New Acyclic 12-Hydroxygeranylgeraniol-Derived Diterpenoids from the Seeds of *Carpesium triste*

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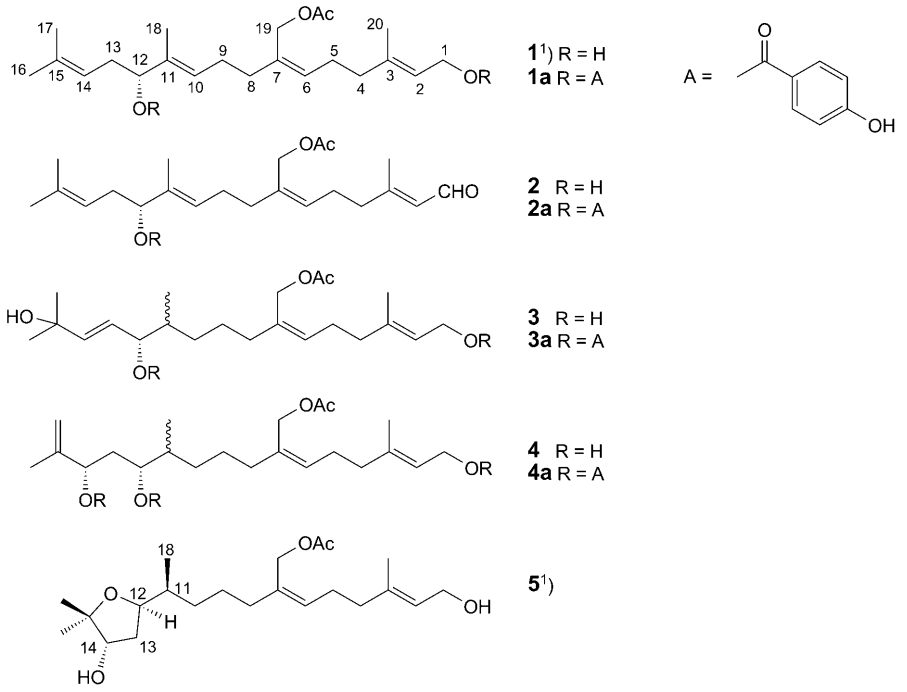
Five new acyclic 12-hydroxygeranylgeraniol-derived diterpenoids, *i.e.*, **1**–**5**, were isolated from the seeds of *Carpesium triste*. The structures including the absolute configurations of the new compounds were elucidated by spectroscopic methods. All the compounds, except for **2**, were evaluated for their *in vitro* cytotoxic activity against cultured SMMC-7721 (human hepatoma), HL-60 (human promyelocytic leukemia), and L02 (human hepatocyte) cells.

Introduction. – The genus *Carpesium* (Compositae) has been reported as a rich source of antifungal, antibacterial, and antitumor sesquiterpene lactones [1][2]. Only one cytotoxic acyclic diterpene was reported from *C. divaricatum* [3]. *C. triste* MAXIM is a Chinese herbal medicine that is used to treat sore throat, toothache, urinary-tract infection, diarrhea, and mastitis [4]. Recently, we reported the structure determination of germacranolides and acyclic diterpenes from *C. triste* [5]. This kind of acyclic 12-hydroxygeranylgeraniol-derived diterpenoids was mainly found before in the Atlantic brown alga *Bifurcaria bifurcata* (Phaeophyceae) [6][7]. In a continuation of our phytochemical studies of acyclic diterpenes, we report herein the isolation and structural elucidation of the five acyclic 12-hydroxygeranylgeraniol-derived diterpenoids **1**–**5**[1]) from the seeds of *C. triste* MAXIM. Thus, for the first time, a series of acyclic 12-hydroxygeranylgeraniol-derived diterpenoids were found in a terrestrial plant. All the compounds, except for **2**, were evaluated against a small panel of human-cancer cell lines for their cytotoxic effects.

Results and Discussion. – The pulverized air-dried seeds of *C. triste* were extracted with MeOH. Extensive purification by column chromatography (silica gel) of the extract afforded compounds **1**–**5**.

Compound **1** has the molecular formula $C_{22}H_{36}O_4$ as deduced by HR-ESI-MS (*m*/*z* 387.2510 ($[M+Na]^+$)). The IR spectrum of **1** displayed OH (3410 cm^{-1}), carbonyl (1737 cm^{-1}), and C=C bond (1669 cm^{-1}) absorptions. Analysis of its NMR data (*Tables 1* and *2*) and circular-dichroism (CD) data of its 4-hydroxybenzoate derivative **1a** enabled us to elucidate the structure of **1** as (2*E*,6*Z*,10*E*,12*R*)-7-[(acetyloxy)methyl]-3,11,15-trimethylhexadeca-2,6,10,14-tetraene-1,12-diol.

The ^{1}H- and ^{13}C-NMR (DEPT) spectra of **1**[1]) showed resonances for an acetyloxy group (δ(H) 2.05 (*s*); δ(C) 171.1 (C) and 20.8 (Me)), as well as resonances for four C=C bonds (δ(H) 5.41, 5.37, 5.10 (each



br. t, $J = 7.2$ Hz, 1 H), and 5.39 (br. t, $J = 6.8$ Hz, 1 H); δ(C) 124.0 (CH), 137.1 (C), 130.3 (CH), 133.4 (C), 125.2 (CH), 138.0 (C), 120.1 (CH), and 134.1 (C)), two oxygenated CH_2 groups (δ(H) 4.12 (d, $J =$ 7.2 Hz) and 4.69 (br. s); δ(C) 58.9 (CH_2) and 61.8 (CH_2)), an oxygenated CH group (δ(H) 3.97 (t, $J =$ 6.8 Hz); δ(C) 76.9 (CH)), and four Me groups (δ(H) 1.71, 1.63, 1.60, and 1.62 (4 br. s); δ(C) 25.7, 17.8, 11.5, and 16.0 (4 Me)). Considering the above information, **1** was deduced to represent an acyclic geranylgeraniol-derived diterpene, with a structure similar to that of bifurcadiol [7], except that a Me group (Me(19)) was absent, and an oxygenated CH_2 and a corresponding acetyloxy group were present. In the HMBC plot, the correlations CH_2(1)/C(2) and C(3), Me(20)/C(2), C(4), and C(3), CH_2(19)/C(6), C(8), C(7), and C=O of Ac, Me(18)/C(10), C(12), and C(11), H–C(12)/C(10), C(14), and C(18), and Me(16)(Me(17))/C(14), C(15), and C(17)(C(16)) were used to establish that **1** is an acyclic geranylgeraniol-derived diterpene. The characteristic ^{13}C-NMR signals of the Me groups of linear (E)-terpenes resonate at δ *ca.* 16, while those in the (Z)-configuration resonate near δ 23 [8]. Thus the (E)-configuration at C(2) and C(10) were indicated by the δ(C) of Me(18) and Me(20). The (Z)-configuration at C(6) was deduced by an NOE difference spectrum: irradiating H–C(6) enhanced the signals of CH_2(8) by 2.67%.

To deduce the absolute configuration at C(12), compound **1** was 4-hydroxybenzoylated to yield 4-hydroxybenzoate **1a**. The CD spectrum of **1a** showed a negative *Cotton* effect in the $\pi \rightarrow \pi^*$ region around 244 nm, which allowed us to deduce the absolute configuration of **1a** to be (12R) [9][10].

The HR-ESI-MS of compound **2** displayed the $[M + Na]^+$ signal at m/z 385.2351 which, in combination with the NMR data (*Tables 1* and *2*) suggested a molecular

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

Table 1. *^{1}H-NMR Data* ($CHCl_3$, 400 MHz) *of Compounds* **1**–**5**[1]). δ in ppm, J in Hz.

	1	**2**	**3**	**4**	**5**
CH_2(1) or	4.12 (*d*,	9.98 (*d*,	4.12 (*d*,	4.12 (*d*,	4.10 (*d*,
H–C(1)	J = 7.2)	J = 8.0)	J = 7.2)	J = 7.2)	J = 7.2)
H–C(2)	5.41 (br. *t*,	5.87 (br. *d*,	5.39 (br. *t*,	5.35 (br. *t*,	5.38 (br. *t*,
	J = 7.2)	J = 8.0)	J = 7.2)	J = 7.2)	J = 7.2)
CH_2(4)	2.07 (*m*)[a])	2.27 (*m*)[a])	2.07 (*m*)[a])	2.08 (*m*)[a])	2.07 (*m*)[a])
CH_2(5)	2.21 (*m*)[a])	2.29 (*m*)[a])	2.18–2.24 (*m*)	2.17–2.23 (*m*)	2.17–2.23 (*m*)
H–C(6)	5.39 (br. *t*,	5.37 (br. *t*,	5.38 (br. *t*,	5.37 (br. *t*,	5.37 (br. *t*,
	J = 6.8)	J = 6.8)	J = 6.8)	J = 6.8)	J = 6.8)
CH_2(8)	2.01 (*m*)[a])	2.13 (*m*)[a])	2.00 (*m*)[a])	2.00 (*m*)[a])	2.00 (*m*)[a])
CH_2(9)	2.08 (*m*)[a])	1.95 (*m*)[a])	1.30–1.38 (*m*)	1.31–1.39 (*m*)	1.29–1.37 (*m*)
			1.99 (*m*)[a])	2.00 (*m*)[a])	2.00 (*m*)[a])
H–C(10) or	5.37 (br. *t*,	5.37 (br. *t*,	1.05–1.11 (*m*)	1.05–1.11 (*m*)	1.03–1.09 (*m*)
CH_2(10)	J = 7.2)	J = 7.2)	1.44–1.54 (*m*)	1.46–1.56 (*m*)	1.44–1.54 (*m*)
H–C(11)			1.54–1.64 (*m*)	1.53–1.63 (*m*)	1.52–1.62 (*m*)
H–C(12)	3.97 (*t*,	3.97 (*t*,	3.89 (*d*,	3.67 (*dt*,	3.94 (*dt*,
	J = 6.8)	J = 6.8)	J = 7.2)	J = 7.6, 5.2)	J = 2.4, 6.8)
CH_2(13) or	2.20 (*m*)[a])	2.20 (*m*)[a])	5.62 (*dd*,	1.66 (*m*)[a])	1.93 (*m*)[a])
H–C(13)			J = 15.6, 7.2)		
H–C(14)	5.10 (br. *t*,	5.09 (br. *t*,	5.78 (br. *d*,	4.25 (br. *d*,	3.89 (*dd*,
	J = 7.2)	J = 7.2)	J = 15.6)	J = 9.6)	J = 5.6, 3.2)
Me(16)	1.71 (br. *s*)	1.71 (br. *s*)	1.31 (*s*)	4.98,	1.17 (*s*)
				4.81 (2 br. *s*)	
Me(17)	1.63 (br. *s*)	1.63 (br. *s*)	1.31 (*s*)	1.70 (br. *s*)	1.22 (*s*)
Me(18)	1.60 (br. *s*)	1.61 (br. *s*)	0.84 (*d*,	0.86 (*d*,	0.80 (*d*,
			J = 6.6)	J = 6.6)	J = 6.8)
CH_2(19)	4.69 (br. *s*)	4.59 (br. *s*)	4.57 (br. *s*)	4.57 (br. *s*)	4.56 (br. *s*)
Me(20)	1.62 (br. *s*)	2.17 (br. *s*)	1.65 (br. *s*)	1.65 (br. *s*)	1.64 (br. *s*)
AcO	2.05 (*s*)	2.05 (*s*)	2.05 (*s*)	2.04 (*s*)	2.02 (*s*)

[a]) Overlapped signals.

formula $C_{22}H_{34}O_4$. The IR-absorption bands of **2** indicated the presence of OH (3411 cm^{-1}), C=O (1738 cm^{-1}), and C=C (1688 cm^{-1}) groups. Compound **2** was deduced to be (2*E*,6*Z*,10*E*,12*R*)-7-[(acetyloxy)methyl]-12-hydroxy-3,11,15-trimethylhexadeca-2,6,10,14-tetraenal from further spectral data.

The ^{1}H- and ^{13}C-NMR spectra of **2**[1]) were very similar to those of **1**, except that the CH_2(1)OH moiety of **1** was replaced by an aldehyde group (δ(H) 9.98 (*d*, J = 8.0 Hz); δ(C) 191.4 (CH)) in **2**. For that reason, the chemical shifts of the C(2)=C(3) bond were shifted downfield (δ(H) 5.87 (br. *d*, J = 8.0 Hz); δ(C) 127.8 (CH) and 163.0 (C)). The (*E*)-configuration at C(2) was deduced by comparing the chemical shifts of the implicated isoprene unit with those reported for (2*E*,6*E*,10*E*,12*S*)-12-hydroxy-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraenal and (2*Z*,6*E*,10*E*,12*S*)-12-hydroxy-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraenal [6]. The CD spectrum of the 4-hydroxybenzoate **2a** of **2** showed a negative *Cotton* effect in the $\pi \rightarrow \pi^*$ region around 245 nm, pointing to the absolute configuration of (12*R*) for **2a**.

The molecular formula of compound **3** was determined as $C_{22}H_{38}O_5$ based on the HR-ESI-MS (*m*/*z* 400.3065 ($[M + NH_4]^+$)). Its IR spectrum showed absorption bands for an ester group (1737 cm^{-1}), a C=C bond (1667 cm^{-1}), and OH groups (3375 cm^{-1}).

Table 2. *^{13}C-NMR and DEPT NMR Data* ($CHCl_3$, 100 MHz) *of* **1**–**5**[1]). δ in ppm.

	1	**2**	**3**	**4**	**5**[a])
C(1)	58.9 (*t*)	191.4 (*d*)	59.1 (*t*)	59.2 (*t*)	59.2 (*t*)
C(2)	124.0 (*d*)	127.8 (*d*)	124.2 (*d*)	124.2 (*d*)	124.2 (*d*)
C(3)	137.1 (*s*)	163.0 (*s*)	138.2 (*s*)	138.3 (*s*)	138.4 (*s*)
C(4)	39.2 (*t*)	40.6 (*t*)	39.3 (*t*)	39.3 (*t*)	39.4 (*t*)
C(5)	26.0 (*t*)	26.1 (*t*)	25.7 (*t*)	25.7 (*t*)	25.8 (*t*)
C(6)	130.3 (*d*)	129.1 (*d*)	130.3 (*d*)	130.4 (*d*)	130.2 (*d*)
C(7)	133.4 (*s*)	135.2 (*s*)	133.9 (*s*)	133.9 (*s*)	134.0 (*s*)
C(8)	34.0 (*t*)	35.1 (*t*)	35.3 (*t*)	35.4 (*t*)	35.3 (*t*)
C(9)	25.8 (*t*)	25.5 (*t*)	25.3 (*t*)	25.4 (*t*)	25.3 (*t*)
C(10)	125.2 (*t*)	125.3 (*d*)	31.8 (*t*)	31.4 (*t*)	32.9 (*t*)
C(11)	138.0 (*s*)	137.6 (*s*)	38.7 (*d*)	39.1 (*d*)	37.9 (*d*)
C(12)	76.9 (*d*)	77.2 (*d*)	76.3 (*d*)	72.7 (*d*)	80.3 (*d*)
C(13)	34.6 (*t*)	34.5 (*t*)	127.5 (*d*)	37.0 (*t*)	36.8 (*t*)
C(14	120.1 (*d*)	120.4 (*d*)	139.8 (*d*)	76.8 (*d*)	78.2 (*d*)
C(15)	134.1 (*s*)	134.7 (*s*)	70.5 (*s*)	147.5 (*s*)	82.3 (*s*)
C(16)	25.7 (*q*)	25.5 (*q*)	29.8 (*q*)	110.6 (*t*)	21.4 (*q*)
C(17)	17.8 (*q*)	18.2 (*q*)	29.6 (*q*)	17.8 (*q*)	27.9 (*q*)
C(18)	11.5 (*q*)	12.0 (*q*)	15.1 (*q*)	15.1 (*q*)	14.4 (*q*)
C(19)	61.8 (*t*)	61.8 (*t*)	61.8 (*t*)	61.9 (*t*)	61.9 (*t*)
C(20)	16.0 (*q*)	17.7 (*q*)	16.1 (*q*)	16.1 (*q*)	16.1 (*q*)
AcO	20.8 (*q*), 171.1 (*s*)	21.1 (*q*), 171.2 (*s*)	20.9 (*q*), 171.2 (*s*)	20.9 (*q*), 171.2 (*s*)	20.9 (*q*), 171.1 (*s*)

The structure of **3** was assigned as (2*E*,6*Z*,12*S*,13*E*)-7-[(acetyloxy)methyl]-3,11,15-trimethylhexadeca-2,6,13-triene-1,12,15-triol from further spectral data.

The NMR data of **3**[1]) (*Tables 1* and *2*) were similar to those of (2*E*,6*Z*,11*S*,12*R*)-7-[(acetyloxy)-methyl]-3,11,15-trimethylhexadeca-2,6,14-triene-1,12-diol [5], except for the difference of the terminal isoprene unit in **3**, in which the C(14)=C(15) bond of the known compound was transformed into an (*E*)-configured C(13)=C(14) bond (δ(H) 5.62 (*dd*, J = 15.6, 7.2 Hz) and 5.78 (*d*, J = 15.6 Hz); δ(C) 127.5 (CH) and 139.8 (CH)), and in which an OH group was present at the quaternary C(15) atom (δ(C) 70.5). In the HMBC plot, the correlations H–C(13)/C(11), C(15), C(12), and C(14) and H–C(14)/C(12), C(16), C(17), C(13), and C(15) supported the structure of the terminal isoprene unit. The CD spectrum of the 4-hydroxybenzoate **3a** of **3** showed a positive *Cotton* effect around 243 nm, which allowed to deduce the absolute configuration (12*S*) for **3a** [9][10].

The molecular formula of compound **4** was determined as $C_{22}H_{38}O_5$ by HR-ESI-MS (m/z 383.2798 ($[M+H]^+$, $C_{22}H_{39}O_5^+$)). The IR spectrum showed absorption bands for an ester group (1737 cm^{-1}), C=C bonds (1657 cm^{-1}), and OH groups (3372 cm^{-1}). Compound **4** was assigned as (2*E*,6*Z*,12*R*,14*S*)-7-[(acetyloxy)methyl]-3,11,15-trimethylhexadeca-2,6,15-triene-1,12,14-triol from further spectral data.

The NMR data of **4**[1]) (*Tables 1* and *2*) were similar to those of **3**, except for the resonances of the terminal isoprene unit, in which the (13*E*)-C(13)=C(14) bond and OH–C(15) of **3** were replaced in **4** by a terminal CH_2(16)=C(15) bond (δ(H) 4.98 and 4.81 (2 br. *s*); δ(C) 147.5 (C) and 110.6 (CH_2)) and an oxygenated CH group (δ(H) 4.25 (br. *d*, J = 9.6 Hz); δ(C) 76.8 (CH)). In the HMBC plot, the correlations H–C(14)/C(17), C(12), and C(13), and Me(17)(CH_2(16))/C(14) and C(16)(C(17)) supported the structure of the terminal isoprene unit. The CD spectrum of the 4-hydroxybenzoate **4a**

of **4** also showed a positive *Cotton* effect around 243 nm; therefore the absolute configuration (14*S*) was deduced for **4a**.

The HR-ESI-MS of **5** revealed $[M+H]^+$ at *m/z* 383.2785, establishing the molecular formula $C_{22}H_{38}O_5$. Its IR spectrum indicated the presence of an ester group (1737 cm^{-1}), C=C bonds (1663 cm^{-1}), and OH groups (3394 cm^{-1}). According to four degrees of unsaturation, **5** was confirmed as *rel*-(3*R*,5*S*)-5-{(1*R*,5*Z*,9*E*)-5-[(acetyloxy)methyl]-11-hydroxy-1,9-dimethylundeca-5,9-dien-1-yl}tetrahydro-2,2-dimethylfuran-3-ol.

The NMR data of **5**[1]) (*Tables 1* and *2*) were similar to those of **4**, the main difference being due to the terminal isoprene unit, in which the C(15)=C(16) bond of **4** was replaced in **5** by an oxygenated quaternary C-atom (δ(C) 82.3) and one more Me group. In the HMBC plot, the correlations Me(18)/C(10), C(12), and C(11), H–C(14)/C(12), and Me(16)(Me(17)) with C(14), C(15), and C(17)(C(16)) supported the structure of the terminal isoprene unit. In the NOE difference experiments, no NOE effects between H–C(12) and Me(18) were observed, hence H–C(12) and Me(18) were on opposite faces of the ring. The coupling constants (J(12,13a) = J(12,13b) = 6.8 Hz, J(14,13a) = 5.6 Hz, and J(14,13b) = 3.2 Hz) were similar to those of sachalinol B [11], which indicated that they had similar relative configurations of the furan ring. On the other hand, the absolute configurations of **5** were assumed to be the same as those in **4** because **5** is considered to be biosynthesized from **4** by an epoxidation of the olefin, followed by the ether-bond formation.

All the compounds, except for **2**, were assayed for their *in vitro* cytotoxic activities towards human hepatoma SMMC-7721 cells, human promyelocytic leukemia HL-60 cells, and human hepatocytes L02 cells according to the sulforhodamine B (SRB) [12] method. Vincristine sulfate was used as a positive control which exhibited IC_{50} values of 26.7 ± 4.1, 11.2 ± 1.9, and 28.4 ± 4.2 μg/ml for SMMC-7721, HL-60, and L02 cells, respectively. The new compounds were inactive towards SMMC-7721 and L02 cells ($IC_{50} > 100$ μg/ml); but the IC_{50} of **1** and **3** against HL-60 cells were 40.7 ± 6.9 and 65.6 ± 8.1 μg/ml, respectively. Thus, **1** and **3** may exhibit weak cytotoxicity. As to compound **2**, so little material was left after the 4-hydroxybenzoylation that its *in vitro* cytotoxic activity could not be determined.

Experimental Part

General. Column chromatography (CC): silica gel (200–300 mesh). TLC: silica gel GF_{254} (10–40 μ); detection under UV light or by heating after spraying with 5% H_2SO_4 in EtOH. Optical rotation: *Perkin-Elmer 341* Polarimeter. IR Spectra: *Nicolet 170sx Nexus 670* FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1}. CD Spectra: *Olis-RSM-1000CD* spectrometer; $\lambda([\theta])$ in nm. NMR Spectra: *Varian Mercury* spectrometer; δ in ppm rel. to Me_4Si as internal standard, J in Hz. EI-MS: *HP 5988A* GC/MS instrument; *m/z* (rel. %). HR-ESI-MS: *Bruker Apex* spectrometer.

Plant Material. The seeds of *C. triste* were collected from Chongqing, P. R. China, in August 2005, and identified by Prof. *Guo-Liang Zhang* of the Department of Biology, Lanzhou University. A voucher specimen was deposited with the Institute of Organic Chemistry, Lanzhou University.

Extraction and Isolation. The air-dried seeds of *C. triste* (3.7 kg) were pulverized and extracted 3 × with MeOH (7 d each time) at r.t. The combined extract was concentrated, and the residue (130 g) subjected to CC (silica gel (200–300 mesh; 1300 g), petroleum ether (bp. 60–90°)/acetone 30:1, 15:1, 8:1, and 2:1): *Fractions 1–4*. *Fr. 2* (petroleum ether (60–90°)/acetone 15:1; 20 g) was separated by CC (silica gel (200–300 mesh; 200 g), petroleum ether (60–90°)/AcOEt 15:1 and 8:1): *Fr. 2.1* and *2.2*. *Fr. 2.1* (petroleum ether (60–90°)/AcOEt 10:1; 7.8 g) was purified by repeated CC (silica gel, petroleum

ether (60–90°)/AcOEt 18:1): *Fr. 2.1.1–2.1.4*. *Fr. 2.1.4* was further purified by repeated CC (silica gel, petroleum ether (60–90°)/AcOEt 15:1): **2** (10 mg). *Fr. 2.2* (petroleum ether (60–90°)/AcOEt 4:1; 9.2 g), after further CC (silica gel (200–300 mesh; 92 g), petroleum ether (60–90°)/AcOEt 12:1) gave *Fr. 2.2.1* and *2.2.2*. *Fr. 2.2.2*, after further CC (silica gel, petroleum ether (60–90°)/AcOEt 12:1), gave **1** (48 mg). *Fr. 3* (petroleum ether (60–90°)/acetone 8:1; 32 g) was separated by CC (silica gel (200–300 mesh; 320 g), $CHCl_3$/AcOEt 1:0, 15:1 and 10:1): *Fr. 3.1–3.3*. *Fr. 3.3* was purified by repeated CC (silica gel, petroleum ether (60–90°)/AcOEt/MeOH 10:2:0.2): *Fr. 3.3.1–3.3.3*. *Fr. 3.3.2* was further purified by prep. TLC (petroleum ether (60–90°)/AcOEt/MeOH 10:3:0.1): **5** (18 mg; R_f 0.4) and **4** (22 mg; R_f 0.35). *Fr. 3.3.3* afforded **3** (20 mg; R_f 0.33) by prep. TLC (petroleum ether (60–90°)/AcOEt/MeOH 10:5:0.1).

4-Hydroxybenzoates from Allylic Alcohols. To a soln. of pure compound **1**, **2**, **3**, or **4** (*ca.* 4 mg) in dry pyridine and CH_2Cl_2 under Ar in a dry test tube fitted with a rubber septum, a slight excess of 4-hydroxybenzoyl chloride was added. After 4 h under magnetic stirring at r.t., the 4-hydroxybenzoate was isolated by prep. TLC: **1a**, **2a**, **3a**, and **4a**.

*(2*E*,6*Z*,10*E*,12*R*)-7-[(Acetyloxy)methyl]-3,11,15-trimethylhexadeca-2,6,10,14-tetraene-1,12-diol* (**1**). Colorless gum. $[\alpha]_D^{20} = -0.3$ ($c = 2.0$, $CHCl_3$). IR (KBr): 3410, 2926, 1737, 1669. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 387.2510 ($[M+Na]^+$, $C_{22}H_{36}NaO_4^+$; calc. 387.2506).

CD of **1a** ($c = 1.1$ g/l, MeOH): 244 (−2316).

*(2*E*,6*Z*,10*E*,12*R*)-7-[(Acetyloxy)methyl]-12-hydroxy-3,11,15-trimethylhexadeca-2,6,10,14-tetraenal* (**2**). Colorless gum. $[\alpha]_D^{20} = -1.6$ ($c = 1.6$, $CHCl_3$). IR (KBr): 3411, 2965, 1738, 1668. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 385.2351 ($[M+Na]^+$, $C_{22}H_{34}NaO_4^+$; calc. 385.2350).

CD of **2a** ($c = 1.8$ g/l, MeOH): 245 (−4424).

*(2*E*,6*Z*,12*S*,13*E*)-7-[(Acetyloxy)methyl]-3,11,15-trimethylhexadeca-2,6,13-triene-1,12,15-triol* (**3**). Colorless gum. $[\alpha]_D^{20} = -4.0$ ($c = 2.0$, $CHCl_3$). IR (KBr): 3375, 2929, 1737, 1719, 1667. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 400.3065 ($[M+NH_4]^+$, $C_{22}H_{42}NO_5^+$; calc. 400.3057).

CD of **3a** ($c = 1.5$ g/l, MeOH): 243 (+5093).

*(2*E*,6*Z*,12*R*,14*S*)-7-[(Acetyloxy)methyl]-3,11,15-trimethylhexadeca-2,6,15-triene-1,12,14-triol* (**4**). Colorless gum. $[\alpha]_D^{20} = +4.0$ ($c = 4.0$, $CHCl_3$). IR (KBr): 3372, 2926, 1737, 1712, 1657. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 383.2798 ($[M+H]^+$, $C_{22}H_{39}O_5^+$; calc. 383.2792).

CD of **4a** ($c = 1.4$ g/l, MeOH): 243 (+4092).

rel-*(3*R*,5*S*)-5-{(1*R*,5*Z*,9*E*)-5-[(Acetyloxy)methyl]-11-hydroxy-1,9-dimethylundeca-5,9-dien-1-yl}tetrahydro-2,2-dimethylfuran-3-ol* (**5**). Colorless gum. $[\alpha]_D^{20} = -10.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3394, 2923, 1737, 1663. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 383.2785 ($[M+H]^+$, $C_{22}H_{39}O_5^+$; calc. 383.2792).

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