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Letter

Chemical Constituents from Leaves of *Oplopanax horridus*

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ABSTRACT

Objective To study the chemical constituents from the leaves of *Oplopanax horridus*. **Methods** The chemical constituents were isolated and purified by column chromatography on silica gel and Sephadex LH-20 gel columns, ^{1}H-NMR and ^{13}C-NMR were applied for the identification of chemical structure. **Results** Ten compounds were isolated and identified as dammara-20,24-dien-3β-ol acetate (**1**), phytol (**2**), 16*Z*,19*Z*-pentacosadienoic acid (**3**), β-sitosterol (**4**), (3*S*,8*S*)-falcarindiol (**5**), maltol (**6**), acankoreagenin (**7**), daucosterol (**8**), stigmasterol-3-*O*-β-*D*-glucopyranoside (**9**), and acankoreoside A (**10**). **Conclusion** Compounds **1**-**3**, **6**, and **10** are isolated from this plant for the first time. Compounds **1**-**3** and **6** are isolated from the plants in genus *Oplopanax* Miq. for the first time. Moreover, Compounds **1**, **3**, and **6** are isolated from the plants in the family of Araliaceae for the first time.

Key words

Araliaceae; chemotaxonomy; *Oplopanax horridus*; triterpenoid

1. Introduction

Plants of the genus *Oplopanax* Miq. (Araliaceae) are mainly distributed in eastern Asia and northwestern America. This genus consists of three species, such as *Oplopanax elatus* Nakai, *O. japonicus* (Nakai) Nakai, *O. horridus* (Smith) Miq. (Calway et al, 2012). *O. horridus*, or Devil's club, is a commonly used traditional folk herb by indigenous people native to the Pacific Northwest of North America. Until now, *O. horridus* has been used for the treatment of respiratory diseases, cardiovascular diseases, gastrointestinal diseases, diabetes, arthritis, and cancer (Calway et al, 2012). Previous phytochemical investigations on *O. horridus* mainly focus on the root bark, which have revealed the presence of polyynes, triterpene glycosides, phenolic glycosides, sesquiterpenes, lignans, and polyenes (Calway et al, 2012). Actually, leaf of *O. horridus* is a traditionally used medicinal part to treat arthritis and rheumatism (Trevor et al, 2004). Moreover, bioactive study showed triterpenoids from the leaves of *O. horridus* has significant inhibitory effects on human hepatoma carcinoma cells (HepG-2), human colon cancer cells (HCT116), human lung carcinoma cells (NCI-H460), and human gastric cancer cells (MGC803) (Liu et al, 2012). However, the phytochemical investigation on the leaves of this plant is rarely reported. To further investigate the chemical constituents from the leaves, we isolated and identified 10 compounds in this study and discussed their chemotaxonomic significance.

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2. Materials and methods

2.1 Apparatus and reagents

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AV−500 Spectrometer (Germany) with tetramethylsilane (TMS) as an internal standard. Silica gel (100−200 and 200−300 mesh) (Qingdao Marine Chemical Co., Ltd., China) and Alltech RP-C_{18} silica gel (40−63 μm, USA) were used for column chromatography (CC). Precoated silica gel GF_{254} plates (Qingdao Marine Co., Ltd., China) were used for TLC.

2.2 Plant material

Leaves of *Oplopanax horridus* (Smith) Miq. were obtained from Alaska, USA, in September 2012, and were identified by Dr. Chun-su Yuan. A voucher specimen was deposited at the State Key Laboratory of Quality Research in Chinese Medicine, Institute of Chinese Medical Sciences, University of Macau, Macao SAR, China.

2.3 Extraction and isolation

Air-dried and powdered leaves of *O. horridus* (2.2 kg) were extracted with 70% ethanol at room temperature for three times. After the removal of ethanol by concentration, the extract (550 g) was suspended in water and partitioned sequentially with petroleum ether, EtOAc, and *n*-BuOH, respectively.

The petroleum ether extract (39.51 g) was separated into 16 fractions (Frs. 1−16) by using silica gel column (petroleum ether-EtOAC, 20:1→1:1). Frs. 1 and 2 were purified by repeated silica gel and Sephadex LH-20 (MeOH-$CHCl_3$) to give compounds **1** (126 mg), **2** (200 mg), and **3** (900 mg).

The EtOAc extract (39.78 g) was separated into 17 fractions (Frs. 1−17) by using silica gel column (petroleum ether-EtOAC, 20:1→1:1). Frs. 3−5 were purified by Sephadex LH-20 column (MeOH) to give compound **4** (205 mg), the same method was applied to obtain compounds **5** (65 mg) and **6** (33 mg) from Frs. 6 and 7. Frs. 13−16 were subjected to MCI gel column (MeOH), followed by MPLC over on silica gel ($CHCl_3$-acetone 20:1→1:1) and Sephadex LH-20 column (MeOH) to give compound **7** (260 mg).

The *n*-BuOH extract (162.68 g) was separated over silica gel ($CHCl_3$-MeOH 100:1→0:1) to afford 15 fractions (Frs. 1−15). Compounds **8** and **9** (mixed, 30 mg) were obtained from Fr. 9 as precipitate in MeOH. Frs. 14 and 15 were subjected to MPLC over on silica gel ($CHCl_3$-MeOH 100:1→0:1), ODS gel (MeOH-H_2O 1:8→1:0) and Sephadex LH-20 (MeOH) column to give compound **10** (1.4 g). The chemical structures of compounds **1**−**10** are shown in Figure 1.

3. Results and discussion

3.1 Structure identification

Compound **1**: white crystal. ^{1}H-NMR (400 Hz, $CDCl_3$) δ: 5.13 (1H, t, J = 6.9 Hz, H-24), 4.74 (1H, s, H-21a), 4.71 (1H, s, H-21b), 4.48 (1H, m, H-3α), 2.04 (3H, s), 1.69 (3H, s), 1.61 (3H, s), 0.97 (3H, s), 0.87 (3H, s), 0.86 (3H, s), 0.85 (6H, s). ^{13}C-NMR (100 Hz, $CDCl_3$) δ: 38.8 (C-1), 23.7 (C-2), 80.9 (C-3), 37.9 (C-4), 56.0 (C-5), 18.2 (C-6), 35.4 (C-7), 40.5 (C-8), 50.9 (C-9), 37.2 (C-10), 21.4 (C-11), 24.9 (C-12), 47.8 (C-13), 49.4 (C-14), 31.4 (C-15), 27.1 (C-16), 45.3 (C-17), 15.9 (C-18), 16.3 (C-19), 152.7 (C-20), 107.5 (C-21), 34.2 (C-22), 28.9 (C-23), 124.5 (C-24), 131.4 (C-25), 25.7 (C-26), 17.7 (C-27), 28.0 (C-28), 15.6 (C-29), 16.5 (C-30), 170.9 (C-1′), 21.3 (C-2′). The ^{1}H-NMR and ^{13}C-NMR data were in agreement with those given in literature (Zhang and Chen, 2011), and compound **1** was identified as dammara-20,24-dien-3β-ol acetate.

Compound **2**: colorless oil. ^{1}H-NMR (400 Hz, $CDCl_3$) δ: 5.41 (1H, dt, J = 6.9 Hz, 1.2 Hz, H-2), 4.15 (2H, d, J = 6.9 Hz, H-1), 1.98 (2H, m, H-4), 1.66 (3H, s, H-20), 1.52 (1H, m, H-15), 0.83−0.87 (12H, m, H-16, H-17, H-18, H-19). ^{13}C-NMR

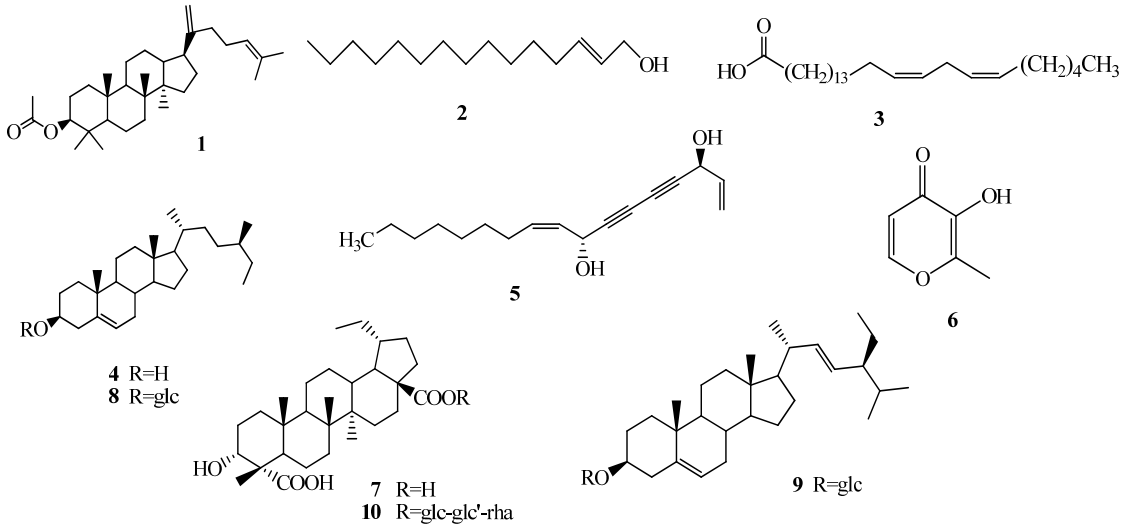

Figure 1 Chemical structures of compounds 1−10

(100 Hz, $CDCl_3$) δ: 59.4 (C-1), 123.1 (C-2), 140.2 (C-3), 39.8 (C-4), 39.3 (C-5), 37.4 (C-6), 32.8 (C-7), 37.3 (C-8), 37.3 (C-9), 36.6 (C-10), 32.7 (C-11), 24.4 (C-12), 24.8 (C-13), 25.1 (C-14), 27.9 (C-15), 19.7 (C-16), 22.6 (C-17), 22.6 (C-18), 19.7 (C-19), 16.1 (C-20). The ^{1}H-NMR and ^{13}C-NMR data were in agreement with those given in literature (Feng et al, 2008), and compound **2** was identified as phytol.

Compound **3**: colorless crystal. ^{1}H-NMR (400 Hz, $CDCl_3$) δ: 5.35 (4H, m, H-16, H-17, H-19, H-20), 2.77 (2H, m, H-18), 2.34 (2H, t, J = 7.5 Hz, H-2), 2.04 (4H, m, H-15, H-21), 1.63 (2H, quint, J = 7.2 Hz, H-3), 1.20−1.30 (28H, m, H-4−H-14, H-22−H-24), 0.87 (3H, t, J = 6.4, H-25). ^{13}C-NMR (100 Hz, $CDCl_3$) δ: 180.0 (C-1), 34.0 (C-2), 24.7 (C-3), 29.0−29.6 (C-4−C-14), 27.1 (C-15), 130.0 (C-16), 128.0 (C-17), 25.6 (C-18), 130.2 (C-19), 127.8 (C-20), 27.1 (C-21), 29.7 (C-22), 31.9 (C-23), 22.6 (C-24), 14.0 (C-25). The ^{1}H-NMR and ^{13}C-NMR data were in agreement with those given in literature (Huang et al, 2007), and compound **3** was identified as 16*Z*,19*Z*-pentacosadienoic acid.

Compound **4**: colorless needle crystal. Its Rf value is in accordance with that of reference substance (β-sitosterol), and compound **4** was identified as β-sitosterol.

Compound **5**: colorless oil. ^{1}H-NMR (400 Hz, $CDCl_3$) δ: 5.94 (1H, ddd, J = 15.6, 10.2, 5.4 Hz, H-2), 5.60 (1H, dt, J = 10.6, 7.4 Hz, H-10), 5.51 (1H, d, J = 8.2 Hz, H-9), 5.47 (1H, d, J = 16.8 Hz, H-1a), 5.25 (1H, d, J = 10.2 Hz, H-1b), 5.20 (1H, d, J = 8.2 Hz, H-8), 4.94 (1H, d, J = 5.3 Hz, H-3), 2.11 (2H, m, H-11), 1.38 (2H, m, H-12), 1.27 (8H, m, H-13, H-14, H-15, H-16), 0.88 (3H, t, J = 7.0 Hz, H-17). The ^{1}H-NMR data was in agreement with that given in literature (Tamura et al, 2010), and compound **5** was identified as (3*S*,8*S*)-falcarindiol.

Compound **6**: white needle crystal. ^{1}H-NMR (400 Hz, CD_3OD) δ: 7.92 (1H, d, J = 5.5 Hz, H-6), 6.37 (1H, d, J = 5.5 Hz, H-5), 2.33 (3H, s, 2-CH_3). ^{13}C-NMR (100 Hz, CD_3OD) δ: 152.1 (C-2), 144.5 (C-3), 175.2 (C-4), 114.4 (C-5), 156.2 (C-6), 14.2 (2-CH_3). The ^{1}H-NMR and ^{13}C-NMR data were in agreement with those given in literature (Sun et al, 1995), and compound **6** was identified as maltol.

Compound **7**: white needle crystal. ^{1}H-NMR (400 Hz, CD_3OD) δ: 4.71 (1H, d, J = 1.4 Hz, H-29b), 4.59 (1H, s, H-29a), 3.72 (1H, s, H-3), 3.05 (1H, m, H-19), 1.70 (3H, s, H-30), 1.15 (3H, s, H-24), 1.07 (3H, s, H-26), 0.98 (3H, s, H-25), 0.91 (3H, s, H-27). ^{13}C-NMR (100 Hz, CD_3OD) δ: 33.4 (C-1), 26.1 (C-2), 73.8 (C-3), 52.4 (C-4), 45.4 (C-5), 21.8 (C-6), 35.1 (C-7), 42.4 (C-8), 51.8 (C-9), 38.0 (C-10), 22.3 (C-11), 26.8 (C-12), 39.6 (C-13), 43.8 (C-14), 30.8 (C-15), 33.3 (C-16), 57.5 (C-17), 50.4 (C-18), 48.5 (C-19), 151.9 (C-20), 31.7 (C-21), 38.1 (C-22), 180.3 (C-23), 17.7 (C-24), 16.9 (C-25), 16.8 (C-26), 15.1 (C-27), 180.0 (C-28), 110.1 (C-29), 19.5 (C-30). The ^{1}H-NMR and ^{13}C-NMR data were in agreement with those given in literature (An et al, 2009), and compound **7** was identified as acankoreagenin.

Compound **8**: white solid. ^{13}C-NMR (100 Hz, CD_3OD) δ: 37.4 (C-1), 29.4 (C-2), 78.5 (C-3), 39.9 (C-4), 140.8 (C-5), 121.8 (C-6), 30.2 (C-7), 29.8 (C-8), 50.3 (C-9), 36.3 (C-10), 19.9 (C-11), 39.3 (C-12), 42.4 (C-13), 56.2 (C-14), 24.4 (C-15), 28.4 (C-16), 56.0 (C-17), 12.0 (C-18), 19.1 (C-19), 36.8 (C-20), 18.9 (C-21), 34.1 (C-22), 25.6 (C-23), 46.0 (C-24), 29.2 (C-25), 18.9 (C-26), 19.3 (C-27), 23.3 (C-28), 12.4 (C-29), 102.5 (C-1′), 75.2 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.5 (C-5′), 62.8 (C-6′). The ^{13}C-NMR data was in agreement with that given in literature (Yoo et al, 2006), and compound **8** was identified as daucosterol.

Compound **9**: white solid. ^{13}C-NMR (100 Hz, CD_3OD) δ: 37.4 (C-1), 29.4 (C-2), 78.5 (C-3), 40.6 (C-4), 140.8 (C-5), 122.8 (C-6), 32.1 (C-7), 32.0 (C-8), 51.3 (C-9), 36.3 (C-10), 21.4 (C-11), 42.3 (C-12), 42.4 (C-13), 56.8 (C-14), 24.4 (C-15), 26.4 (C-16), 56.7 (C-17), 12.0 (C-18), 19.1 (C-19), 36.8 (C-20), 18.9 (C-21), 138.7 (C-22), 129.4 (C-23), 46.0 (C-24), 29.2 (C-25), 21.2 (C-26), 19.3 (C-27), 23.3 (C-28), 11.9 (C-29), 102.5 (C-1′), 75.2 (C-2′), 78.3 (C-3′), 71.6 (C-4′), 78.5 (C-5′), 62.8 (C-6′). The ^{13}C-NMR data was in agreement with that given in literature (Liu et al, 2005), and compound **9** was identified as stigmasterol-3-*O*-β-*D*-glucopyranoside.

Compound **10**: white solid. ^{1}H-NMR (400 Hz, CD_3OD) δ: 5.45 (1H, d, J = 8.0 Hz, H-1 of Glc), 4.73 (1H, s, H-1 of Rha), 4.60 (1H, s, H-29b), 4.36 (1H, d, J = 8.0 Hz, H-1 of Glc′), 4.10 (1H, m, H-29a), 1.69 (3H, s, H-30), 1.24 (3H, d, J = 6.4 Hz, CH_3 of Rha), 1.13 (3H, s, H-24), 1.04 (3H, s, H-26), 0.96 (3H, s, H-25), 0.89 (3H, s, H-27). ^{13}C-NMR (100 Hz, CD_3OD) δ: 33.5 (C-1), 26.8 (C-2), 73.7 (C-3), 52.3 (C-4), 45.6 (C-5), 22.2 (C-6), 35.1 (C-7), 42.5 (C-8), 51.8 (C-9), 38.0 (C-10), 21.8 (C-11), 26.1 (C-12), 39.3 (C-13), 43.7 (C-14), 30.8 (C-15), 32.8 (C-16), 57.9 (C-17), 50.5 (C-18), 48.3 (C-19), 151.7 (C-20), 31.5 (C-21), 37.6 (C-22), 181.0 (C-23), 17.8 (C-24), 17.0 (C-25), 16.9 (C-26), 15.1 (C-27), 176.3 (C-28), 110.4 (C-29), 19.5 (C-30), 95.2 (C-1 glc), 73.9 (C-2 glc), 79.6 (C-3 glc), 71.0 (C-4 glc), 78.0 (C-5 glc), 69.5 (C-6 glc), 104.5 (C-1 glc'), 75.2 (C-2 glc'), 76.7 (C-3 glc'), 78.2 (C-4 glc'), 76.8 (C-5 glc'), 61.9 (C-6 glc'), 102.9 (C-1 rha), 72.2 (C-2 rha), 72.4 (C-3 rha), 73.7 (C-4 rha), 70.6 (C-5 rha), 17.8 (C-6 rha). The ^{1}H-NMR and ^{13}C-NMR data were in agreement with those given in literature (Van Kiem et al, 2003), and compound **10** was identified as acankoreoside A.

3.2 Chemotaxonomic significance

Ten compounds were isolated and identified from the leaves of *O. horridus*, including three triterpenoids (**1**, **7**, **10**), one diterpenoid (**2**), one polyyne (**5**), one pyrone (**6**), one unsaturated fatty acid (**3**) and three steroids (**4**, **8**, **9**). Compounds **1**−**3**, **6**, and **10** were reported from this species for the first time. Compounds **1**−**3** and **6** are isolated from the genus *Oplopanax* Miq. for the first time. Moreover, Compounds **1**, **3**, and **6** are isolated from the family of Araliaceae for the first time.

Araliaceae, a big family of medicinal plants, comprises about 700 species in 55 genera, and is rich in triterpenoids which are the most representative components from this family (Hansen and Boll, 1986). In this study, two triterpenoids with high content (compounds **7** and **10**) were isolated from *O. horridus* previously reported from the genera *Schefflera* J. R. et G. Forst. (Sung et al, 1991; Wanas et al, 2010), *Brassaiopsis* Decne. et Planch. (Van Kiem et al, 2003) *Acanthopanax* Miq. (Chang et al, 1998; Liu et al, 2002), and

Oplopanax Miq. (Hirai et al, 1995; Liu et al, 2010; 2012). The similarity of triterpenoids suggests a potential close relationship among these genera.

Dammara-20,24-dien-3β-ol acetate (**1**) has been mainly reported from the family Asteraceae, including *Taraxacum* Weber. (Saeki et al, 2013), *Santolina* Tourn. (Ferrari et al, 2005), *Microglossa* DC. (Schmidt et al, 2003), etc. In addition, some plants of Cruciferae, Boraginaceae, and Theaceae contain this compound as well. Although dammarane triterpenoid is very common in the family Araliaceae, especially in the genus *Panax* Linn., this component is the first report from the family Araliaceae. 16*Z*,19*Z*-Pentacosadienoic acid (**3**) has been reported from *Tagetes erecta* L. (Asteraceae) (Huang et al, 2007) and freshwater Israeli sponges (Rezanka and Dembitsky, 2002). To our best knowledge, this is the second report about this component from natural herbs and first report from Araliaceae. Maltol (**6**) has been reported from many medicinal plants. Theoretically, it is considered as a product of Maillard reaction (Yaylayan and Mandeville, 1994). An example is that maltol exists in the red ginseng (steamed *P. ginseng*) but could not be detected in the fresh *P. ginseng* (Li et al, 1999). It indicates that maltol is a significant compound in red ginseng. In this study, as a natural product, this is the first report from Araliaceae. However, limited data on these three components are within other species of Araliaceae, and these data suggest further work on different species of Araliaceae is justified.

Phytol (**2**) exists commonly in many medicinal plants in different families. In Araliaceae, this compound has previously been isolated from *Schefflera* J. R. et G. Forst. (Kuo et al, 2002), *Panax* Linn. (Lai et al, 2010), *Acanthopanax* Miq. (Zhang and Liu, 2001), etc. This is the first report from the genus *Oplopanax* Miq.

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