18 .....	73.5	58.2	72.6	71.8	72.4
C-19 .....	27.0	26.7	26.6	26.1	26.9
C-20 .....	26.0	26.7	26.2	25.3	26.0
OAc .....					170.9
					20.8

<sup>a</sup>Solvent  $\text{CDCl}_3$ ;  $\delta$  values from TMS.<sup>b</sup>Data taken from Dunlop and Wells (14) and reinterpreted.

those of **4** suggested that terpenoid **3** is also a lobane derivative. The presence of two more hydrogens and an oxygen in the molecular formula of terpenoid **3** compared to that of **4** and the appearance of relatively deshielded carbon resonances for C-17 and C-18 indicated the replacement of an epoxide moiety of **4** by a 1,2-diol unit in terpenoid **3** [7]. The presence of the diol functionality was supported by acetylation of **6** using pyridine/ $\text{Ac}_2\text{O}$  to give a mixture of diacetyl **8** and triacetyl **9** derivatives. Terpenoid **3** was therefore loba-8,10,13(15)-triene-16,17,18-triol [7]. The stereochemistry at C-1, C-2, and C-4 is the same as in **4** based on comparison of  $^{13}\text{C}$ -nmr spectral data for the two compounds, and the stereochemistry at C-16 and C-17 is undefined. Moreover, it was found that a  $\text{CDCl}_3$  solution (nmr sample) of **4** was converted almost entirely into **7** on storage for long time (nearly 6 months) in a refrigerator. An

attempted acid-catalyzed hydrolysis (14) of the epoxide in **4**, however, led to the formation of an inseparable mixture of compounds.

#### EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting point was determined on a Mel-Temp apparatus and is uncorrected. The ir spectra were recorded on a Perkin-Elmer 1760 FT-IR spectrometer as neat or as  $\text{CHCl}_3$  solution.  $^1\text{H}$ -nmr spectra were recorded on Bruker 500 MHz or Bruker AF 200 MHz nmr spectrometer operating at 499.843 or 200.133 MHz, respectively, in  $\text{CDCl}_3$  using TMS as internal standard and  $^{13}\text{C}$ -nmr spectra on Bruker 500 MHz or Bruker AF 200 MHz nmr spectrometer operating at 125 or 50.3 MHz. Cims spectra were recorded on a Biospect Mass spectrometer (Scientific Research Instruments Corp., Baltimore, MD) using methane as reagent gas, and optical rotations were measured on a Perkin-Elmer 141 polarimeter.

Collection, extraction, and isolation.—Specimens of soft coral, a new Lobophyllum species (Voucher No. NTM C 10016-MF/CBR/109, Northern Territory Museum of Arts and Sciences, Darwin, Australia), were collected at low tide in

the intertidal region of Neill Island (E 93°20'; N 11°48') of the Andaman and Nicobar coasts during March 1989. Voucher specimens are also deposited in the chemistry departments, Andhra University, India and Sri Venkateswara University, Tirupati, India.

The gross morphology of the new *Lobophytum* species (NTM C 10016) reported in this paper is similar to that of *Lobophytum pauciflorum* var. Philippinense and *Lobophytum hirsutum*. Some of the skeletal characteristics are similar to those of *L. pauciflorum*, but samples also show elements whose particular characteristics are not reported from that species. The subsequent discovery of another specimen with similar characters prompted a reexamination of NTM C 10016 that showed extraordinary variability in samples but a consistent preponderance of particular skeletal elements that clearly indicate that it is not *L. pauciflorum*, nor a variety, although there appears to be a complex of *pauciflorum*-like species. As none of the known species of *Lobophytum* have the same characters as NTM C 10016, it is proposed to describe the specimen as a new taxon.

The animals (wet wt ca. 15 kg) were cut into thin slices and soaked in 95% EtOH at the site of collection. The residue obtained by the concentration of EtOH extract under reduced pressure was digested in EtOAc, and the EtOAc-soluble portion, after removal of the solvent, was extracted with CHCl<sub>3</sub> and EtOAc. The CHCl<sub>3</sub>-soluble fraction was concentrated under reduced pressure, and the gummy residue (ca. 80 g) was chromatographed repeatedly over Si gel (ACME 100–200 mesh) columns using mixtures of C<sub>6</sub>H<sub>6</sub> and EtOAc, in increasing polarity, as eluents, to give three pure terpenoids, **1** (200 mg), **4** (100 mg), and **7** (70 mg).

**15-Nor-13-keto-β-elemene [1].**—Oil: [α]<sub>D</sub> +16° (c=0.5, CHCl<sub>3</sub>) [lit. (13) +14.1° (c=1.0, CHCl<sub>3</sub>)]; ir (neat) 1709, 1638, 1375, 1159, 1003, 907 cm<sup>-1</sup>; <sup>1</sup>H nmr (CDCl<sub>3</sub>, 200 MHz) δ 1.00 (3H, s, H-7), 1.71 (3H, s, H-12), 2.18 (3H, s, H-14), 4.60 (1H, br s, H-11), 4.85 (1H, br s, H-11), 4.91 (2H, m, H-9), 5.80 (1H, dd, J=10.5, 17.8, H-8); <sup>13</sup>C nmr see Table 1; cims (positive, CH<sub>4</sub>+NH<sub>4</sub>Cl, 180°) m/z (%) [M+NH<sub>4</sub>]<sup>+</sup> 224; (CH<sub>4</sub>+<sup>15</sup>NH<sub>4</sub>Cl, 180°) [M+<sup>15</sup>NH<sub>4</sub>]<sup>+</sup> 225 (94), [M+<sup>14</sup>NH<sub>4</sub>]<sup>+</sup> 224 (97), [M+H]<sup>+</sup> 207 (100); (negative, CH<sub>4</sub>+NH<sub>4</sub>Cl, 180°) [M-H]<sup>-</sup> 205.

**17,18-Epoxyloba-8,10,13(15)-trien-16-ol [4].**—Colorless oil: Anal. found C 79.02, H 10.74% (C<sub>20</sub>H<sub>32</sub>O<sub>2</sub> requires C 78.95, H 10.53%). [α]<sub>D</sub> +10.7° (c=1.4, CHCl<sub>3</sub>); ir (neat) 3425, 1659, 1638, 1439, 1375, 1003, 904 cm<sup>-1</sup>; <sup>1</sup>H nmr see Table 2; <sup>13</sup>C nmr see Table 2; cims (positive, CH<sub>4</sub>, 180°) m/z [M-H<sub>2</sub>O]<sup>+</sup> 286; (positive, CH<sub>4</sub>+NH<sub>4</sub>Cl, 200°) [M+H-H<sub>2</sub>O]<sup>+</sup> 287.

ACETYLATION OF **4**.—Compound **4** (20 mg)

was acetylated using pyridine and Ac<sub>2</sub>O at room temperature for 24 h. Usual workup followed by chromatography over Si gel gave a monoacetate **5** (8 mg): colorless oil; <sup>1</sup>H nmr (CDCl<sub>3</sub>, 200 MHz) δ 1.00 (3H, s, H-7), 1.32 (3H, s, H-19), 1.33 (3H, s, H-20), 1.71 (3H, s, H-12), 1.79 (3H, s, H-14), 2.07 (3H, s, -OAc), 2.95 (1H, d, J=8.2, H-17), 4.59 (1H, br s, H-11), 4.85 (1H, br s, H-11), 4.90 (2H, m, H-9), 5.21 (1H, d, J=9.6, H-15), 5.37 (1H, dd, J=8.2, 9.6, H-16), 5.81 (1H, dd, J=10.5, 17.7, H-8); <sup>13</sup>C nmr (CDCl<sub>3</sub>, 50 MHz) δ 39.7 (C-1), 52.8 (C-2), 32.6 (C-3), 47.8 (C-4), 26.8 (C-5), 39.8 (C-6), 16.7 (C-7), 150.0 (C-8), 110.0 (C-9), 147.5 (C-10), 112.2 (C-11), 24.7 (C-12), 147.4 (C-13), 15.5 (C-14), 117.5 (C-15), 71.4 (C-16), 64.7 (C-17), 58.0 (C-18), 24.7 (C-19), 19.6 (C-20), 169.9 (OCOMe), 21.1 (OCOCH<sub>3</sub>).

**Loba-8,10,13(15)-triene-16,17,18-triol [7].**—Colorless crystals, mp 73–75°. Anal. found C 74.58, H 10.67% (C<sub>20</sub>H<sub>34</sub>O<sub>3</sub> requires C 74.53, H 10.56%). [α]<sub>D</sub> -14.1° (c=1.0, CHCl<sub>3</sub>); ir (CHCl<sub>3</sub>) 3559, 3418, 1543, 1418, 1119, 1028, 931, 647 cm<sup>-1</sup>; <sup>1</sup>H nmr (CDCl<sub>3</sub>, 200 MHz) δ 1.00 (3H, s, H-7), 1.27 (6H, s, 19, H-20), 1.69 (3H, s, H-12), 1.73 (3H, s, H-14), 2.00 (1H, dd, J=4.2, 11.5, H-2), 3.19 (1H, br s, H-17), 4.57 (1H, br s, H-11), 4.65 (1H, dd, J=2.2, 8.5, H-16), 4.81 (1H, br s, H-11), 4.89 (2H, m, H-9), 5.48 (1H, d, J=8.4, H-15), 5.81 (1H, dd, J=10.5, 17.7, H-8); <sup>13</sup>C nmr see Table 3; cims (positive, CH<sub>4</sub>, 160°) m/z (%) [M-H<sub>2</sub>O]<sup>+</sup> 304 (60), [M-2H<sub>2</sub>O]<sup>+</sup> 286 (33), 246 (100), 228 (47); (positive, NH<sub>4</sub>Cl+CH<sub>4</sub>, 160°) [M+NH<sub>4</sub>]<sup>+</sup> 340 (10), [M]<sup>+</sup> 322 (65), [M-H<sub>2</sub>O]<sup>+</sup> 304 (43), [M-2H<sub>2</sub>O]<sup>+</sup> 286 (26), [M-3H<sub>2</sub>O]<sup>+</sup> 268 (12), 246 (100), 228 (36).

Acetylation of **7** (20 mg) was carried out using pyridine and Ac<sub>2</sub>O at room temperature for 24 h. Usual workup, including chromatography over Si gel, yielded a diacetate **8** (10 mg) and a triacetate **9** (8 mg).

**Loba-8,10,13(15)-triene-16,17,18-triol 16,17-diacetate [8].**—Oil: <sup>1</sup>H nmr (CDCl<sub>3</sub>, 200 MHz) δ 0.98 (3H, s, H-7), 1.22 (6H, s, H-19, -20), 1.70 (3H, s, H-12), 1.82 (3H, s, H-14), 2.05, 2.14 (s, 3H, each, 2×OAc), 4.58 (1H, br s, H-11), 4.81 (1H, br s, H-11), 4.85 (2H, m, H-9), 4.94 (1H, m, H-17), 5.19 (1H, d, J=9.1, H-15), 5.80 (1H, dd, J=10.2, 17.7, H-8), 5.88 (1H, dd, J=6.7, 9.1, H-16); <sup>13</sup>C nmr (CDCl<sub>3</sub>, 50 MHz) δ 39.7 (C-1), 52.7 (C-2), 32.4 (C-3), 47.4 (C-4), 26.5 (C-5), 39.8 (C-6), 16.7 (C-7), 150.0 (C-8), 110.0 (C-9), 147.3 (C-10), 112.2 (C-11), 24.7 (C-12), 146.6 (C-13), 15.7 (C-14), 118.9 (C-15), 69.5 (C-16), 79.0 (C-17), 71.9 (C-18), 26.4 (C-19), 26.9 (C-20), 170.1, 169.7 (2×OCOMe), 21.1, 20.7 (2×OCOCH<sub>3</sub>).

**Loba-8,10,13(15)-triene-16,17,18-triol 16,17,18-triacetate [9].**—Oil: <sup>1</sup>H nmr (CDCl<sub>3</sub>, 200 MHz) δ 0.98 (3H, m, H-7), 1.46 (3H, s, H-19), 1.51 (3H, s, H-20), 1.69 (3H, s, H-12), 1.79

(3H, s, H-14), 1.97, 2.05, 2.13 (s, 3H each, 3×OAc), 4.58 (1H, brs, H-11), 4.81 (1H, brs, H-11), 4.90 (2H, m, H-9), 5.13 (1H, d,  $J=9.2$ , H-15), 5.35 (1H, d,  $J=5.4$  Hz, H-17), 5.80 (1H, dd,  $J=10.7$ , 18.0, H-8), 5.88 (1H, dd,  $J=9.2$ , 5.2, H-16);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  39.7 (C-1), 52.0 (C-2), 32.4 (C-3), 47.4 (C-4), 26.5 (C-5), 39.8 (C-6), 16.8 (C-7), 150.0 (C-8), 110.0 (C-9), 147.4 (C-10), 112.3 (C-11), 24.7 (C-12), 145.9 (C-13), 15.6 (C-14), 118.9 (C-15), 69.2 (C-16), 76.6 (C-17), 82.2 (C-18), 23.0 (C-19), 23.7 (C-20), 169.9, 169.8, 169.5 (3×OCOMe), 21.2, 20.6, 22.3 (3×OCOCH<sub>3</sub>).

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