Phytochemistry Letters 12 (2015) 168–172

Contents lists available at ScienceDirect

Phytochemistry Letters

journal homepage: www.elsevier.com/locate/phytol

Two new triterpene rhamnosides from *Euphorbia dracunculoides* Lam.

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ARTICLE INFO

Article history:
Received 18 December 2014
Received in revised form 18 March 2015
Accepted 30 March 2015
Available online 14 April 2015

Keywords:
Euphorbiaceae
Euphorbia dracunculoides
Taraxerene-type
Triterpene rhamnosides

ABSTRACT

Two new triterpene rhamnosides, 3β-*O*-[α-L-(2′,3′,4′-*O*-triacetyl)-rhamnopyranosyl]-aleuritolic acid (**1**), and 3β-*O*-[α-L-(2′,3′-*O*-diacetyl)-rhamnopyranosyl]-aleuritolic acid (**2**), together with four known triterpenoids (**3**–**6**) were isolated from the petroleum ether fraction of the 70% aqueous acetone extract of the aerial parts of *E. dracunculoides* Lam. Their structures were elucidated by means of extensive spectroscopic analysis, acid hydrolysis, and comparison with data reported in the literatures. Among them, compounds **1** and **2** are the first examples of taraxerene-type triterpene rhamnosides, and compounds **3**–**6** were isolated from this plant for the first time.

1. Introduction

The genus *Euphorbia* is the largest genera of the family Euphorbiaceae, comprising of more than 2000 species, which distribute around the world, particularly in Africa and Central and South America (Li, 1994). There are 80 species distributed in China, most of which are native to southwest region and the northwest dry areas in China (Ma and Cheng, 1997a). Some plants of this genus are known to be used as folk medicine in Asian countries for the treatment of skin diseases, diarrhea and edemas, *etc.* (Shi et al., 2008a; Zhang et al., 2010). Previous phytochemical investigations have demonstrated that triterpenoids, with many different parent skeletons including lanostanes, cycloartanes, euphanes, tirucallanes, oleananes, *etc.* (Shi et al., 2008b; Zhang et al., 2010), are rich in this genus.

Euphorbia dracunculoides Lam., belonging to the genus *Euphorbia*, is a perennial herb mainly located in riverbanks, valleys and roadsides of sandy areas in Tropical African, South Europe and Southwest Asia (Ma and Cheng, 1997b). The earlier biological studies showed that the EtOH extract of the seeds from this plant exhibited antimicrobial activity (Chawla et al., 1982). However, phytochemical reports on this plant are rare over the last three decades. To the best of our knowledge, only three triterpenes, named lupeol, betulinic acid, and oleanolic acid, respectively, were reported from this plant in 1982 (Chawla et al., 1982). This paper deals with the isolation and structure elucidation of two new taraxerene-type triterpene rhamnosides (**1** and **2**) and four known triterpenoids (**3**–**6**) (Fig. 1) from the aerial parts of *E. dracunculoides*.

2. Results and discussion

Two new triterpene rhamnosides, 3β-*O*-[α-L-(2′,3′,4′-*O*-triacetyl)-rhamnopyranosyl]-aleuritolic acid (**1**), and 3β-*O*-[α-L-(2′,3′-*O*-diacetyl)-rhamnopyranosyl]-aleuritolic acid (**2**), along with four known triterpenoids (**3–6**) were isolated from the petroleum ether fraction of the 70% aqueous acetone extract of the aerial parts of *E. dracunculoides* Lam. The structures of known compounds were determined to be 24-methylene-cycloart-3β-ol (**3**) (Sara et al., 2013), cycloeucalenol (**4**) (Lee et al., 2007), cycloart-23*Z*-ene-3β,25-diol (**5**) (Greca et al., 1994), and euphol (**6**) (Liang et al., 2008), by comparing their spectroscopic data with those reported in the literatures. Among them, compounds **1** and **2** are the first examples of taraxerene-type triterpene rhamnosides, and compounds **3–6** were firstly reported from this plant.

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http://dx.doi.org/10.1016/j.phytol.2015.03.015
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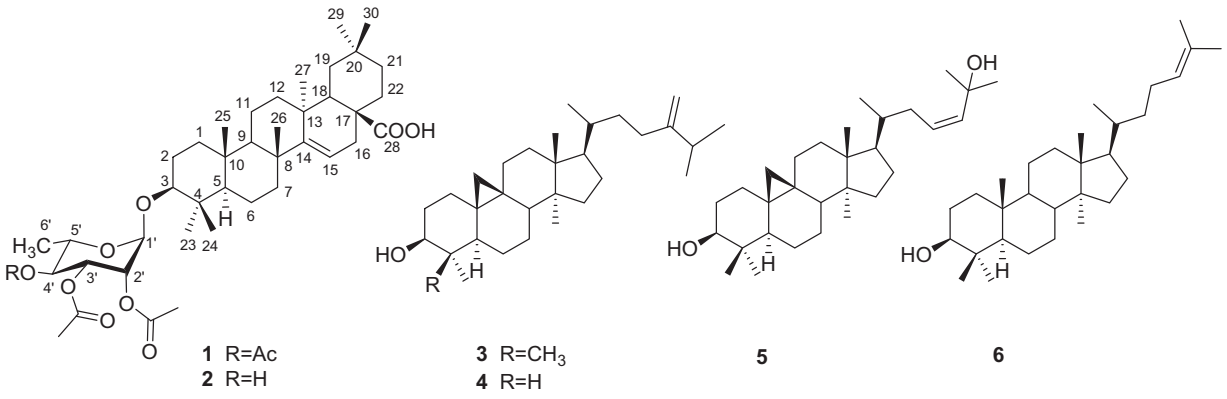

Fig. 1. Structures of compounds **1**–**6**.

Compound **1**, $[\alpha]_D^{23.1}$ −28.5 (*c* 0.14, MeOH), was obtained as white flakes from MeOH. The HR-ESI-MS of **1** exhibited a pseudo-molecular ion peak at *m/z* 751.4391 $[M+Na]^+$, consistent with a molecular formula $C_{42}H_{64}O_{10}$ (calcd 751.4397), indicating 11° of unsaturation. The IR spectrum of **1** showed bands at 3440 and 1753 cm^{-1}, corresponding to hydroxyl and carbonyl group absorption, respectively. The analysis of its ^1H NMR spectrum (Table 1) indicated the presence of seven tertiary methyl protons at δ_H 0.93 × 4, 0.90, 0.89 and 0.84, an olefinic proton at δ_H 5.50, and an anomeric proton at δ_H 4.77 (1H, br s). The ^{13}C NMR spectrum of **1** showed 42 carbon signals, of which 30 might be assigned for the triterpenoid aglycon, six for three acetyl groups (δ_C 170.3, 20.1; 170.2, 21.0; 170.1, 20.9), and the remaining six for a sugar moiety. In addition, the DEPT spectrum of **1** exhibited diagnostic seven methyl signals at δ_C 32.0, 28.8, 28.3, 26.3, 22.6, 16.4, and 15.7, ten methylenes, three methines (δ_C 55.8, 49.2, and 41.5), six quaternary carbons (δ_C 51.6, 39.1, 39.1, 37.8, 37.4, and 29.4), an oxidized methine (δ_C 89.8), a carboxylic group at δ_C 184.7, and olefinic carbons at δ_C 160.7 (C), 116.9 (CH). These evidences suggested **1** to be a taraxer-14-ene derivative (Fröhlich et al., 2013; Momo et al., 2013; Swapan et al., 1995).

Further NMR analysis of **1** was performed with the aid of 2D-NMR (^1H–^1H COSY, HSQC, HMBC and ROESY, Fig. 2). The sugar moiety of **1** was supposed to be α-rhamnopyranose based on the anomeric proton (δ_H 4.77, 1H, br s) and the ^{13}C NMR data (δ_C 99.8, 70.4, 69.3, 71.6, 66.5, 17.4) as well as comparison of TLC with standard substance (Agrawal, 1992). The absolute configuration of the sugar was simultaneously identified as L-series by the [α] of its hydrolysate (see Section 3.4). The long-range correlations in the HMBC spectrum between the anomeric proton (δ_H 4.77, 1H, br s) and an oxygen-bearing methine (δ_C 89.8) revealed that the rhamnopyranose was attached to C-3 through an *O*-glycosidic bond (Fig. 2, Supplementary material, Fig. S5). Moreover, the ROESY correlation of H-3 (δ_H 3.07) with H-1′ (δ_H 4.77) also supported this deduction. Compared with acetyl aleuritolic acid (Fröhlich et al., 2013), the significantly downfield shift (Δ 9 ppm) of ^{13}C NMR for C-3 in **1** was consistent with this conclusion. The position of double bond was determined to be located at C-14 by the correlations from H-15 (δ_H 5.50) to C-8 (δ_C 37.4), C-13 (δ_C 39.1), and C-17 (δ_C 51.6) observed in the HMBC spectrum. Furthermore, the HMBC correlations from three methine protons (δ_H 5.21, 5.30, 5.04) in the sugar moiety to three carbonyl carbons (δ_C 170.3, 170.1, and 170.2) in corresponding acyl groups (Fig. 2, Supplementary material, Fig. S5), implied that three acetoxy groups were located at C-2′, C-3′, and C-4′, respectively.

The relative configuration of **1** was determined by the ROESY experiments (Fig. 2), as well as literature report (Shi et al., 2008b; Zhang et al., 2010). For the reported pentacyclic triterpenoids having this taraxer-14-ene skeleton, A/B, B/C, and C/D rings are all *trans*-fused, while the D/E rings were *cis*-fused, and H-5 is α-oriented. The ROESY correlations observed for H-3/H-5 and Me-23 supported the α-orientations of H-3. Consequently, compound **1** was elucidated as 3β-*O*-[α-L-(2′,3′,4′-*O*-triacetyl)-rhamnopyranosyl]-aleuritolic acid.

Compound **2**, white amorphous powder ($CHCl_3$), $[\alpha]_D^{23.2}$ −17.5 (*c* 0.11, MeOH), was found to possess the molecular formula $C_{40}H_{62}O_9$ from the HR-ESI-MS data (*m/z* 709.4292 $[M+Na]^+$, calcd. 709.4292), inferring 10° of unsaturation. Seven tertiary methyl protons at δ_H 0.94, 0.93 × 2, 0.92, 0.91 × 2, and 0.82, an olefinic proton at δ_H 5.51, and an anomeric proton at δ_H 4.75 (1H, br s) were also observed in the ^1H NMR spectrum (Table 1). In the ^{13}C NMR spectrum, except for 10 carbon signals covering two acetyl groups (δ_C 171.6, 21.1; 170.3, 21.1) and a sugar moiety (δ_C 99.9, 72.6, 71.7, 70.6, 68.8, and 17.5), the remaining 30 carbon signals including diagnostic seven methyl signals at δ_C 32.0, 28.8, 28.3, 26.3, 22.6, 16.4, and 15.7, ten methylenes, three methines (δ_C 55.8, 49.2, and 41.5), six quaternary carbons (δ_C 51.5, 39.1, 39.1, 37.8, 37.4, and 29.4), an oxidized methine (δ_C 89.7), a carboxylic group at δ_C 183.8, and olefinic carbons at δ_C 160.7 (C), 116.9 (CH), might be assigned for the triterpenoid aglycon. These evidences disclosed that **2** was also a taraxer-14-ene derivative.

The ^1H and ^{13}C NMR spectra of **2** were surprisingly similar to those of **1**, except for the presence of a hydroxyl group in **2** instead of an acetoxyl one in **1** at C-4′, which was proved by the HMBC correlations of Me-6′ (δ_H 1.31) and H-3′ (δ_H 5.13) with C-4′ (δ_C 71.7). The fact that the chemical shift of H-4′ (δ_H 3.60) in **2** was upfield (Δ 1.4 ppm) because of the deacetylation at C-4′, along with the molecular weight was lower (Δ 42) than that of **1** confirmed this conclusion. Further 2D NMR experiments allowed a determination of **2** as 3β-*O*-[α-L-(2′,3′-*O*-diacetyl)-rhamnopyranosyl]-aleuritolic acid.

3. Experimental

3.1. General experimental procedures

Melting points were measured *via* a XR4A micro melting point apparatus (Shanghai Yongheng optical equipment manufacture Corp. Ltd., China). Optical rotations were recorded in MeOH using a JASCO P-1020 Polarimeter (Jasco Corp., Japan). IR spectra were measured on a Bruker Tensor 27 FTIR Spectrometer with KBr disks (Bruker Corp., Germany). ^1H NMR, ^{13}C NMR and 2D NMR spectra were recorded in $CDCl_3$ using a Bruker AVANCE III-600 spectrometer (Bruker Corp., Switzerland), and TMS was used as internal

Table 1
NMR data for compounds **1** and **2** (TMS as the internal standard, δ in ppm, J in Hz).[a,b]

No.	**1**		**2**	
	δ_H	δ_C	δ_H	δ_C
1a	1.59 (1H, overlapped)	37.8 (t)	1.59 (1H, overlapped)	37.8 (t)
1b	0.91 (1H, overlapped)		0.92 (1H, overlapped)	
2	1.68 (2H, overlapped)	25.3 (t)	1.70 (2H, overlapped)	25.4 (t)
3	3.07 (1H, t, J = 8.0)	89.8 (d)	3.06 (1H, dd, J = 10.4, 5.9)	89.7 (d)
4		39.1 (s)		39.1 (s)
5	0.75 (1H, br d, J = 11.9)	55.8 (d)	0.76 (1H, dd, J = 11.8, 1.2)	55.8 (d)
6a	1.59 (1H, overlapped)	18.8 (t)	1.59 (1H, overlapped)	18.9 (t)
6b	1.44 (1H, overlapped)		1.45 (1H, overlapped)	
7a	1.94 (1H, overlapped)	41.0 (t)	1.95 (1H, m)	41.0 (t)
7b	1.27 (1H, m)		1.28 (1H, m)	
8		37.4 (s)		37.4 (s)
9	1.37 (1H, m)	49.2 (d)	1.37 (1H, m)	49.2 (d)
10		37.8 (s)		37.8 (s)
11a	1.60 (1H, overlapped)	17.4 (t)	1.60 (1H, overlapped)	17.4 (t)
11b	1.46 (1H, overlapped)		1.47 (1H, overlapped)	
12a	1.74 (1H, m)	33.4 (t)	1.76 (1H, m)	33.5 (t)
12b	1.59 (1H, overlapped)		1.59 (1H, overlapped)	
13		39.1 (s)		39.1 (s)
14		160.7 (s)		160.7 (s)
15	5.50 (1H, dd, J = 7.7, 2.6)	116.9 (d)	5.51 (1H, dd, J = 7.9, 3.4)	116.9 (d)
16a	2.35 (1H, dd, J = 14.2, 7.7)	31.5 (t)	2.36 (1H, dd, J = 14.4, 7.9)	31.5 (t)
16b	1.90 (1H, dd, J = 14.2, 2.6)		1.91 (1H, dd, J = 14.4, 3.4)	
17		51.6 (s)		51.5 (s)
18	2.26 (1H, br d, J = 13.8)	41.5 (d)	2.27 (1H, dd, J = 13.7, 2.7)	41.5 (d)
19a	1.22 (1H, overlapped)	35.5 (t)	1.24 (1H, overlapped)	35.5 (t)
19b	1.08 (1H, overlapped)		1.09 (1H, dd, J = 13.4, 2.7)	
20		29.4 (s)		29.4 (s)
21a	1.13 (1H, overlapped)	33.8 (t)	1.15 (1H, m)	33.8 (t)
21b	1.03 (1H, overlapped)		1.06 (1H, overlapped)	
22a	1.67 (1H, m)	30.8 (t)	1.69 (1H, dd, J = 14.0, 2.8)	30.8 (t)
22b	1.44 (1H, br d, J = 13.7)		1.43 (1H, dd, J = 14.0, 3.2)	
23	0.93 (3H, overlapped)	28.3 (q)	0.93 (3H, overlapped)	28.3 (q)
24	0.84 (3H, s)	16.4 (q)	0.92 (3H, s)	16.4 (q)
25	0.93 (3H, overlapped)	15.7 (q)	0.82 (3H, s)	15.7 (q)
26	0.93 (3H, overlapped)	26.3 (q)	0.94 (3H, s)	26.3 (q)
27	0.90 (3H, s)	22.6 (q)	0.91 (3H, overlapped)	22.6 (q)
28		184.7 (s)		183.8 (s)
29	0.93 (3H, overlapped)	32.0 (q)	0.93 (3H, overlapped)	32.0 (q)
30	0.89 (3H, s)	28.8 (q)	0.91 (3H, overlapped)	28.8 (q)
1′	4.77 (1H, br s)	99.8 (d)	4.75 (1H, d, J = 1.3)	99.9 (d)
2′	5.21 (1H, dd, J = 2.9, 1.6)	70.4 (d)	5.20 (1H, dd, J = 3.3, 1.3)	70.6 (d)
3′	5.30 (1H, dd, J = 9.9, 2.9)	69.3 (d)	5.13 (1H, dd, J = 9.7, 3.3)	72.6 (d)
4′	5.04 (1H, t like, J = 11.0)	71.6 (d)	3.60 (1H, t, J = 9.7)	71.7 (d)
5′	3.99 (1H, dq, J = 12.5, 6.2)	66.5 (d)	3.87 (1H, dq, J = 9.7, 6.2)	68.8 (d)
6′	1.17 (3H, d, J = 6.2)	17.4 (q)	1.31 (3H, d, J = 6.2)	17.5 (q)
2′-OAc		170.3 (s)		170.3 (s)
	2.13 (3H, s)	21.1 (q)	2.11 (3H, s)	21.1 (q)
3′-OAc		170.1 (s)		171.6 (s)
	1.97 (3H, s)	20.9 (q)	2.07 (3H, s)	21.1 (q)
4′-OAc		170.2 (s)		
	2.03 (3H, s)	21.0 (q)		

[a] ^{1}H NMR and ^{13}C NMR data were recorded in $CDCl_3$ at 600 MHz and 150 MHz, respectively.
[b] The assignments were based on HSQC, ^{1}H–^{1}H COSY, and HMBC experiments.

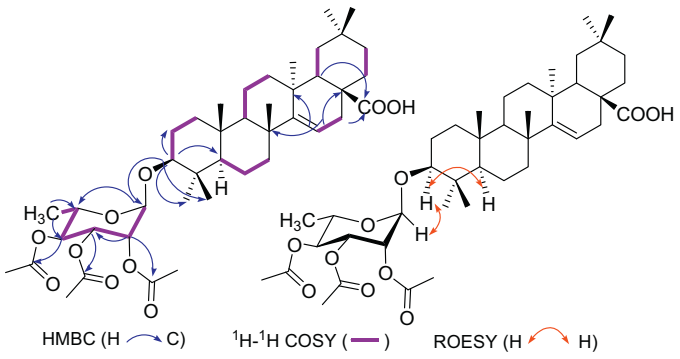

Fig. 2. Key COSY (left), HMBC (left), and ROESY (right) correlations of **1**.

standard. ESI-MS spectra were recorded using a Waters Xevo TQ-S Ultrahigh Pressure Liquid Chromatography Triple Quadrupole Mass Spectrometer (Waters Corp., UK). HR-ESI-MS data were obtained using an Agilent G6230 Q-TOF mass instrument (Agilent Corp., USA). Column chromatography (CC) was performed using silica gel (100–200 mesh and 200–300 mesh, Qingdao Marine Chemical Inc., China), silica gel 60 RP-18 (EMD Chemicals Inc., Germany) and Sephadex LH-20 (25–100 μm, Pharmacia Biotech Ltd., Sweden). Thin-layer chromatography (TLC) was performed using precoated silica gel GF254 plates (0.25 mm in thickness for analysis and 0.60 mm in thickness for preparation, Qingdao Marine Chemical Inc., China) with various solvent systems, and spots were visualized by UV light (254 nm) and colorated by iodine, or by spraying heated silica gel plates with 10% H_2SO_4 in MeOH. Preparative

HPLC separations were performed on a CXTH system, equipped with a UV3000 detector at 203 nm (Beijing Chuangxintongheng Instruments Co. Ltd., China), and a Kromasil C_{18} column (250 mm × 20 mm i.d., 5 μm, EKA Chemicals Corp., Sweden), using a flow rate of 12.0 mL/min at a column temperature of 28 °C. Semipreparative HPLC was conducted on a HITACHI Chromaster system (Hitachi Ltd., Japan) equipped with an Agilent ZORBAX SB-C_{18} column (150 mm × 9.4 mm i.d., 5 μm, Agilent Corp., USA), using a flow rate of 3.0 mL/min at a column temperature of 25 °C, and the detection was performed with a DAD detector.

3.2. Plant material

The aerial parts of *E. dracunculoides* Lam. were collected in September 2012 from Xishuang Banna prefecture, Yunnan Province, People's Republic of China, and authenticated by Mr. Shun-Cheng Zhang, Xishuang Banna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen (No. Zhang 20120927) was deposited at Kunming Institute of Botany, Chinese Academy of Sciences.

3.3. Extraction and isolation

The air-dried and powdered aerial parts of *E. dracunculoides* Lam. (4.0 kg) were extracted with 70% aqueous acetone (8 L × 2 d × 3) at room temperature. The extracts were concentrated by a rotary evaporator under reduced pressure to remove organic solvent. The aqueous residue was then partitioned with petroleum ether (4 × 1.0 L), EtOAc (4 × 1.0 L), and *n*-BuOH (4 × 1.0 L) sequentially.

The petroleum ether layer (72.0 g) was subjected to silica gel CC (0.8 Kg, 100–200 mesh), eluting with petroleum ether–acetone (1:0–0:1) to afford six fractions (A–F) based on TLC analysis. Fraction B (petroleum ether–acetone 25:1, 5.0 g) was then divided into two subfractions (Fr. B-1 and Fr. B-2) by a flash silica gel CC (200–300 mesh) eluting with petroleum ether – CH_2Cl_2 100:7 and 100:20, respectively, followed by Sephadex LH-20 CC (MeOH – $CHCl_3$ 1:1). Fr. B-1 was further purified by preparative TLC ($CHCl_3$ – MeOH 45:2, visualized with by iodine to locate the band, R_f = 0.78) to yield compound **6** (34.0 mg). Compounds **3** (305.0 mg) and **4** (5.0 mg) were obtained from Fr. B-2 by repeated silica gel CC (200–300 mesh) eluting with petroleum ether – EtOAc (20:1). Fraction C (petroleum ether–acetone 12:1, 4.2 g) was further chromatographed on silica gel column (200–300 mesh, eluting with petroleum ether – acetone 20:1 and 10:1, respectively) and Sephadex LH-20 column (MeOH – $CHCl_3$ 1:1) orderly, to give subfractions Fr. C-1 and Fr. C-2. Compound **5** (26.2 mg) was isolated from Fr. C-1 by recrystallization (MeOH – $CHCl_3$ 1:2). Fr. C-2 was submitted to preparative HPLC (MeOH – H_2O 98:2), and then preparative HPLC (MeOH – H_2O 91:9) to yield compound **1** (70.0 mg, t_R = 18.0 min). Compound **2** (8.0 mg, t_R = 20.2 min) was isolated from fraction D (petroleum ether–acetone 12:1, 7.2 g) by undergoing a protocol of Sephadex LH-20 CC (eluting with MeOH), preparative HPLC (MeOH – H_2O 98:2) and semipreparative HPLC (MeOH – H_2O 88:12) in sequence.

3.3.1. 3β-O-[α-L-(2′,3′,4′-O-triacetyl)-rhamnopyranosyl]-aleuritolic acid (**1**)

White flakes (MeOH), mp 162 – 165 °C; $[\alpha]_D^{23.1}$ −28.5 (*c* 0.14, MeOH); IR (KBr) ν_{max} 3440, 2941, 1753, 1696, 1454, 1370, 1225, 1134, 1079 and 1052 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) data, see Table 1; ESIMS *m/z* 751 $[M+Na]^+$; HR-ESI-MS *m/z* 751.4391 $[M+Na]^+$ (calcd for $C_{42}H_{64}O_{10}Na$, 751.4397).

3.3.2. 3-β-O-[α-L-(2′,3′-O-diacetyl)-rhamnopyranosyl]-aleuritolic acid (**2**)

White amorphous powder ($CHCl_3$); $[\alpha]_D^{23.2}$ −17.5 (*c* 0.11, MeOH); IR (KBr) ν_{max} 3441, 2939, 1751, 1694, 1453, 1372, 1229, 1131, 1077 and 1059 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) data, see Table 1; ESIMS *m/z* 709 $[M+Na]^+$; HR-ESI-MS *m/z* 709.4292 $[M+Na]^+$ (calcd for $C_{40}H_{62}O_9Na$, 709.4292).

3.4. Analysis of the sugar moiety

The absolute configuration determination of the carbohydrate units of **1** and **2** were completed using acid hydrolysis. Each compound (5.0 mg) was hydrolyzed *via* refluxing in 10% HCl–THF (1:2, v/v, 3 mL) at 80 °C for 7–8 h. After removing the organic solvent and the residual HCl by a rotary evaporator under reduced pressure, the reaction mixture was then chromatographed on a RP-18 column eluting with 2% MeOH to yield the sugars, respectively. The purified sugars were then dissolved in H_2O (0.5 mL) and compared with the authentic one on TLC using CH_2Cl_2–MeOH–H_2O (10:6:1, v/v) (Huan et al., 1998) and EtOAc–*n*-BuOH–H_2O (2:7:1, v/v) (Bedir et al., 2001) as solvent systems. The purified sugars were finally submitted to optical rotation measurements. The results of $[\alpha]_D^{20.2}$ +1.8 (*c* 0.06, H_2O) and $[\alpha]_D^{20.3}$ +2.2 (*c* 0.04, H_2O) were obtained for **1** and **2**, respectively. Accordingly, it could be inferred that the sugar moieties in compounds **1** and **2** were all L-rhamnose.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 21162044), High-end Science and Technology Talents Program of Yunnan Province to S.-X. H (No. 2013HA022), and Mid-aged and Young Academic and Technical Leader Raising Foundation of Yunnan Province (No. 2010CI040), China.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.phytol.2015.03.015.

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