Highly Acylated 3,4-Secograyanane Diterpenoids from the Fruits of *Pieris formosa*

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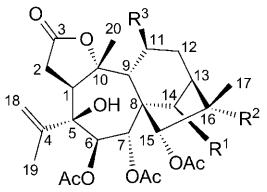
From the fruits of *Pieris formosa*, four new highly acylated 3,4-secograyanane diterpenoids, secorhodomollolides E–H (**1**–**4**, resp.), along with two known ones, secorhodomollolides C and D (**5** and **6**, resp.), were obtained. Their structures were established mainly by spectroscopic methods, including 1D- and 2D-NMR spectroscopy, and mass spectrometry.

Introduction. – Plants of the genus *Pieris*, evergreen shrubs or small trees, containing only seven species, mainly grow in East Asia, East of North America, and West Indies [1]. Although a small genus of the big family of Ericaceae, *Pieris* has attracted much attention due to its toxic constituents, grayanane diterpenoids. Since the first investigation by *Eykman* [2], *ca.* 40 grayanane diterpenoids have been isolated from the plants of genus *Pieris*.

Pieris formosa (WALL) D. DON, a well-known toxic plant, is distributed mainly in hilly and valley regions of South and Southwest China [3]. In folk practice, the juice of the fresh leaves of *P. formosa* can be used as insecticide or lotion for the treatment of ring worm and scabies [4]. Thirteen grayanane diterpenoids, pierisformosins A–D and pierisformosides A–I, were obtained from the flowers and leaves of *P. formosa* [5–9]. Recently, two new highly acylated 3,4-secograyanane diterpenoids (pierisoids A and B) [10] and a new grayanane diterpenoid (grayanotoxin XXII) [11] from the flowers of *P. formosa* were reported. Biological investigations showed that some of these diterpenoids displayed significant physiological properties, including potent acute toxicity in mammals [12][13], antifeedant, growth-inhibitory, and insecticidal activities [14][15].

Our previous phytochemical studies on the flowers of *P. formosa* led to the identification of pierisformotoxins A–D, along with 26 known compounds [16]. We now investigated the fruits of this plant, searching for further structurally unique diterpenoids. As a result, four new highly acylated 3,4-secograyanane diterpenoids, secorhodomollolides E–H (**1**–**4**, resp.), together with two known ones, secorhodomollolides C and D (**5** and **6**, resp.), were isolated from the fruits of *P. formosa*. Here, we describe the isolation and structure elucidation of compounds **1**–**6** (*Fig. 1*).

Results and Discussion. – A 75% aqueous acetone extract of the fruits of *P. formosa* was partitioned between AcOEt and H_2O (1:1). The AcOEt layer was subjected repeatedly to column chromatography on silica gel and *Sephadex LH-20*, and then



	R^1	R^2	R^3
1	Propanoyloxy	OH	AcO
2	Propanoyloxy	AcO	OH
3	AcO	AcO	AcO
4	AcO	AcO	H
5	Propanoyloxy	AcO	H
6	Propanoyloxy	AcO	AcO

Fig. 1. *Structures of compounds* **1**–**6**

purified by semipreparative HPLC to afford four new 3,4-secograyanane diterpenoids **1**–**4**, together with two known ones, secorhodomollolide C (**5**) and secorhodomollolide D (**6**).

Compound **1**, $[\alpha]_D^{24} = -30$ ($c = 0.17$, $CHCl_3$), was isolated as a white amorphous powder. The HR-ESI-MS (negative-ion mode; m/z 637.2512 ($[M-H]^-$)), together with the NMR data, provided the molecular formula of **1** as $C_{31}H_{42}O_{14}$. The ^{1}H-NMR spectrum of **1** (*Table 1*) exhibited signals for a propanoyloxy group at δ(H) 1.25 (t, $J =$ 7.5, 3 H), 2.66 (*dd*, $J = 16.9$, 7.6, 1 H), and 2.55 (*dd*, $J = 16.8$, 7.7, 1 H), and four AcO groups at δ(H) 1.73, 2.14, 2.18, and 2.21 (*s*, each 3 H). In addition, three *singlet*s for Me groups at δ(H) 1.56, 1.95 and 2.09, and signals of five O-bearing CH groups (δ(H) 5.43, 5.74, 5.75, 6.62, and 6.91) and two olefinic CH signals (δ(H) 5.13 and 5.67) were also observed. Besides C-atom resonances of four AcO and one propanoyloxy moieties, the ^{13}C-NMR and DEPT spectra (*Table 2*) showed 20 C-atom signals, including those of three Me, three CH_2 (one olefinic), and eight CH groups (five O-bearing), as well as of six quaternary C-atoms (one COO, one olefinic, and three O-bearing), suggesting that compound **1** is probably a highly acylated diterpenoid.

The ^{13}C-NMR data of compound **1** showed that signals due to an AcO unit was absent, and the resonances for C(13), C(14), C(16), and C(17) were shifted by $\Delta\delta$(C) $+6.3$, $+2.2$, -7.1, and $+4.7$ ppm, respectively, as compared with those of compound **6** (*Table 2*). These data revealed that the AcO group at C(16) in **6** was replaced by a OH group in **1**, which was confirmed by the following 2D-NMR data. Signal at δ(H) 4.41, showing no correlation with any C-atoms in the HSQC spectrum, was assigned to an exchangeable OH H-atom. Further, in the HMBC spectrum of **1** (*Fig. 2*), correlations from δ(H) 4.41 to C(16) (δ(C) 81.1) and C(17) (δ(C) 23.7) implied a OH group at C(16), which resulted in the change of the chemical shifts of C(13), C(14), C(16), and C(17).

The relative configurations of the stereogenic centers of **1** were assigned to be the same as those of **6** based on the similarity of the chemical shifts in ^{1}H- and ^{13}C-NMR

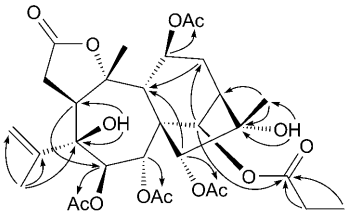


Fig. 2. *Key HMBCs of compound* **1**

Table 1. *^{1}H-NMR Data of Compounds* **1**–**6** *in (D$_6$)Pyridine*[a]). δ in ppm, J in Hz.

Position	**1**	**2**	**3**	**4**	**5**	**6**
1	3.64 (*dd*, *J* = 12.6, 7.5)	4.41 (*dd*, *J* = 13.4, 7.0)	3.71 (*dd*, *J* = 13.5, 7.6)	3.17–3.21 (*m*)	3.19 (overlapped)	3.71 (*dd*, *J* = 13.5, 8.0)
2α	3.11 (*dd*, *J* = 17.1, 13.5)	3.10 (*dd*, *J* = 16.4, 14.3)	3.10 (*dd*, *J* = 15.9, 13.5)	3.08 (*dd*, *J* = 16.6, 13.4)	3.07 (*dd*, *J* = 17.0, 13.0)	3.09 (*dd*, *J* = 17.5, 13.5)
2β	2.50 (overlapped)	2.35 (*dd*, *J* = 16.2, 7.1)	2.13 (overlapped)	2.50 (*dd*, *J* = 16.9, 6.8)	2.50 (*dd*, *J* = 17.0, 7.0)	2.10 (overlapped)
5-OH	7.33 (*s*)	7.13 (*s*)	7.24 (*s*)	7.14 (*s*)	7.02 (*s*)	
6	5.74 (*d*, *J* = 9.6)	6.00 (*d*, *J* = 8.9)	5.65 (*d*, *J* = 9.7)	5.59 (*d*, *J* = 9.9)	5.56 (*d*, *J* = 9.8)	5.60 (*d*, *J* = 9.6)
7	6.62 (*d*, *J* = 9.5)	6.80 (*d*, *J* = 8.8)	6.39 (*d*, *J* = 9.5)	6.26 (*d*, *J* = 9.6)	6.26 (*d*, *J* = 9.7)	6.37 (*d*, *J* = 9.6)
9	3.20 (*d*, *J* = 3.8)	2.44 (overlapped)	3.56 (*d*, *J* = 4.7)	3.26–3.28 (*m*)	3.21 (overlapped)	3.55 (*d*, *J* = 5.0)
11	5.75 (*t*, *J* = 4.3)	4.68 (br. *s*)	5.68 (*t*, *J* = 4.8)	1.75 (overlapped)	1.94 (overlapped, H$_\alpha$), 1.66 (overlapped, H$_\beta$)	5.61–5.66 (*m*)
12	2.46 (overlapped, H$_\alpha$), 2.20 (overlapped, H$_\beta$)	2.34 (overlapped, H$_\alpha$), 2.08 (overlapped, H$_\beta$)	2.42–2.29 (*m*)	2.00 (overlapped, H$_\alpha$), 1.48–1.54 (*m*, H$_\beta$)	2.02 (overlapped, H$_\alpha$), 1.50–1.56 (*m*, H$_\beta$)	2.46 (*dd*, *J* = 13.6, 10.8, H$_\alpha$), 2.10–2.66 (*m*, H$_\beta$)
13	2.47 (br. *s*)	3.40 (*d*, *J* = 9.2)	3.61 (*d*, *J* = 10.5)	3.57 (br. *s*)	3.52 (*d*, *J* = 10.2)	3.59 (*dd*, *J* = 19.0, 8.5)
14	6.91 (*s*)	7.35 (*s*)	6.95 (*s*)	6.05 (*s*)	6.08 (*s*)	7.00 (*s*)
15	5.43 (*s*)	5.62 (*s*)	5.34 (*s*)	5.28 (*s*)	5.32 (*s*)	5.32 (*s*)
HO–C(16)	4.41 (*s*)					
17	1.56 (*s*)	1.90 (*s*)	1.70 (*s*)	1.67 (*s*)	1.69 (*s*)	1.70 (*s*)
18	5.67 (*s*), 5.13 (*s*)	5.61 (*s*), 5.02 (*s*)	5.66 (*s*), 5.10 (*s*)	5.59 (*s*), 5.03 (*s*)	5.59 (*s*), 5.05 (*s*)	5.65 (*s*), 5.10 (*s*)
19	1.95 (*s*)	1.79 (*s*)	1.98 (*s*)	1.91 (*s*)	1.91 (*s*)	1.98 (*s*)
20	2.09 (*s*)	2.12 (*s*)	2.09 (*s*)	2.03 (*s*)	2.01 (*s*)	2.08 (*s*)
AcO–C(6)	1.73 (*s*)	1.72 (*s*)	1.67 (*s*)	1.64 (*s*)	1.68 (*s*)	1.68 (*s*)
AcO–C(7)	2.18 (*s*)	2.13 (*s*)	2.22 (*s*)	2.20 (*s*)	2.20 (*s*)	2.15 (*s*)
AcO–C(11)	2.14 (*s*)		2.14 (*s*)			2.16 (*s*)
Propanoyl-oxy–C(14) or AcO–C(14)	1.25 (*t*, *J* = 7.5), 2.66 (*dd*, *J* = 16.9, 7.6), 2.55 (*dd*, *J* = 16.8, 7.7)	1.27 (*t*, *J* = 7.5), 2.57 (*dd*, *J* = 15.9, 7.4), 2.44 (overlapped)	2.28 (*s*)	2.29 (*s*)	1.31 (*t*, *J* = 7.5), 2.78 (*dd*, *J* = 16.8, 7.5), 2.41 (*dd*, *J* = 16.8, 7.5)	1.32 (*t*, *J* = 7.2), 2.72–2.77 (*m*), 2.39–2.44 (*m*)
AcO–C(15)	2.21 (*s*)	2.20 (*s*)	2.22 (*s*)	2.21 (*s*)	2.22 (*s*)	2.22 (*s*)
AcO–C(16)		2.03 (*s*)	2.14 (*s*)	2.12 (*s*)	2.13 (*s*)	2.29 (*s*)

[a]) The ^{1}H-NMR spectra of compounds **1**, **3**, **4**, **5**, and **6** were recorded at 500 MHz, and that of **2** was recorded at 400 MHz.

Table 2. *^{13}C-NMR Data of Compounds* **1**–**6** *in (D$_5$)Pyridine*[a]). δ in ppm.

C-Atom	**1**	**2**	**3**	**4**	**5**	**6**
1	43.3 (*d*)	42.8 (*d*)	42.9 (*d*)	40.9 (*d*)	41.0 (*d*)	42.8 (*d*)
2	30.7 (*t*)	31.1 (*t*)	30.7 (*t*)	31.7 (*t*)	31.7 (*t*)	30.7 (*t*)
3	173.9 (*s*)	174.9 (*s*)	174.0 (*s*)	174.3 (*s*)	174.3 (*s*)	174.1 (*s*)
4	147.7 (*s*)	148.5 (*s*)	147.9 (*s*)	148.1 (*s*)	148.2 (*s*)	148.0 (*s*)
5	76.4 (*s*)	76.7 (*s*)	76.4 (*s*)	76.2 (*s*)	76.2 (*s*)	76.3 (*s*)
6	74.0 (*d*)	74.1 (*d*)	74.1 (*d*)	74.3 (*d*)	74.4 (*d*)	74.0 (*d*)
7	67.5 (*d*)	66.7 (*d*)	67.6 (*d*)	68.4 (*d*)	68.5 (*d*)	67.6 (*d*)
8	53.4 (*s*)	53.1 (*s*)	53.4 (*s*)	52.9 (*s*)	53.0 (*s*)	53.4 (*s*)
9	58.9 (*d*)	57.6 (*d*)	60.9 (*d*)	57.6 (*d*)	57.3 (*d*)	60.8 (*d*)
10	88.1 (*s*)	89.3 (*s*)	88.3 (*s*)	89.1 (*s*)	89.2 (*s*)	88.3 (*s*)
11	68.4 (*d*)	62.8 (*d*)	68.6 (*d*)	18.8 (*t*)	18.9 (*t*)	68.7 (*d*)
12	31.4 (*t*)	35.2 (*t*)	30.6 (*t*)	22.6 (*t*)	22.7 (*t*)	30.5 (*t*)
13	47.8 (*d*)	45.0 (*d*)	41.6 (*d*)	42.2 (*d*)	42.5 (*d*)	41.5 (*d*)
14	77.8 (*d*)	78.1 (*d*)	76.0 (*d*)	77.0 (*d*)	76.9 (*d*)	75.6 (*d*)
15	90.7 (*d*)	88.9 (*d*)	92.3 (*d*)	91.7 (*d*)	91.4 (*d*)	92.2 (*d*)
16	81.1 (*s*)	90.0 (*s*)	88.3 (*s*)	88.2 (*s*)	88.3 (*s*)	88.2 (*s*)
17	23.7 (*q*)	22.8 (*q*)	19.2 (*q*)	18.7 (*q*)	18.9 (*q*)	19.0 (*q*)
18	113.9 (*t*)	113.1 (*t*)	113.9 (*t*)	113.6 (*t*)	113.5 (*t*)	113.9 (*t*)
19	19.1 (*q*)	18.8 (*q*)	19.1 (*q*)	18.7 (*q*)	18.9 (*q*)	19.3 (*q*)
20	28.8 (*q*)	27.4 (*q*)	30.2 (*q*)	29.9 (*q*)	29.7 (*q*)	30.2 (*q*)
*Ac*O–C(6)	19.9 (*q*), 169.2 (*s*)	20.1 (*q*), 169.1 (*s*)	19.9 (*q*), 169.1 (*s*)	19.9 (*q*), 169.0 (*s*)	19.9 (*q*), 169.1 (*s*)	19.9 (*q*), 169.1 (*s*)
*Ac*O–C(7)	21.4 (*q*), 170.2 (*s*)	21.7 (*q*), 170.2 (*s*)	21.3 (*q*), 170.7 (*s*)	21.6 (*q*), 170.7 (*s*)	21.6 (*q*), 170.7 (*s*)	21.6 (*q*), 170.8 (*s*)
*Ac*O–C(11)	21.4 (*q*), 169.0 (*s*)		21.6 (*q*), 168.9 (*s*)			21.3 (*q*), 168.9 (*s*)
*Ac*O–C(14) or Propanoyloxy–C(14)	9.1 (*q*), 28.4 (*t*), 173.2 (*s*)	9.6 (*q*), 28.6 (*t*), 173.6 (*s*)	21.9 (*q*), 171.2 (*s*)	21.9 (*q*), 171.2 (*s*)	9.2 (*q*), 28.3 (*t*), 174.8 (*s*)	9.3 (*q*), 28.3 (*t*), 174.8 (*s*)
*Ac*O–C(15)	20.9 (*q*), 171.5 (*s*)	21.1 (*q*), 171.1 (*s*)	20.8 (*q*), 171.9 (*s*)	20.8 (*q*), 171.7 (*s*)	20.8 (*q*), 171.7 (*s*)	20.8 (*q*), 171.9 (*s*)
*Ac*O–C(16)		22.5 (*q*), 169.9 (*s*)	22.9 (*q*), 170.3 (*s*)	22.9 (*q*), 170.2 (*s*)	22.9 (*q*), 170.3 (*s*)	23.0 (*q*), 170.4 (*s*)

[a]) The ^{13}C-NMR spectra of compounds **1**, **3**, **4**, **5**, and **6** were recorded at 125 MHz, and that of **2** was recorded at 100 MHz.

spectra, as well as ^{1}H-NMR multiplicities for both compounds. In the ROESY spectrum of **1**, cross-peaks between H–C(1) with H–C(6) and H–C(14); H–C(6) with Me(19); H–C(14) with H–C(11) and H–C(13); and H–C(13) with HO–C(16) confirmed that H–C(1), H–C(6), H–C(11), H–C(13), H–C(14), HO–C(16), and Me(19) are α-oriented. Meanwhile, ROESY correlations HO–C(5)/H–C(7), H–C(7)/Me(20), Me(20)/H–C(9), H–C(9)/H–C(15), and H–C(15)/Me(17) indicated that HO–C(5), H–C(7), H–C(9), H–C(15), Me(17), and Me(20) were β-configured. Thus, the structure of compound **1** was assigned and designated as secorhodomollolide E.

Compound **2**, $[\alpha]_D^{25} = -25.7$ ($c = 0.11$, $CHCl_3$), also obtained as white amorphous powder, had the same molecular formula ($C_{31}H_{42}O_{14}$) as compound **1**, based on HR-

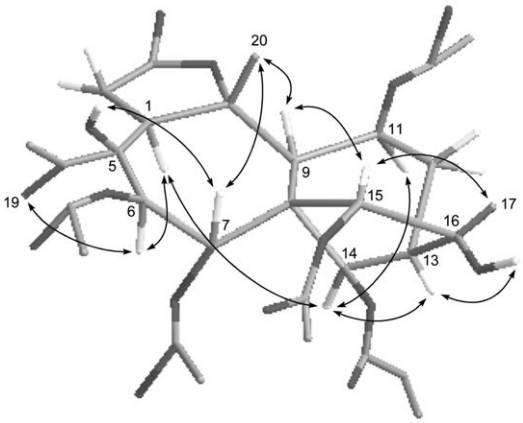


Fig. 3. *Key ROESY correlations of compound* **1**

ESI-MS (*m*/*z* 637.2495 ([*M* – H]$^-$)). The similarity of the NMR spectra of **2** to those of **1** indicated that **2** was an isomer of **1**, with **2** differing only by the position of one of the AcO groups. The upfield resonance of CH(11) (δ(H) 4.68 (br. *s*); δ(C) 62.8), coupled with the obvious downfield resonance of C(16) (δ(C) 90.0), suggested that the AcO group was at C(16) in **2**, rather than at C(11) as in **1**, and, accordingly, the OH group was at C(11). The very similar coupling patterns and ROESY data of **2** and **1** also indicated their identical configuration. Therefore, the structure of compound **2** was established as shown and named as secorhodomollolide F.

Compound **3**, a white amorphous powder, $[\alpha]_D^{23} = -20$ ($c = 0.12$, $CHCl_3$), had the molecular formula of $C_{32}H_{42}O_{15}$, deduced from HR-ESI-MS (negative-ion mode; *m*/*z* 665.2445 ([*M* – H]$^-$)). The ^{13}C-NMR data of compound **3** were quite similar to those of **6** (*Table 2*), and the difference was that **3** contained six AcO groups and no *O*-propanoyl moiety. The 2D-NMR data of **3** revealed that, as compared to **6**, an AcO instead of a propanoyloxy group was located at C(14). On comparing the coupling constants and ROESY data with those of compounds **1** and **6**, the configuration of **3** was found to be identical to those of **1** and **6**. Consequently, the structure of **3** was established and named as secorhodomollolide G.

Compound **4**, isolated as a white amorphous powder, $[\alpha]_D^{23} = +5.7$ ($c = 0.12$, $CHCl_3$), had the molecular formula $C_{30}H_{40}O_{13}$, based on its HR-ESI-MS (negative-ion mode; at *m*/*z* 607.2392 ([*M* – H]$^-$)). The ^{13}C-NMR analysis of **4** (*Table 2*) revealed similarities between the structures of **4** and **5**. The obvious difference was that the propanoyloxy group at C(14) in **5** was replaced by an AcO group in **4**. This observation was confirmed by the correlation from H–C(14) (δ(H) 6.05) to the AcO CO group at (δ(C) 171.2) in the HMBC spectrum of **4**. The ROESY spectrum demonstrated that compound **4** had the same configuration as those of compounds **1**–**3**. Then, the structure of compound **4** was established and named as secorhodomollolide H.

Compound **5** (ESI-MS: *m*/*z* 621 ([*M* – H]$^-$)) was identified as secorhodomollolide C, which was previously isolated from the flower buds of *Rhododendron molle* [17]. The reported NMR assignments for C(1) (δ(C) 56.0) and C(9) (δ(C) 40.3) of **5** had to

be revised because of strong HMBCs from HO–C(5) (δ(H) 7.02 (*s*)), H_α–C(2) (δ(H) 3.07 (*dd*, $J = 17.0, 13.0$)), H_β–C(2) (δ(H) 2.50 (*dd*, $J = 17.0, 7.0$)), and Me(20) (δ(H) 2.01 (*s*)) to δ(C) 41.0, and from H–C(7) (δ(H) 6.26 (*d*, $J = 9.7$)), H–C(14) (δ(H) 6.08 (*s*)), H–C(15) (δ(H) 5.32 (*s*)) to δ(C) 57.3. The above correlations implied the assignments of δ(C) 41.0 to C(1) and of δ(C) 57.3 to C(9); therefore, the published assignments should be revised.

Compound **6** (ESI-MS: *m*/*z* 715 ($[M + Cl]^+$) was identified as secorhodomollolide D by comparison of the NMR data with those reported in the literature [17].

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Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 or 100–200 mesh, *Qingdao Marine Chemical Factory*, P. R. China) and *Sephadex LH-20* (*Amersham Biosciences AB*, S-Uppsala). TLC: silical-gel *GF-254* plates (*Qingdao Marine Chemical Factory*, P. R. China), visualization by spraying with 10% H_2SO_4/EtOH, followed by heating on a hot plate. Semiprep. HPLC: *Agilent 1200* system with a *Zorbax SB-C_{18}* column (5 μm, 9.4 × 250 mm). Optical rotations: *Jasco DIP-370* digital polarimeter. 1D- and 2D-NMR Spectra: *Bruker-DRX-500* and *-AM-400* spectrometers. ESI-MS and HR-ESI-MS Spectra: *API Qstar Pulsar* instrument.

Plant Material. The fruits of *P. formosa* were collected in Jindian, Kunming, Yunnan Province, P. R. China, in October 2009. The sample was identified by Dr. *Yong-Peng Ma*, Kunming Institute of Botany, Chinese Academy of Sciences, and a voucher specimen (KMUST 2009100801) has been deposited with the Laboratory of Phytochemistry, Biotechnology Research Center, Kunming University of Science and Technology.

Extraction and Isolation. The air-dried and powdered fruits of *P. formosa* (6 kg) were extracted with 75% aq. acetone (3 × 18 l, 24 h each) at r.t. The filtrate was concentrated under reduced pressure to give a crude extract, which was then partitioned between H_2O and AcOEt (1:1; 3 × 4 l). The AcOEt extract (350 g) was chromatographed on *Sephadex LH-20* (MeOH/H_2O 3:7, 6:4, 9:1, 1:0) to afford *Frs. I–VI*. *Fr. I* (MeOH/H_2O 3:7; 45 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 20:0, 19:1, 9:1, 4:1, 0:20) to give five fractions, *Frs. A–E*. Mixed crystals were obtained from *Fr. B* ($CHCl_3$/MeOH 19:1; 9 g), and were further chromatographed on SiO_2 ($CHCl_3$/MeOH 180:1, 150:1, 100:1), to obtain compounds **5** (94 mg) and **6** (115 mg). The mother liquor of *Fr. B* was subjected to CC (SiO_2; petroleum ether (PE)/Me_2CO 9:1, 8:2, 7:3, 6:4) to afford four subfractions, *Subfrs. B1–B4*. *Subfr. B1* was then purified by semiprep. HPLC (45–55% MeOH/H_2O; 3 ml/min) to give compound **4** (3 mg). *Subfr. B2* was separated by CC (SiO_2; PE/Me_2CO 10:1), and then by semiprep. HPLC (40% MeOH/H_2O; 3 ml/min) to yield compounds **1** (11 mg) and **3** (6 mg). *Subfr. B3* was repeatedly recrystallized with MeOH to afford compound **2** (19 mg).

Secorhodomollolide E (= rel-*(3a*R,*5*R,*6*S,*6a*S,*7*R,*9*R,*11a*S,*11b*R*)-5,6,7,11-Tetrakis(acetyloxy)dodecahydro-4,8-dihydroxy-8,11b-dimethyl-2-oxo-4-(prop-1-en-2-yl)-4*H*-6a,9-methanoheptaleno[1,2-b]furan-12-yl Propanoate*; **1**). White amorphous powder. $[\alpha]_D^{24} = -30$ ($c = 0.17$, $CHCl_3$). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. ESI-MS (neg.): 637 ($[M - H]^-$). HR-ESI-MS (neg.): 637.2512 ($[M - H]^-$, $C_{31}H_{41}O_{14}^-$; calc. 637.2496).

Secorhodomollolide F (= rel-*(3a*R,*5*R,*6*S,*6a*S,*7*R,*9*R,*11a*S,*11b*R*)-5,6,7,8-Tetrakis(acetyloxy)dodecahydro-4,11-dihydroxy-8,11b-dimethyl-2-oxo-4-(prop-1-en-2-yl)-4*H*-6a,9-methanoheptaleno[1,2-b]furan-12-yl Propanoate*; **2**). Colorless prisms (MeOH). M.p. 278–279°. $[\alpha]_D^{25} = -26$ ($c = 0.11$, $CHCl_3$). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. ESI-MS (neg.): 637 ($[M - H]^-$). HR-ESI-MS (neg.): 637.2495 ($[M - H]^-$, $C_{31}H_{41}O_{14}^-$; calc. 637.2496).

Secorhodomollolide G (= rel-*(3a*R,*5*R,*6*S,*6a*S,*7*R,*9*R,*11a*S,*11b*R*)-Dodecahydro-4-hydroxy-8,11b-dimethyl-2-oxo-4-(prop-1-en-2-yl)-4*H-*6a,9-methanoheptaleno[1,2-*b*]*furan-5,6,7,8,11,12-hexayl Hexaacetate*; **3**). White amorphous powder. $[\alpha]_D^{23} = -20$ ($c = 0.12$, $CHCl_3$). ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. ESI-MS (neg.): 665 ($[M-H]^-$). HR-ESI-MS (neg.): 665.2445 ($[M-H]^-$, $C_{32}H_{41}O_{15}^-$; calc. 665.2445).

Secorhodomollolide H (= rel-*(3a*R,*5*R,*6*S,*6a*S,*7*R,*9*R,*11a*S,*11b*R*)-Dodecahydro-4,11-dihydroxy-8,11b-dimethyl-2-oxo-4-(prop-1-en-2-yl)-4*H-*6a,9-methanoheptaleno[1,2-*b*]*furan-5,6,7,8,12-pentayl Pentaacetate*; **4**). White amorphous powder. $[\alpha]_D^{23} = +6$ ($c = 0.12$, $CHCl_3$). ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. ESI-MS (neg.): 607 ($[M-H]^-$). HR-ESI-MS (neg.): 607.2392 ($[M-H]^-$, $C_{30}H_{39}O_{13}^-$; calc. 607.2390).

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