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Short communication

Two new monoterpenes and one dicaffeic acid ester from *Sibiraea angustata* with hypolipidemic activities in HepG2 cells *in Vitro*

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ABSTRACT

Two new monoterpenes, named sibiscolacton B (**1**) and sibiscolacton C (**2**), together with a sorbate obtained from the natural product 1, 6-sorbitol-*O*-dicaffeic acid ester (**3**), were isolated from an aqueous extract of the aerial portion of *Sibiraea angustata*. The compounds' structures were elucidated on the basis of extensive spectroscopic analysis, as well as literature comparisons. A preliminary *in vitro* bioassay showed that all of the compounds exhibited hypolipidemic effects in HepG2 cells.

1. Introduction

Sibiraea angustata is a shrub of the Rosaceae family and is widely distributed in the western part of China. The aerial part of the plant is called "Liucha", which is typically used to treat indigestion and obesity in Tibetan folk medicine of China (Institute of Botany, 1985). Thus, thorough chemical and bioactive studies have been performed on this plant, leading to the identification of one monoterpene glycoside (Ito et al., 2009), two monoterpenes (Li et al., 2010) and eight monoterpene acylglucosides (Wang et al., 2013) from the plant. In the current investigation, two new monoterpenes named sibiscolacton B and sibiscolacton C(**1–2**) (Fig. 1) along with 1,6-sorbitol-*O*-C acid ester (**3**) (He et al., 2013) were isolated from this plant. Compound **3** was obtained from natural products even though it has been synthesized previously. The structural elucidation was based on extensive two dimensional NMR and High resolution ESI–MS spectra as well as literature comparisons. In addition, a preliminary evaluation of the hypolipidemic activities of these compounds in HepG2 cells was presented, demonstrating that all of the compounds exhibited an effect in the *in vitro* bioassay.

2. Results and discussion

The ethanol extract of the powder residue from the aqueous extract of *S. angustata* was concentrated under reduced pressure to yield a solid brown material, which was applied to a Diaion HP-20 chromatography column and eluted gradiently with EtOH/H_2O. Fortunately, by following modern column chromatography, two new monoterpenes, sibiscolactone B (**1**) and sibiscolactone C (**2**), were isolated from the 95% EtOH fraction, and a natural product, 1,6-sorbitol-*O*-dicaffeic acid ester (**3**), was obtained from the 50% EtOH fraction.

Compound **1** was obtained as a white powder with a $[\alpha]_D^{25}$ value of −21.5 ($CHCl_3$), the molecular formula of which was determined to be $C_{10}H_{16}O_3$ from the molecular ion peak at *m/z* 184.1112 $[M]^+$ (calc'd for 184.1100) in the HR–EI–MS. The IR spectrum also showed characteristic absorption bands for OH (3424 cm^{-1}) and lactone (1726 cm^{-1}). The ^1H NMR, ^{13}C NMR and HSQC spectra of **1** (Table 1) exhibited signals attributed to two vinyl methyls at δ_H 1.73 (δ_C 25.7) and 1.70 (δ_C 18.5); one olefinic methine signal with a proton at δ_H 5.19 (H-7) and a carbon at δ_C 125.1 (C-7); an oxygenated methylene group with protons at δ_H 3.90, 3.69 (H-1)

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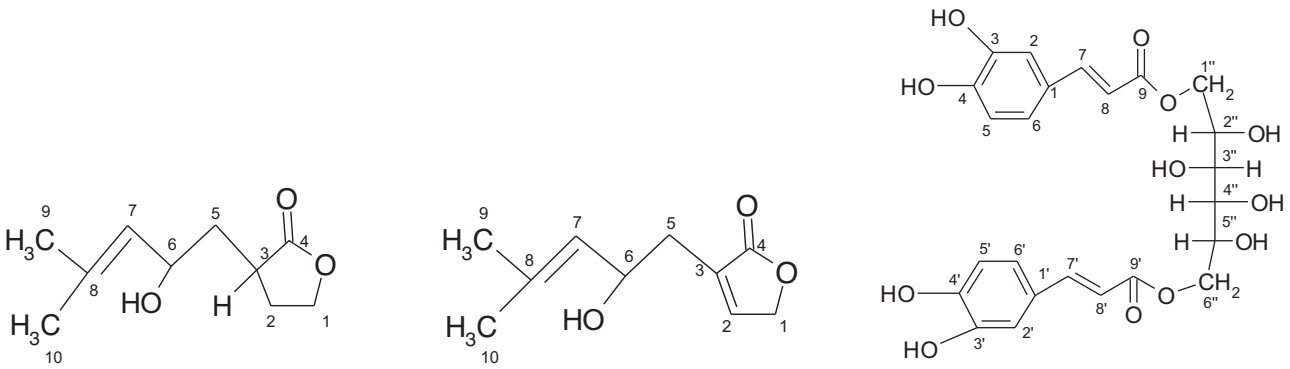

Fig. 1. Structures of compounds **1–3**.

Table 1
NMR spectral data of compound **1** ($CDCl_3$, 400 MHz, 100 MHz) and 2 ($CDCl_3$, 500 MHz, 125 MHz) [δ_H mult[a]. J (Hz)].

No.	**1**				**2**			
	^{1}H	^{13}C	HMBC	COSY	^{1}H	^{13}C	HMBC	COSY
1	3.90 ddd(12.0, 8.4,3.6) 3.69 m	71.2	2, 3, 4	2	4.80 d(1.5)	70.5	2, 3, 4	2
2	1.96 m, 1.89 m	26.9	1, 3, 4	1, 3	7.44 dd(2.0, 1.0)	148.8	1, 3, 4	1
3	2.91 m	36.7	2, 4, 5	2, 5		128.9		
4		179.7				174.5		
5	2.00 m, 1.69 m	32.5	2, 3, 4, 6, 7	3, 6	2.36 ddd (14.5, 7.5, 1.5) 2.22 ddd (14.5, 7.5, 1.5)	33.5	2, 4, 6, 7	6
6	4.29 ddd(8.8, 8.0, 2.2)	64.3	7, 8	7, 5	4.40 m	65.2	3, 8	7, 5
7	5.19 dd(6.4, 1.6)	125.1	5, 9, 10	5	5.10 dd(8.5, 1.5)	128.8	5, 9, 10	6
8		136.5				132.2		
9	1.73 d(1.2)	25.7	7, 8, 10		1.63 d (1.0)	25.5	7, 8, 10	
10	1.70 d(1.2)	18.5	7, 8, 9		1.56 d (1.0)	18.0	7, 8, 9	

[a] Multiplicity: s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet.

and carbon at δ_C 71.2 (C-1); an oxygenated methenyl with signals at δ_H 4.29 (H-6) and δ_C 64.3 (C-6); two methylenes with signals at δ_H 2.00, 1.69 (H-5), δ_C 32.5(C-5), and δ_H 1.96, 1.89 (H-2), δ_C 26.9 (C-2); and a methenyl with signals at δ_H 2.91 (H-3) and δ_C 36.7 (C-3). ^{13}C NMR and DEPT spectra showed an olefinic quaternary carbon at δ_C 136.5 (C-8) and a carbonyl carbon at δ_C 179.7 (C-4) in addition to the above carbons. These spectroscopic features along with two sp2 carbon signals (one double bond) at δ_C 136.5 (C-8) and δ_C 125.1 (C-7) in the ^{13}C NMR spectrum and the ^{1}H–^{1}H COSY correlations (H-1/H-2; H-2/H-1, -3; H-3/H-2, -5; H-5/H-3, -6; H-6/H-5, -7; and

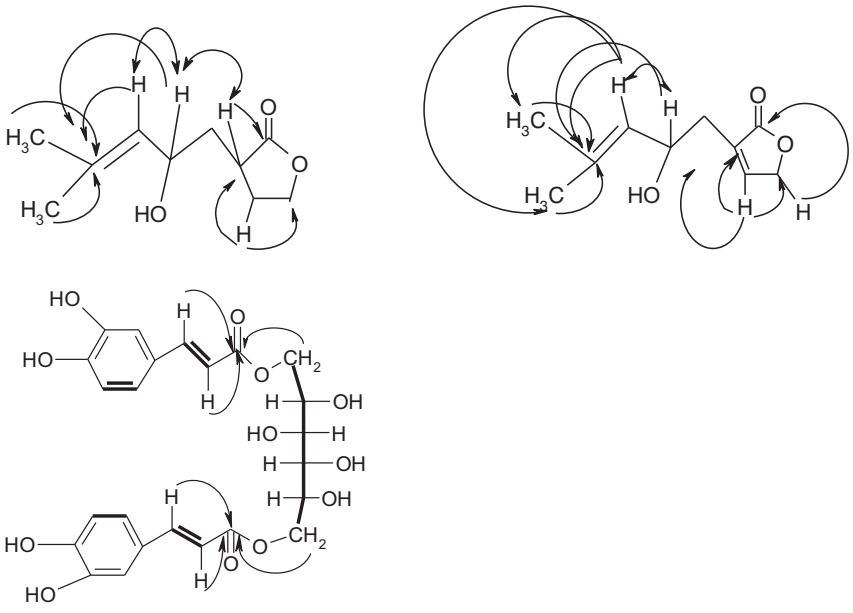

Fig. 2. Key HMBC (→), COSY (—) and NOE (↔) correlations observed for compounds **1–3**.

H-7/H-6) suggested that compound **1** is a oxygenated geraniol-monoterpene with a carboxy monocyclic skeleton. The HMBC spectrum (Fig. 2) showed key long-range correlations between the following proton and carbon signals: H-1 and C-2, C-3, C-4; H-2 and C-1, C-3, C-4; H-3 and C-2, C-4, C-5; H-5 and C-2, C-3, C-4, C-6, C-7; H-6 and C-7, C-8; and H-7 and C-5, C-9, C-10 as shown in Fig. 1. Furthermore, two methyl singlets (H-9 and H-10) showed correlations to the olefinic carbon signals at C-8 and C-7, indicating two vinyl methyls were connected to C-8. The coupling constant of 8.0 Hz between the two protons of H-6 and H-7 suggests that the protons occupied the same side, which was further confirmed by the appearance of a signal between H-6 and H-7 in the NOSEY spectrum. The presence of a signal between H-6 and H-3 in the NOSEY spectrum concluded that these two protons were on the same ring side. Compound **1** possesses the relative configuration presented in Fig. 2 with an [a] 25 D value of −21.5, which is similar to the reference compound's value of −20 (Ito et al., 2009), suggesting that they have the same configuration at the furan-lactone moiety. However, when compound **1** was separated into two enantiomorphs, which possess enol structures that easily transform into one another, no optical isomer was obtained; therefore, the absolute configuration of compound **1** was not clarified. Thus, the structure of **1** was determined to be 3-(2-hydroxyl-4-methyl-3-pentenyl)furan-5H-2-one and named sibiscolactone B.

Compound **2** was isolated as a colorless oil with an $[\alpha]_D^{25}$ value of +8.9 (MeOH), the molecular formula of which, $C_{10}H_{14}O_3$, was derived on the base of positive HR–ESI–MS (*m/z* 182.0942 $[M]^+$, calculated for 182.0943), which is equivalent to 4 degrees of unsaturation. The IR spectrum showed the presence of a hydroxyl group (3419 cm^{-1}) and a conjugated ester carbonyl group (1747 cm^{-1}). Analysis of the ^1H- and ^{13}C NMR spectra indicated that **2** was structurally similar to **1,** except that **2** had a molecular weight 2 mass units less than **1** because of the loss of two hydrogens. The NMR spectrum of compound **2** (Table 1) showed an extra olefinic proton signal at δ_H 7.44 (H-2) and two extra olefinic carbon signals at δ_C 148.8 (C-2) and δ_C128.9 (C-3) compared to a methylene signal at δ_H 1.96, 1.89 (δ_C 26.9) and a methenyl signal at δ_H 2.91 (δ_C 36.7) in compound **1**, indicating that compound **2** was hydrogenated to form a double bond between C-2 and C-3. The appearance of a signal between H-6 and H-7 in the NOSEY spectrum suggested that the signals were on same side. Furthermore, **2** has an [a] 25 D value of +8.9, which is the opposite sign rotation as that reported in the literature data (Ito et al., 2009). Additionally, separation of compound **2** into two enantiomorphs was attempted. The enol type structures easily transform into one another, thus the absolute configuration of **2** could not be obtained. Therefore, the structure of **2** was elucidated as 3-(2-hydroxyl-4-methyl-3-pentenyl)furan-2-en-2(5H)-one and named sibiscolactone C.

Compound **3** was a light yellow powder with a molecular formula of $C_{24}H_{26}O_{12}$ determined by positive HR–ESI–MS ($[M]^+$ at *m/z* 506.1433, calculated for 506.1424), indicating 12 degrees of unsaturation. The IR spectrum showed the presence of a hydroxyl group (3428 cm^{-1}), two conjugated ester carbonyl groups (1689 and 1701 cm^{-1}) and an aromatic ring (1632, 1598, 1515, 1444, 1612, 1588, and 1516 cm^{-1}). The UV spectrum exhibited absorption maxima at 203, 213, 296 (sh), and 322 nm, suggesting the presence of an extensive conjugated system. ^{13}C NMR data showed 21 carbons signals, revealing that **3** possessed a symmetrical structure when compared with the HR-ESI–MS results. The ^1H- and ^{13}C NMR and DEPT spectra of **3** (Table 2) indicated the presence of four trans olefinic proton signals at δ_H 6.22 (2H, d, *J* = 16.0 Hz, H-8, 8′), and δ_H 7.55 (2H, d, *J* = 16.0 Hz, H-7, 7′) and their corresponding olefinic carbon signals of δ_C 147.2 (C-7), 147.1 (C-7′), 116.5 (C-8), and 116.5 (C-8′); six aromatic protons at δ_H 6.98 (2H, brs, H-2, 2′), 6.72 (2H, d, *J* = 8.0 Hz, H-5, 5′), 6.89 (2H, d, *J* = 8.0 Hz, H-6, 6′) and their corresponding aromatic carbons at δ_C 115.1 (C-2), 115.0 (C-2′), 115.2 (C-5), 115.3 (C-5′), 123.0 (C-6), and 122.9(C-6′); four oxygenated olefinic carbons at δ_C 146.8 (C-3), 146.8 (C-3′), 149.6 (C-4), and 149.5 (C-4′); two quaternary aromatic carbons at δ_C 127.8 (C-1) and 127.7 (C-1′); and two carbonyl carbons at δ_C 169.2 (C-9) and 169.2 (C-9′). All of these signals revealed that there were two ABX coupled signals characteristic of two caffeic moieties. An additional four oxygenated aliphatic carbons and two oxymethylenes, which were similar to the signals of sorbitol (Tao et al., 2006; Zhang et al., 1993; Li et al., 2000), except for the downfield shift of C-1″ and C-6″ (δ_C 67.3, cf. δ_C 66.7 for compound **3** and δ_C 62.1, cf. δ_C 63.3 for the reference), revealing that the C-1″ and C-6″ of sorbitol in compound **3** were all substituted. Furthermore, comparing the spectral data of compound **3** with the reference compound sibirate (Zhang et al., 1993) showed their structural similarities, except that the molecular structure of **3** was 148 mass units greater than sibirate. Furthermore, the disappearance of proton and carbon signals of OCH_3 in **3,** which existed in sibirate, verified that the ferulic acid section in sibirate was replaced by two caffeic acid residues in compound **3**, and two caffeic acid moieties were attached to the head and tail of sorbitol by ester linkages. The sorbitol portion was further confirmed by the alkaloid hydrolysis of compound **3**, from which a polyhydric alcohol was obtained and identified as sorbitol by TLC comparison with the reference as well as comparison of NMR analysis in the literature data (Li et al., 2000). The HMBC spectrum showed key long-range correlations between the following proton and carbon signals: H-7 and C-1, C-2, C-6, C-8, C-9; H-8 and C-1, C-7, C-9; H-7′ and C-1′, C-2′, C-6′, C-8′, C-9′; H-8′ and C-1′, C-7′, C-9′; H-1″, C-9; and H-6″ and C-9′ as shown in Fig. 2. Thus, compound **3** was composed of two caffeic acid moieties and a sorbitol with a head-tail connection, i.e., 1,6-sorbitol-*O*-dicaffeic acid ester, which had been previously synthesized and reported but was obtained from natural products for the first time and its spectral data were described.

Table 2
NMR spectral data 0f compound **3** (CD_3OD, 400 MHz, 100 MHz) and compound Sibirate.

No.	3		Sibirate	
	δ_H mult[a]. *J* (Hz)	^{13}C	δ_H mult[a]. *J* (Hz)	^{13}C
1		127.8		126.8
2	6.98 brs	115.1	7.15 brs	112.0
3		146.8		146.6
4		149.6		150.0
5	6.72 d(8.0)	115.2	6.86 d(8.0)	115.3
6	6.89 d(8.0)	123.0	7.04 d(8.0)	121.1
7	7.55 d(16.0)	147.2	7.57 d(16.0)	144.5
8	6.27 d(16.0)	116.5	6.29 d(16.0)	114.1
9		169.5		166.4
1′		127.7		
2′	6.98 bars	115.0		
3′		146.8		
4′		149.5		
5′	6.72 d(8.0)	115.2		
6′	6.89 d(8.0)	122.9		
7′	7.55 d(16.0)	147.1		
8′	6.27 d(16.0)	116.5		
9′		169.2		
1″	3.92 dd(12.0,8.0) 3.69 dd(12.0,4.0)	67.3		66.8
2”	4.02 dd(8.0,4.0)	73.0		71.4
3”	4.24 dd(8.0,4.0)	70.7		69.4
4”	4.24 dd(8.0,4.0)	72.7		71.3
5”	4.32 dd(8.0,4.0)	70.8		70.7
6”	4.02 dd(12.0,8.0) 3.95 dd(12.0,4.0)	66.7		63.3

[a] Multiplicity: s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet.

The compounds were isolated by bioassay guiding, and the ethanol extract of the aqueous extract of *S. angustata* showed effects on lipid-lowering. Additionally, the new compound sibiskoside exhibited an anti-obesity effect (Ito et al., 2009). Therefore, compounds from the ethanol extract were preliminarily evaluated for hypolipidemic activities by assessing their triglyceride content in HepG2 cells (Table 3). Fortunately, compared to the control group, compounds **1–3** all showed moderate activities ($p < 0.01$) in HepG2 cells, which were in accordance with our previously reported results. The structural analysis declared that these compounds were all esters, possibly leading to their similar activities, and further investigations continue in our laboratory.

3. Experimental

3.1. General experimental procedures

Optical rotations were measured on a JASCO P-2000 polarimeter using MeOH as the solvent. CD spectra were obtained on a JASCO J-815 spectrometer. UV spectra were obtained on a JASCO V650 spectrophotometer. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer by the microscope transmission method. NMR spectra were obtained on an INOVA-500 MHz NMR spectrometer operating at 500 MHz for ^{1}H and at 125 MHz for ^{13}C. Chemical shifts are given in δ (ppm) with solvent (DMSO-d_6 or CD_3COCD_3) peaks used as references. GC was conducted using an Agilent 7890A instrument (Agilent). ESI–MS spectra were measured on an Agilent 1100 Series LC/MSD ion trap mass spectrometer. HRESIMS data were recorded on an Autospec Ultima-TOF mass spectrometer. Analytical HPLC was run on an Agilent 1100 series instrument with a UV/DAD detector using a YMC column (RP-C_{18}, 4.6 × 250 mm, 5 μm). Preparative HPLC was performed on a Shimadzu LC-6AD instrument with an SPD-10A detector using a YMC-Pack ODS-A column (20 × 250 mm, 5 μm). The Sephadex LH-20 was obtained from Amersham Pharmacia Biotech AB Factory, Sweden. ODS (45–70 μm, Merck KGaA, Darmstadt, Germany), Diaion HP20 macroporous resin (Mitsuboshi Chemical Industries, Tokyo, Japan), and silica gel (200–300 mesh, Qingdao Marine Chemical Inc., PR China) were used for column chromatography. TLC was performed on glass pre-coated with silica gel GF_{254} (200–300 mesh, Qingdao Marine Chemical Inc., PR, China). Spots were visualized under UV light or by spraying with 10% H_2SO_4 in 95% EtOH, followed by heating.

3.2. Plant Materials

S.angustata (Rehd.) Hand.-Mazz was collected in the Sichuan province, China in 2002 and identified by professor Wang Tianzhi in West China School of Pharmacy, Sichuan University, China.

3.3. Extraction and Isolation

The air-dried and powdered aerial portion of *S. angustata* (25.5 kg) was extracted with 250 L of boiling water (3 × 1 h), and the decoction was then spray-dried to yield 3.0 kg of extract. Part of the extract (1.3 kg) was extracted with EtOH under reflux (3 × 1.5 h), and the EtOH-soluble portion was concentrated under reduced pressure to give a brown solid material (500 g). This material was applied to a Diaion HP 20 chromatography column and eluted successively with a gradient of EtOH/H_2O. Then, 25.8 g of the 50% EtOH elution was further subjected to silica gel column chromatography eluted with $CHCl_3$ and MeOH in a stepwise gradient mode, the eluate of which were monitored by TLC and similar fractions were combined to afford 10 subfractions. Subfraction 2 (0.36 g) was refractioned on a silica gel column (5.0 cm i.d., 57 cm, 360–420 mesh) eluted gradiently with $CHCl_3$/MeOH, and refractions 21–25 were finally purified on a silica gel column eluted gradiently with C_6H_6/$(Me)_2CO$ (9:1, 8:2, 7:3). Compound **1** was obtained from the C_6H_6/$(Me)_2CO$ (8:2) eluate (25 mg, recrystallized in hexane). Subfraction 4 (2.8 g) was dissolved in methanol and repartitioned to a silica gel column eluted gradiently with $CHCl_3$/MeOH (20:1–1:1) to obtain 30 fractions. Fraction 15 (0.7 g) was subjected to silica gel column chromatography (5.0 cm i.d., 100 cm, 200–300 mesh) eluted gradiently with $CHCl_3$/MeOH, from which eluate 4 was precipitated and recrystallized by methanol to afford **3** (60 mg). 70 g of the 20% EtOH elution was subjected to silica gel column chromatography (2000 g) and eluted with $CHCl_3$/MeOH/H_2O to give 15 fractions (A–O). Fraction B (15.0 g) was fractionated on an ODS column (50 μm, 400 g) eluted with a MeOH/H_2O solvent system (5:95 → 50:50) to give 10 subfractions. Subfraction B-10 (0.7 g) was purified by preparative HPLC and eluted with 13% CAN at a flow rate of 7 ml/min (210 nm) to obtain **2** (20 mg).

Table 3
Hypolipdaemic effects of compounds **1–3** on triglyceride content in HepG2.

Group	Concentration	Results
model		0.3410 ± 0.0113
simvastatin	10^{-5} M	0.1799 ± 0.0109**
1	10^{-5} M	0.2185 ± 0.0072*
2	10^{-5} M	0.2130 ± 0.0183*
3	10^{-5} M	0.2221 ± 0.0133*

Data were expressed as mean ± S.E.
* $p < 0.05$.
** $p < 0.01$ vs control group.

3.4. Alkaloid hydrolysis and sugar analysis of compounds 3

Compound **3** (20 mg) was refluxed in 2 M KOH (0.5 ml) at 100 °C for 1 h and neutralized with HCl. The neutralization solution was then partitioned by polyamide column chromatography and eluted with MeOH to obtain caffeic acid (6 mg) and D-glucitol (5 mg), the NMR spectral data of which match the reference values.

3.5. Hypolipidemic activity assays

The hypolipidemic activities of compounds **1**–**3** were assayed as described previously (Wang et al., 2013).

3.5.1. 3-(2-hydroxyl-4-methyl-3-pentenyl)furan-5H-2-one (*1*)

Colorless needles (Hexane); mp 68–70 °C, $[\alpha]^{25}_{D}$ -21.5 (c 1.30, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 284 (1.53), 308 (1.36) nm; IR (KBr) ν_{max} 3424 (OH), 1726 (CO) cm^{-1}; ^{1}HNMR (CD_3OD, 400 MHz) δ: 5.19 (1H, dd, J = 6.4, 1.6 Hz, H-7), 4.29 (1H, ddd, J = 8.8, 8.0, 2.2 Hz, H-6), 3.90 (1H, ddd, J = 12.0, 8.4, 3.6 Hz, H-1a), 3.69 (1H, m, H-1b), 2.91 (1H, m, H-3), 1.96, 1.89 (each 1H, m, H-2), 2.00, 1.69 (each 1H, m, H-5), 1.73 (3H, d, J = 1.2 Hz, CH_3-9), 1.70 (3H, d, J = 1.2 Hz, CH_3-10); EIMS (+) *m/z* 184 $[M]^+$ (20), 169 $[M–CH_3]^+$ (100); HREIMS (+) *m/z* 184.1112 (calc'd for $C_{10}H_{16}O_3$, 184.1100).

3.5.2. 3-(2-hydroxyl-4-methyl-3-pentenyl)furan-2-en-2(5H)-one (*2*)

Colorless oil; $[\alpha]^{25}_{D}$ -16.5(c 1.0, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 207 (2.11), 308 (1.15) nm; IR (KBr) ν_{max} 3419 (OH), 1747 (CO) cm^{-1}; ^{1}HNMR (CD_3OD, 400 MHz) δ: 7.44 (1H, dd, J = 2.0, 1.0 Hz, H-2), 5.10 (1H, dd, J = 8.5, 1.5, H-7), 4.80 (2H, d, J = 1.5 Hz, H-1), 4.70(1H, m, OH), 4.40 (1H, m, H-6), 2.36 (1H, ddd, J = 14.5, 7.5, 1.5 Hz, H-5a), 2.22 (1H, ddd, J = 14.5, 7.5, 1.5 Hz, H-5b), 1.63 (3H, d, J = 1.0 Hz, CH_3-9), 1.56 (3H, d, J = 1.0 Hz, CH_3-10); ESIMS (+) *m/z* 205 $[M + Na]^+$ (53), 387 $[2M + Na]^+$ (100); HRESIMS (+) *m/z* 182.0942 $[M]^+$ (calc'd for $C_{10}H_{14}O_3$, 182.0943).

3.5.3. 1,6-sorbitol-O-dicaffeic acid ester (*3*)

Light yellow powder; UV (MeOH) λ_{max} (log ε) 284 (3.32), 308 (2.06) nm; IR (KBr) ν_{max} 3386 (OH), 1686 (CO), 1642 (CO),

1597 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ: 7.55 (2H, d, J = 16.0 Hz, H-7,7′), 6.98 (1H, brs, H-2,2′), 6.89 (2H, d, J = 8.0 Hz, H-6,6′), 6.72 (2H, d, J = 8.0 Hz, H-5, 5′), 6.27 (2H, d, J = 16.0 Hz, H-8,8′); ESI–MS m/z 505 $[M-H]^-$ (100), 529 $[M+Na]^+$ (80); HRESIMS (+) m/z 506.1433 (calc'd For $C_{24}H_{26}O_{12}$, 506.1424).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.phytol.2015.07.009.

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