Molecules **2010**, *15*, 1089-1096; doi:10.3390/molecules15021089

OPEN ACCESS

molecules

ISSN 1420-3049

www.mdpi.com/journal/molecules

Article

Isolation and Identification of Two New Polyynes from a North American Ethnic Medicinal Plant--*Oplopanax horridus* (Smith) Miq.

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Received: 27 December 2009; in revised form: 4 February 2010 / Accepted: 19 February 2010 / Published: 23 February 2010

Abstract: Two new polyynes, named oplopantriol A (**5**) and oplopantriol B (**6**), were isolated from the root bark of *Oplopanax horridus* (Smith) Miq, an ethnic medicinal plant of North America, along with four known polyynes: (3*S*,8*S*)-falcarindiol (**1**), oplopandiol (**2**), (11*S*,16*S*,9*Z*)-9,17-octadecadiene-12,14-diyne-1,11,16-triol, 1-acetate (**3**) and oplopandiol acetate (**4**). The structures of the new compounds were elucidated by detailed spectroscopic analyses, including 1D and 2D NMR techniques and chemical methods. The absolute configurations of the new compounds **5** and **6** were determined by comparing their optical rotation values with the hydrolysis products of the known compounds **3** and **4**, respectively, derived from the same plant. On the basis of an analysis of their physical and chemical properties we show that the alkaline hydrolysis of **3** and **4** afforded the new compounds **5** and **6**, respectively.

Keywords: *Oplopanax horridus*; polyyne; oplopantriol A and B; alkaline hydrolysis

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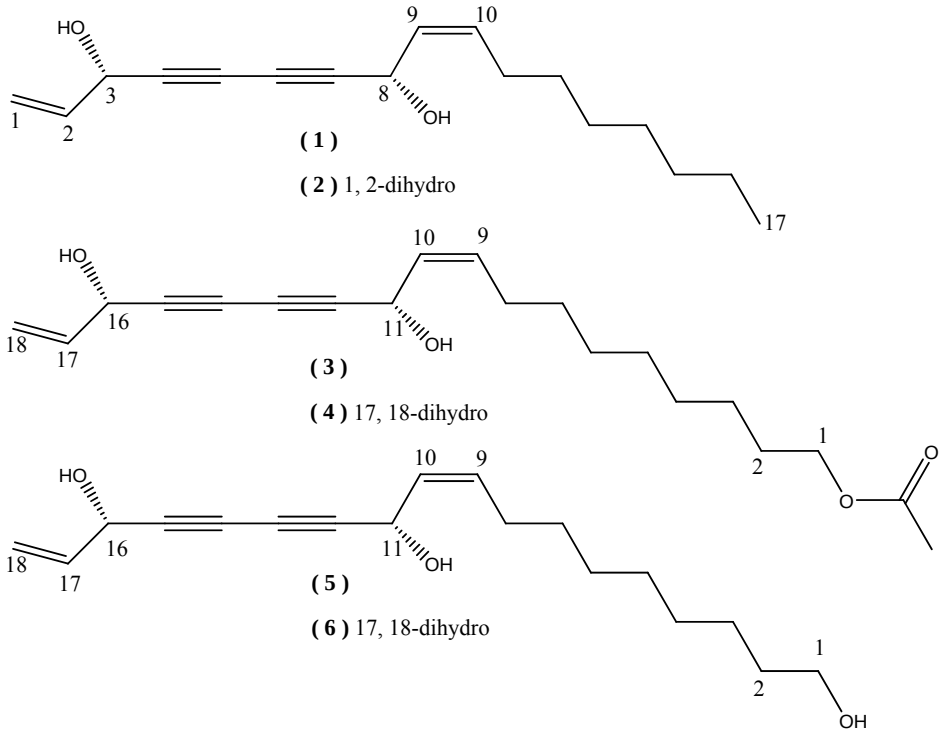
1. Introduction

Plants of the genus *Oplopanax*, belonging to the family Araliaceae, comprise three species which are *Oplopanax japonicus* (Nakai) Nakai. uniquely found in Japan, *Oplopanax elatus* Nakai, only distributed in northeast China, and *Oplopanax horridus* (Smith) Miq. exclusively originated and grown in North America [1-3]. These ethnic medicinal herbs were reported to have anti-tuberculosis, antibiotic, lineae atrophicae relieving, antifungal, anti-psoriasis and anticancer activities [4-9]. *O. horridus*, commonly known as Devil's Club, whose inner bark and roots are used by First Nations peoples for a variety of ailments such as diabetes, rheumatism, tuberculosis, colds, headaches, and lung hemorrhages [10], was reported to afford antimycobacterial and antifungal polyyne ingredients [11]. As a part of our research work on bioactive metabolites from the plants of *Oplopanax*, phytochemical investigation on *O. horridus* was conducted and two new polyynes **5** and **6** were isolated, together with four known polyynes: (3*S*,8*S*)-falcarindiol (**1**), oplopandiol (**2**), (11*S*,16*S*,9*Z*)-9,17-octadecadiene-12,14-diyne-1,11,16 -triol, 1-acetate (**3**) and oplopandiol acetate (**4**) (Figure 1) [11]. Although the planar structure of compound **5** was reported previously, the absolute configuration was not elucidated [12]. The present paper describes the isolation and structural elucidation of compounds **5** and **6** on the basis of the IR, ^{1}H- and ^{13}C-NMR, Hydrogen-Hydrogen Correlation Spectroscopy (H-H COSY), Heteronuclear Multiple Quantum Coherence (HMQC), Heteronuclear Multiple Bond Coherence (HMBC), mass spectroscopic data and chemical methods.

Figure 1. Structures of compounds **1**-**6**.



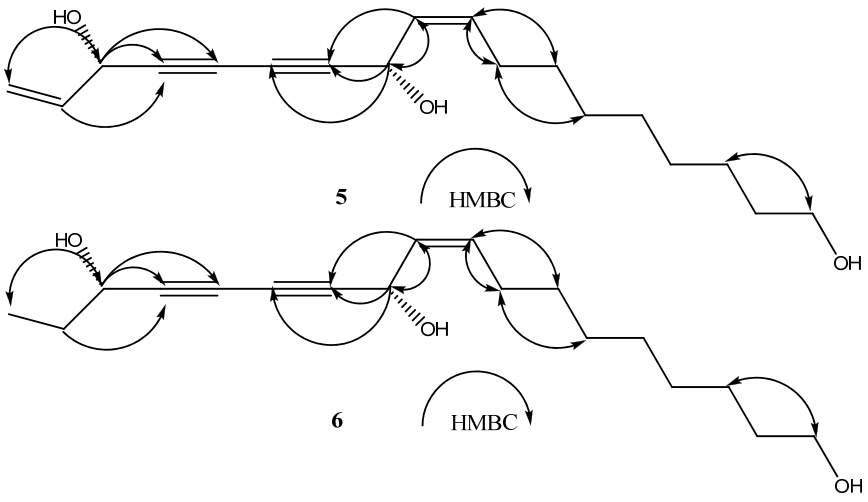
2. Results and Discussion

By successive column chromatography (CC) on silica gel and octadecyl silica gel (ODS gel) and prep-HPLC, an 85% ethanol extract of air-dried root bark of *O. horridus* afforded two new polyynes **5**,

6, along with four known compounds **1-4**. The identification of **5** and **6** were made by spectroscopic data. The absolute configurations of the new compounds **5** and **6** were determined by comparing their optical rotation values with the hydrolysis products of the known compounds **3** and **4,** respectively, derived from the same plant.

Compound **5** was obtained as a yellowish oil. The molecular formula of **5** was determined to be $C_{18}H_{26}O_3$ on the basis of the HR-electrospray ionization (ESI)-MS spectrum (*m/z* 289.1867 $[M-H]^-$, Calcd for $C_{18}H_{25}O_3$: 289.1804). The UV (288, 271, 263, and 253 nm) and IR absorptions (2250 and 1675 cm^{-1}) indicated the presence of two C≡C bonds [13]. The ^{1}H-NMR spectrum of **5** displayed signals due to five olefinic protons at δ_H 5.93 (ddd, J = 17.4, 10.0, 5.5 Hz), 5.58 (ddt, J = 10.6, 7.3, 1.0 Hz), 5.51 (ddt, J = 10.6, 8.2, 1.0 Hz), 5.46 (dt, J = 17.4, 1.0 Hz) and 5.22 (dt, J = 10.0, 1.0 Hz), in addition to a hydroxymethyl group at δ_H 3.64 (2H, t, J = 6.5 Hz), seven methylene groups at δ_H 2.11 (2H, tq, J = 7.1, 1.5 Hz), 1.56 (2H, m), 1.39 (2H, m) and 1.31 (8H, m) (Table 1). Analysis of the ^{13}C-NMR and HMQC spectra revealed the presence of 18 carbons (Table 1), containing seven methylenes carbons (δ_C 25.6-32.6) and one hydroxymethyl at δ_C 63.0, four olefinic carbons at δ_C 136.0, 134.2, 127.9 and 117.1, four unprotonated acetylenic carbons and two oxygen-bearing sp^3 carbons at δ_C 58.5 and 63.3. All protonated C-atoms and their corresponding H-atoms were assigned by the HMQC experiments. The structure elucidation was assisted by analyses of the HMBC experiments (Figure 2). The HMBC correlations between H-16 (δ_H 4.93) and C-18 (δ_C 117.1), C-17 (δ_C 136.0), C-15 (δ_C 78.5) and C-14 (δ_C 70.1) indicated that the hydroxy group was connected to C-16. Furthermore, the correlations between H-11 (δ_H 5.19) and C-13 (δ_C 68.7), C-12 (δ_C 79.8), C-9 (δ_C 127.9) and C-10 (δ_C 134.2) identified that another hydroxyl group was attached to C-11. The correlations in the H-H COSY spectrum between the hydroxy methylene at δ_H 5.19 and olefinic proton at δ_H 5.58 as well as between the other hydroxy methylene at δ_H 4.93 and another olefinic proton at δ_H 5.93 confirmed above findings. The geometry of the double bond between C-9 and C-10 was determined to be *cis* as the alkene bond was fixed to be ***Z*** according to the vicinal coupling constant between H-9 and H-10 ($J_{9,10}$ = 10.6 Hz). On the basis of these structural determinations, the planar structure of **5** was established as 9,17-octadecadien-12,14-diyne-1,11,16-triol. The absolute configuration of compound **5** was not elucidated, but would be determined together with that of compound **6**.

Figure 2. Key HMBC correlations (H → C) of compounds **5** and **6**.



Compound **6** was prepared as yellowish oil. Its molecular formula, $C_{18}H_{28}O_3$, was determined from the $[M-H]^-$ peak at 291.1966 (Calcd for $C_{18}H_{27}O_3$: 291.1960), in the HR-ESI-MS spectrum. The UV (287, 261, 255, and 226 nm) and IR absorptions (2232 and 1656 cm^{-1}) suggested that compound **6** had the same structural skeleton as compound **5**. The ^1H and ^{13}C NMR (Table 1) spectra of **6** were similar to those of **5**, except for the appearance of signals for an ethyl group [δ_H 1.00 (3H, t, J = 7.5 Hz) and 1.74 (2H, m); δ_C 9.3 and 30.6] and the disappearance of the signals for the terminal double bond [δ_H 5.52 (1H, dt, J = 10.0 and 1.0 Hz), 5.46(3H, dt, J = 17.6 and 1.0 Hz) and 5.93 (3H, ddd, J = 17.4, 10.0 and 5.5 Hz); δ_C 117.1 and 136.0], suggesting that **6** was a dihydro derivative of **5**. In the HMBC spectrum (Figure 2), the correlations between H-16 [δ_H 4.37(1H, t, J = 6.6 Hz)] and C-17 (δ_C 30.6), C-18 (δ_C 9.3), C-15 (δ_C 80.9) and C-14 (δ_C 68.8), as well as between H-11 [δ_H 5.19 (1H, br.d, J = 8.2 Hz)] and C-10 (δ_C 134.1), C-9 (δ_C 128.0), C-12 (δ_C 79.1) and C-13 (δ_C 68.8) confirmed the structure as shown in Figure 1. The geometry of the double bond between C-10 and C-9 was determined to be the same as compound **5** as *cis* and ***Z***. According to the above results, the planar structure of **6** was elucidated to be 9-octadecaen-12,14-diyne-1,11,16-triol.

Table 1. ^1H- (500 MHz) and ^{13}C-NMR (125 MHz) data of **5** and **6** in $CDCl_3$[α, β].

Carbon position	compound **5**		compound **6**	
	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
1	3.64, t (2H, 6.5)	63.0	3.64, t (2H, 6.5)	63.0
2	1.56, m (2H)	32.6	1.57, m (2H)	32.6
3	1.31, m (2H)	25.6	1.31, m (2H)	25.6
4	1.31, m (2H)	29.1[a]	1.31, m (2H)	29.1[b]
5	1.31, m (2H)	29.2	1.31, m (2H)	29.2
6	1.31, m (2H)	29.0[a]	1.31, m (2H)	29.0[b]
7	1.39, m (2H)	28.8	1.38, m (2H)	28.8
8	2.11, dq (2H, 7.1, 1.5)	27.5	2.11, dq (2H, 7.1, 1.5)	27.5
9	5.51, ddt (1H, 10.6, 8.2, 1.5)	127.9	5.52, ddt (1H, 10.6, 8.2, 1.5)	128.0
10	5.58, ddt (1H, 10.6, 7.3, 1.5)	134.2	5.58, ddt (1H, 10.6, 7.3, 1.5)	134.1
11	5.19, d (1H, 8.0)	58.5	5.19, br.d (1H, 8.0)	58.5
12	-	79.8	-	79.1
13	-	68.7	-	68.8[c]
14	-	70.1	-	68.8[c]
15	-	78.5	-	80.9
16	4.93, br.d (1H, 5.5)	63.3	4.37, t (1H, 6.6)	63.8
17	5.93, ddd (1H, 17.4, 10.0, 5.5)	136.0	1.74, m (2H)	30.6
18	5.22, dt (1H, 10.0, 1.0); 5.46, dt (1H, 17.4, 1.0)	117.1	1.00, t (3H, 7.5)	9.3

[α] TMS was used as an internal standard in spectra experiments; [β] Assignments based on HMQC and HMBC experiments; [a-c] Assignments may be interchanged.

Alkaline hydrolysis of **3** and **4** afforded their deacetyl derivatives **3a** and **4a**, respectively, which had the same retention times as **5** and **6** by Ultra Performance Liquid Chromatography (UPLC) analysis.

Furthermore, the optical rotation values of **3a** {$[\alpha]_D^{25}$ + 189.3° (*c* = 0.23, $CHCl_3$)} and **4a** {$[\alpha]_D^{25}$ + 230.6° (*c* = 0.11, $CHCl_3$)} were identical with those of the new polyynes **5** {$[\alpha]_D^{25}$ +194.4° (*c* = 0.16, $CHCl_3$)}and **6**{$[\alpha]_D^{25}$ + 233.0° (*c* = 0.3, $CHCl_3$)}, respectively. The above evidence indicated that **5** and **6** should have the same absolute configurations with the known compounds **3** and **4**. Thus, the complete structures of the new polyynes, oplopantriol A (**5**) and oplopantriol B (**6**), were elucidated to be (11*S*,16*S*,9*Z*)-9,17-octadecadien-12,14-diyne-1,11,16-triol and (11*S*,16*S*,9*Z*)-9-octadecaen-12,14-diyne-1,11,16-triol, which were named as oplopantriol A (**5**) and oplopantriol B (**6**), respectively.

Falcarindiol was isolated from several species in Araliaceae, Asteraceae and Apiaceae. The absolute configuration of falcarindiol from *Peucedanum oreoselinum* was assigned as (3*R*,8*S*) by Lemmich in 1981 on the basis of chemical correlation studies [14], and the same result was obtained by Ratnayake and Hemscheidt using olefin cross-metathesis for that isolated from *Tetraplasandra hawaiiensis* [15]. Steroselective synthesis of (3*R*,8*S*)-falcarindiol has been reported by Zheng *et al*. [16] and Sabitha *et al*. [17]. The (3*S*,8*S*) epimer was also reported by Bernart *et al*. and Kobaisy *et al*. from *Dendropanax arboreus* [18] and *O. horridus* [11], respectively. In Mosher's method, the resonances of falcarindiol with a (3*R*,8*S*)-configuration for protons H-9, H-10, and H-11 all showed negative $\Delta\delta$ ($\delta S - \delta R$)values, and those of the resonances for H-1*E*, H-1*Z*, and H-2 were all positive (the data were extracted from the supporting materials of reference [15], and was misinterpreted in the text), while that with a (3*S*,8*S*)-configuration had shown all negative $\Delta\delta$ values [18]. The stereochemistry found for polyynes isolated from Araliaceae with a (3*S*,8*S*)-configuration seems to be entirely different from those with the (3*R*,8*S*) stereochemistry reported from Apiaceae and Asteraceae [14, 19-22]. Consequently the four known polyynes were proposed as (3*S*,8*S*)-falcarindiol (**1**), oplopandiol (**2**), (11*S*,16*S*,9*Z*)-9,17-octadecadiene-12,14-diyne-1,11,16-triol, 1-acetate (**3**) and oplopandiol acetate (**4**) with a (3*S*,8*S*)-configuration or (11*S*,16*S*)-configuration on basis of biosynthesis pathway, optical rotation values and spectroscopic data with those reported from the same plants.

3. Experimental

3.1. General

Optical rotations were measured on a PerkinElmer Model 341 polarimeter. UV spectra were recorded on a Beckman Coulter DU 640 spectrophotometer. IR spectra were obtained with a PerkinElmer Spectrum 100 FT-IR spectrometer with KBr pallets. The ^{1}H-, ^{13}C-, and 2D-NMR spectra were recorded on a Bruker AV-500 spectrometer at room temperature (δ in ppm, *J* in Hz) with tetramethylsilane (TMS) as an internal standard (Bruker, Germany). ESI-MS and HR-ESI-MS measurements were carried out on an Agilent 1100 series LC/MSD Trap VL mass spectrometer and a Wiff Agilent time-of-flight (TOF) mass spectrometer respectively (Agilent, USA). Silica gel (100-200 and 200-300 mesh) (Qingdao Haiyang Chemical Co. Ltd, China) and Alltech Reversed-phase C_{18} (RP-C_{18}) silica gel (40-63 μm) (Alltech, USA) were used for column chromatography (CC). Precoated silica gel GF_{254} plates (Qingdao Haiyang Chemical Co. Ltd, Qingdao, China) were used for TLC. Supercritical fluid extraction was manipulated on a supercritical fluid extractor (SFT-250, Supercritical Fluid Technologies, Inc., USA). Analytical HPLC was performed on an Agilent 1100 liquid chromatograph with an Alltech Alltima RP-C_{18} column (250 mm × 4.6 mm inside diameter (I.D.), 5 μm, Alltech, USA). Preparative HPLC was

carried out with an Agilent 1100 liquid chromatograph with an Alltech Alltima RP-C_{18} column (250 mm × 22 mm I.D., 10 μm). Analytical UPLC was performed on Waters Acquity Ultra performance LC (Waters, Milford, MA), equipped with binary solvent manager, sampler manager, column compartment, and PDA detector, connected to Waters Empower 2 software, with an Acquity UPLC BEH C_{18} column (50 mm × 2.1 mm I.D., 1.7 μm). HPLC-grade methanol was a product of Merck (Merck, Germany). The deionized water used for HPLC was purified by a Milli-Q purification system (Millipore, USA).

3.2. Plant Material

The dried root bark of *O. horridus* was collected and authenticated by one of the authors (C.-Z. Wang) from Chicago, IL of USA in March, 2009. A voucher specimen has been deposited in the Laboratory of Quality Control, Institute of Chinese Medicine Sciences, University of Macau, Macao, China.

3.3. Extraction and Isolation

After the volatile oil was removed from the air-dried, powdered root bark of *O. horridus* (10.5 kg) by supercritical fluid extraction (SFE), the residue (10.2 kg) was extracted by 85% EtOH under refluxing, and the crude extract (1,900 g) was suspended in water and then extracted successively with petroleum ether (60-90°C), EtOAc, and *n*-BuOH to give the corresponding fractions P (124 g), E (570 g) and B (610 g), respectively. The EtOAc-soluble fraction E (510 g) was separated by silica gel (100–200 mesh) CC, eluted with a gradient of $CHCl_3$–MeOH (50:1 to 0:1) to give ten fractions (E1–E10). Fraction E7 (82 g) was then subjected to CC of silica gel (200–300 mesh), eluting with $CHCl_3$–MeOH(10:1, 8:1 and 5:1), to give six subfractions (E7a–E7f). Subfraction E7d (50 g) was chromatographed on RP-C_{18} silica gel CC (MeOH-H_2O, 70:30), then prepared on Prep-HPLC (MeOH-H_2O, 78:22) to afford **1** (1.6g) and **2** (2.5 g)**.** Fraction E8 (75 g) was subjected to silica gel (200–300 mesh) CC, eluting with $CHCl_3$–MeOH(10:1, 6:1 and 4:1), to afford five subfractions (E8a–E8e). Subfraction E8d (45 g) was chromatographed on RP-C_{18} silica gel CC (MeOH-H_2O, 67:33), then by prep-HPLC (MeOH-H_2O, 70:30) to afford **3** (2.6 g) and **4** (3.0 g)**.** Subfraction E9 (68 g) was further separated by CC on silica gel (200–300 mesh), eluting with $CHCl_3$–MeOH(8:1, 5:1 and 3:1), to yield six subfractions (E9a–E9f). Subfraction E9e (36 g) was further purified by prep-HPLC (MeOH-H_2O, 65:35) to afford **5** (1.8 g) and **6** (2.1 g)**.**

3.4. Alkaline Hydrolysis of Compounds **3** *and* **4**

The polyyne ester compound **3** (21 mg) and compound **4** (22 mg) were each dissolved in 95% ethanol (1 mL). Then, NaOH (8 mg) was added to each solution, and the mixtures were heated at 60 °C for 4 hours. The mixtures were diluted with H_2O (5 mL) and each one was extracted with $CHCl_3$ (6 mL × 3). The $CHCl_3$ layer was evaporated and the hydrolysis products were subjected to prep-HPLC (MeOH-H_2O, 65:35) to afford **5** (6 mg) and **6** (5 mg), respectively.

Oplopantriol **A** (**5**), (11*S*,16*S*,9*Z*)-9,17-octadecadien-12,14-diyne-1,11,16-triol yellowish oil; $[\alpha]_D^{25}$ +194.4° (*c* = 0.16, $CHCl_3$); UV ($CHCl_3$) λmax (log ξ): 215 (0.63), 226 (1.10), 255 (4.09) 261 (3.95), 273 (4.13) and 287 (4.07) nm; IR (KBr) ν_{max} : 3357, 3022, 2929, 2855, 2251, 2150, 1675, 1464, 1405, 1303,

1021, 933 and 880 cm^{-1}; ^{1}H and ^{13}C NMR data (Table 1); Positive mode ESI-MS *m/z*: 313 $[M+Na]^+$ (100); Negative mode HR-ESI-MS *m/z*: 289.1867 $[M-H]^-$, Calcd for $C_{18}H_{25}O_3$: 289.1804).

Oplopantriol **B** (**6**), (11*S*,16*S*,9*Z*)-9-octadecaen-12,14-diyne-1,11,16-triol yellowish oil; $[\alpha]_D^{25}$ + 233.0° (*c* = 0.3, $CHCl_3$); UV($CHCl_3$) λmax (log ξ): 207 (1.07), 226 (1.19), 232 (1.17), 253 (4.02), 263 (3.98), 265 (3.95), 272 (4.01) and 288 (3.84) nm; IR (KBr) ν_{max} : 3355, 3021, 2930, 2856, 2232, 2143, 1656, 1463, 1305, 1095, 1017, 970 and 866 cm^{-1}; ^{1}H and ^{13}C NMR data (Table 1); Positive mode ESI-MS *m/z*: 315 $[M+Na]^+$ (100); Negative mode HR-ESI-MS *m/z*: 291.1966 $[M-H]^-$, Calcd for $C_{18}H_{27}O_3$: 291.1960).

4. Conclusions

A detailed phytochemical investigation on *O. horridus* led to the isolation of two new polyynes (11*S*,16*S*,9*Z*)-9,17-Octadecadien-12,14-diyne-1,11,16-triol and (11*S*,16*S*,9*Z*)-9-octadecaen-12,14-diyne-1,11,16-triol named oplopantriol A (**5**) and oplopantriol B (**6**), along with four known polyynes (3*S*,8*S*)-falcarindiol (**1**), oplopandiol (**2**), (11*S*,16*S*,9*Z*)-9,17-octadecadiene-12,14-diyne-1,11,16-triol, 1-acetate (**3**) and oplopandiol acetate (**4**).

Acknowledgements

This research was supported by grants from Macao Science and Technology Development Fund (013/2008/A1 to Q.-W. Zhang) and Research Committee of University of Macau (UL015/09-Y1 to S.-P. Li)

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Sample Availability: Samples of all the compounds are available from the authors.