Phytochemistry 69 (2008) 2993–2997

Contents lists available at ScienceDirect

Phytochemistry

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

Terpenoids from *Dysoxylum densiflorum*

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ARTICLE INFO

Article history:
Received 13 June 2008
Received in revised form 8 September 2008
Available online 29 October 2008

Keywords:
Dysoxylum densiflorum
Meliaceae
Degraded limonoids
Sesquiterpenoids
Dysodensiols A–F

ABSTRACT

Three degraded limonoids, dysodensiols A–C (**1**–**3**), and three sesquiterpenoids, dysodensiols D–F (**4**–**6**), along with 17 known compounds, were isolated from the twigs and leaves of *Dysoxylum densiflorum*. The structures of compounds **1**–**6** were established on the basis of extensive spectroscopic analysis.

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1. Introduction

The genus *Dysoxylum*, belonging to the family Meliaceae, is composed of about 75 species distributed in India, Malaysia, Indonesia, Australia and New Zealand, of which 15 species and one variety grow in the south of China (Chen et al., 1997). Diverse types of compounds have been isolated from this genus, such as triterpenoids (Aalbersberg and Singh, 1991), diterpenoids (Luo et al., 2001), sesquiterpenoids (Russell et al., 1994; Mulholland et al., 1998), and limonoids (Jogia and Andersen, 1987; Luo et al., 2002). *Dysoxylum densiflorum* (Bl.) Miq. has not been chemically investigated previously. In the present research, three new degraded limonoids, dysodensiols A–C (**1**–**3**), and three new sesquiterpenoids, dysodensiols D–F (**4**–**6**), together with 17 known compounds were isolated from the EtOH extract of the twigs and leaves of *D. densiflorum*. Herein we report the isolation and structural elucidation of the new compounds.

2. Results and discussion

Dysodensiol A (**1**) was obtained as a white amorphous powder. The HREIMS displayed a molecular ion peak at *m/z* 278.1149, consistent with a molecular formula of $C_{15}H_{18}O_5$ (calcd 278.1154) with 7 degrees of unsaturation. The IR absorptions at 3466 and 1718 cm^{-1} were ascribable to hydroxyl and ester carbonyl groups, respectively. The ^1H NMR (Table 1) spectrum showed the presence of one tertiary methyl (δ 1.07, *s*), one secondary methyl (δ 1.27, *d*, J = 8.1), a β-substituted furan ring (δ 7.39, 2H, *br s*, H-21, 23; δ 6.33, 1H, *br s*, H-22) which was confirmed by HMBC correlations (Fig. 1), and three protons bonded to oxygenated carbons (δ 3.56, 4.13, and 5.51). In the ^{13}C NMR (Table 1) spectrum, a total of 15 carbon resonances were observed, and were further classified by DEPT and HSQC experiments as two methyls, two sp^3 methylenes, four sp^3 methines (three oxygenated), two sp^3 quaternary carbons (one oxygenated), and an ester carbonyl (δ 167.2), together with the typical signals of a β-substituted furan ring (δ 143.1, 141.1, 119.5, and 109.8). After assignment of all the protons to their directly bonded carbons from HSQC correlations, the structure of **1** then established as a degraded limonoid with a ring-D δ-lactone, mainly by the observed correlations in the HMBC spectrum. In the HMBC (Fig. 1), the correlations of H_2-12/C-11 and H_2-9/C-11 indicated that the hydroxyl group was located at C-11. The oxygenated CH-17 methine was connected with the C-20 of the β-substituted furan ring on the basis of the HMBC correlations of H_3-18/C-17, H-17/C-13, H-17/C-14, H-17/C-20, H-17/C-21 and H-17/C-22. The assignment of a 14,15-epoxyl group was demonstrated by the mutual HMBC correlations from H_2-9, H-15, H_3-18, H_3-30 and H-17 to C-14, and from H-15 to C-16 carbonyl. Although no HMBC correlation between H-17 and C-16 was observed in the HMBC spectrum, the remaining one degree of unsaturation and the severely down-field shifted H-17 resonance (δ 5.51) indicated the linkage of C-16 and C-17 via an oxygen atom to form the six-membered lactone.

The relative configuration of **1** was elucidated by analysis of the ROESY spectrum (Fig. 2). The significant ROESY correlations of CH_3-30/CH_3-18, CH_3-30/H-15, H-11/CH_3-18, and H-11/CH_3-30

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doi:10.1016/j.phytochem.2008.09.017

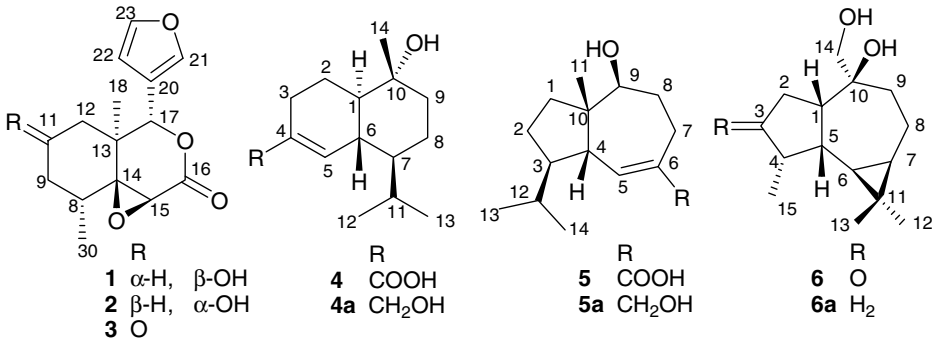

Table 1
^{1}H and ^{13}C NMR spectroscopic data for compounds **1**–**3**[a]

Position	**1**[b]		**2**[b]		**3**[c]	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
8	1.81 (*m*)	36.2	1.69 (*m*)	35.1	2.12 (*m*)	38.2
9α	1.96 (*m*)	38.6	1.87 (*m*)	35.4	2.30 (*ddd*, 1.8, 2.4, 14.0)	45.1
9β	1.79 (*m*)		2.02 (*ddd*, 3.7, 6.9, 14.5)		2.97 (*dd*, 8.0, 14.0)	
11	4.13 (*m*)	63.0	4.38 (*m*)	66.8		206.7
12α	1.72 (*m*)	41.4	1.60 (*m*)	38.4	2.12 (*dd*, 13.3, 2.4)	47.5
12β	1.39 (*t-like*, 11.7)		1.66 (*m*)		2.78 (*d*, 13.3)	
13		38.9		36.8		41.9
14		67.3		68.4		67.3
15	3.56 (*s*)	55.6	3.57 (*s*)	55.6	4.16 (*s*)	56.0
16		167.2		167.6		166.8
17	5.51 (*s*)	78.5	5.43 (*s*)	78.6	5.89 (*s*)	77.7
18	1.07 (*s*, 3H)	15.9	1.30 (*s*, 3H)	17.1	1.05 (*s*, 3H)	16.4
20		119.5		119.7		119.9
21	7.39 (*br s*)	141.1	7.39 (*br s*)	140.9	7.67 (*br d*, 0.7)	141.9
22	6.33 (*br s*)	109.8	6.35 (*br s*)	109.9	6.45 (*br s*)	110.3
23	7.39 (*br s*)	143.1	7.39 (*br s*)	142.9	7.62 (*br s*)	143.9
30	1.27 (*d*, 8.1, 3H)	18.9	1.45 (*d*, 7.4, 3H)	20.2	1.10 (*d*, 7.8, 3H)	19.3

[a] Recorded at 400 and 100 MHz for ^{1}H and ^{13}C NMR, respectively. δ in ppm and *J* in Hz are in the parentheses.
[b] In $CDCl_3$.
[c] In pyridine-d_5.

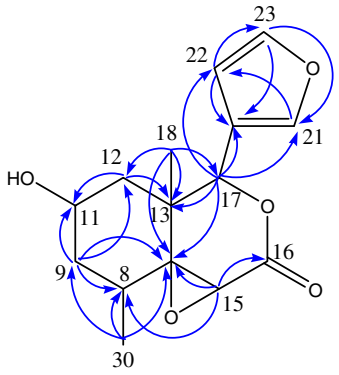

Fig. 1. Key HMBC correlations (H → C) of **1**.

indicated that they were co-facial and randomly assigned as α-oriented. As a consequence, H-17 was assigned the β-configuration by the key ROESY cross-peak of H-17/H-12 β. Thus, the structure of dysodensiol A was determined as **1**.

Dysodensiol B (**2**) had the same molecular formula ($C_{15}H_{18}O_5$) as dysodensiol A (**1**). The ^{1}H and ^{13}C NMR spectroscopic data of both compounds were similar except for the significant changes around CH-11 (CH-8, CH_2-9, CH-11, CH_2-12 and C-13) (Table 1), suggesting that they were likely stereo-isomers at C-11. This was supported by an HMBC experiment (Supplementary data). The ROESY correlations from H-11 to H-9α, H-9β, H-12β and H-12α clearly indicated that H-11 was equatorial and β-oriented (Fig. 2). As a consequence, the C-8 and C-13 of **2** were shielded by 1.1 and 2.1 ppm, respectively, due to the γ-gauche effect of HO-11α, supporting this assignment. The structure of compound **2** was thus established.

Dysodensiol C (**3**) had a molecular formula of $C_{15}H_{16}O_5$, which was two mass units less than that of **1** or **2**. Comparison of its ^{13}C and ^{1}H NMR spectroscopic data (Table 1) with those of **1** or **2** established the presence of a C-11 (δ 206.7) ketone group instead of the C-11 oxymethine in **1** or **2**, and this was further confirmed by the observed HMBC correlations from H_2-12 and H_2-9 to C-11 at δ 206.7 (Supplementary data). The relative stereochemistry at the other stereo centers of **3** was determined to be the same as that of **1** or **2** by ROESY spectrum (Supplementary data).

Dysodensiol D (**4**) was isolated as a white amorphous powder. Its HREIMS at *m/z* 234.1611 $[M–H_2O]^+$ (calcd 234.1620 for $C_{15}H_{22}O_2$ $[M–H_2O]^+$), together with the ^{1}H and ^{13}C NMR spectroscopic data (Table 2), indicated a molecular formula of $C_{15}H_{24}O_3$. The IR spectrum showed absorptions at 3425–2500 cm^{-1} (broad band) and 1687 cm^{-1} for typical carboxylic acid (including hydroxyl), and 1639 cm^{-1} for a double bond. The ^{1}H NMR spectrum showed the presence of two secondary methyls (δ 0.80, *d*, *J* = 7.0; δ 0.93, *d*, *J* = 6.7), one tertiary methyl (δ 1.11, *s*), and one olefinic proton (δ 7.18, *br s*). The ^{13}C NMR and DEPT spectra showed 15 resonances comprising a trisubstituted double bond, three methyls, four sp^3 methylenes, four sp^3 methines, one sp^3 oxygenated quaternary carbon, and one carbonyl group.

Comparison of the ^{1}H and ^{13}C NMR spectroscopic data of **4** with those of 15-hydroxy-α-cadinol (**4a**) (Kuo et al., 2002), also isolated in this study indicated that the structures of both compounds were closely related; the only difference occurred at C-4, where compound **4** bore a carboxylic acid group (C-15) instead of the hydroxymethyl of **4a**. This was verified by HMBC correlations from H-5 to C-3, C-4 and C-15, and from H_2-3 to C-4 and C-15 (Supplementary data). The stereochemistry of **4** was assigned as the same as that of **4a** on the ground of the ROESY correlations (Supplementary data).

Dysodensiol E (**5**) had a molecular formula $C_{15}H_{24}O_3$ as determined by HREIMS at *m/z* 252.1729 $[M]^+$ (calcd 252.1725). The IR spectrum showed absorptions at 3423–2500 cm^{-1} (broad band) and 1696 cm^{-1} for typical carboxylic acid (including hydroxyl), and 1630 cm^{-1} for double bond. The ^{1}H NMR (Table 2) spectrum showed resonances for two secondary methyls (δ 0.90, *d*, *J* = 6.9; δ 0.91, *d*, *J* = 6.6), one tertiary methyl (δ 1.02, *s*), a proton bonding to an oxygenated carbon (δ 3.37, *dd*, *J* = 5.8, 10.1) and one olefinic proton (δ 6.88, *d*, *J* = 4.6). The ^{13}C NMR spectroscopic data, along with the DEPT and HSQC experiments, classified the functionalities

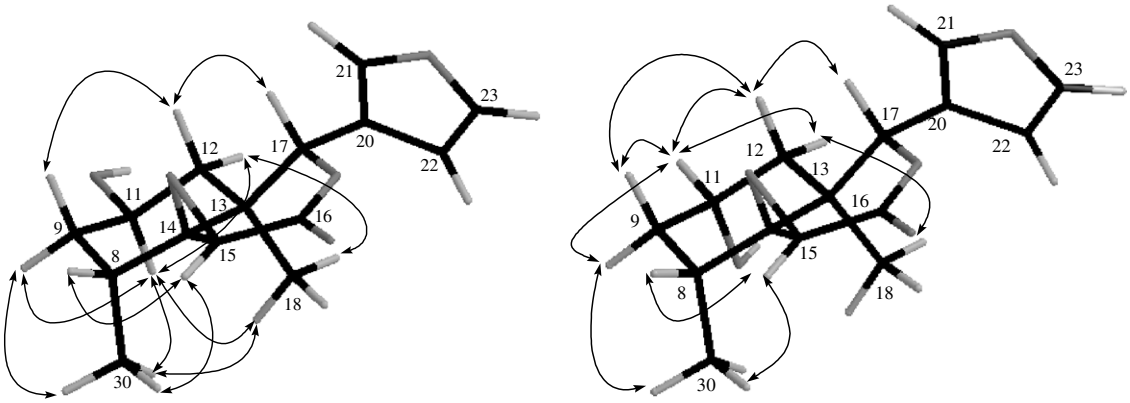

Fig. 2. Key ROESY correlations (H ↔ H) of **1** and **2**.

Table 2
1H and ^{13}C NMR spectroscopic data for compounds **4**–**6**[a]

Position	**4**		**5**		**6**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1α	1.28 (*m*)	48.9	1.43 (*m*)	40.0	2.31 (*m*)	47.9
1β			1.67 (*m*)			
2α	1.23 (*m*)	21.9	1.81 (*m*)	27.5	2.14 (*m*)	37.5
2β	2.14 (*m*)		1.43 (*m*)		2.17 (*m*)	
3α	2.17 (*m*)	24.8	1.79 (*m*)	55.9		219.3
3β	2.48 (*m*)					
4		130.2	2.15 (*m*)	52.8	2.38 (*m*)	37.9
5	7.18 (*br s*)	142.6	6.88 (*d*, 4.6)	151.4	2.35 (*m*)	52.7
6	1.90 (*m*)	40.7		129.8	-0.21 (*t-like*, 9.2)	24.2
7α	1.18 (*m*)	45.7	2.72 (*dd*, 5.8, 13.9)	22.4	0.69 (*m*)	29.7
7β			2.18 (*m*)			
8α	1.67 (*m*)	22.1	1.84 (*m*)	27.1	1.73 (*m*)	17.9
8β	1.20 (*m*)		1.53 (*m*)		1.52 (*m*)	
9α	1.84 (*m*)	41.9	3.37 (*dd*, 5.8, 10.1)	76.1	1.51 (*m*)	32.0
9β	1.44 (*m*)				1.67 (*m*)	
10		72.3		47.0		75.6
11	2.21 (*m*)	26.1	1.02 (*s*, 3H)	19.8		20.0
12	0.80 (*d*, 7.0, 3H)	15.2	1.57 (*m*)	33.2	1.01 (*s*, 3H)	16.0
13	0.93 (*d*, 6.7, 3H)	21.4	0.91 (*d*, 6.6, 3H)	20.1	1.02 (*s*, 3H)	28.3
14	1.11 (*s*, 3H)	20.5	0.90 (*d*, 6.9, 3H)	22.0	a 3.30 (*d*, 11.2); b 3.40 (*d*, 11.2)	70.4
15		172.4		171.6	1.02 (*d*, 6.1, 3H)	9.9

[a] Recorded in $CDCl_3$ at 400 and 100 MHz for ^{1}H and ^{13}C NMR, respectively. δ in ppm and *J* in Hz are in the parentheses.

as a trisubstituted double bond, three methyls, four sp^3 methylenes, four sp^3 methines (one oxygenated), one sp^3 quaternary carbon, and one carboxyl carbon (δ 171.6). The NMR spectroscopic data of **5** resembled those of a coexisting known compound 7-hydroxymethyl-1-isopropyl-3a-methyl-1,2,3,3a,4,5,6,8a-octahydro-azulen-4-ol (**5a**) (Nishizawa et al., 1984), except for the fact that a carboxylic acid group (C-15) was attached to C-6 in **5** instead of hydroxymethyl of **5a**. The structure of **5** was further confirmed by HMBC and ROESY spectra (Supplementary data).

Dysodensiol F (**6**) had a molecular formula $C_{15}H_{24}O_3$ as determined by HREIMS at *m/z* 252.1736 [M]$^+$ (calcd 252.1725). The IR spectrum showed absorptions for hydroxyls (3558 and 3448 cm^{-1}) and carbonyl (1722 cm^{-1}) groups. The ^{1}H NMR (Table 2) spectrum showed two tertiary methyls (δ 1.01 and 1.02), a secondary methyl (δ 1.02, *d*, *J* = 6.1), two geminal protons bonding to an oxygenated carbon (δ 3.30, 3.40, each 1H, *d*, *J* = 11.2), and two protons at δ 0.69 (1H, *m*) and −0.21 (1H, *t-like*, *J* = 9.2) for a characteristic cyclopropane. Inspection of the NMR spectra indicated that **6** was an *allo*-aromadendrane sesquiterpenoid, and its structure was closely related to a coexisting known compound *allo*-aromadendrane-10β,14-diol (**6a**) (de Lima et al., 1999). The only difference was presence of a C-3 (δ 219.3) ketone group in **6** instead of a C-3 methylene in **6a**. The assignment of a C-3 ketone group was confirmed by the strong HMBC correlation from H_3-15 to C-3.

The relative configuration of **6** was established as the same as **6a** by the ROESY spectrum (Fig. 3), in which, the correlations of H-6/H_3-15, H-6/H-7, H-6/H-2α, H-9α /H-7, H-9α /H-2α, H-9β/H-14a, H-14b/H-1, and H-14b/H-2β were observed.

Seventeen known compounds including *allo*-aromadendrane-10β,13,14-triol (de Lima et al., 1999), chromolaevane dione (Misra et al., 1985), eudesm-4(15)-ene-1β,6α-diol (Zhang et al., 2003), aphanamol I (Nishizawa et al., 1984), *allo*-aromadendrane-10β,14-diol (**6a**) (de Lima et al., 1999), alismoxide (Peng et al., 2003), ethyl 3-(3,4-dihydroxyphenyl)prop-2-enoate (Lamidey et al., 2002), 7-hydroxymethyl-1-isopropyl-3a-methyl-1,2,3,3a,4,5,6,8a-octahydroazulen-4-ol (**5a**) (Nishizawa et al., 1984), 2α,3α,19α-trihydroxyurs-12-en-28-oic acid (Seto et al., 1984), 15-hydroxy-α-cadinol (**4a**) (Kuo et al., 2002), clovandiol (Shi et al., 1997), 20S,24S-epoxy-7β,25-dihydroxy-3,4-secodammar-4(28)-en-3-oic acid (de Campos Braga et al., 2006), ficusesquilig-

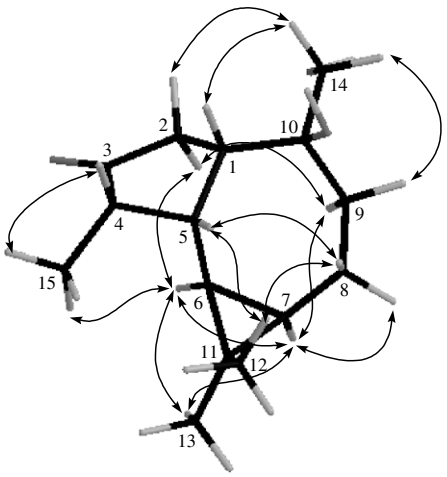

Fig. 3. Key ROESY correlations (H ↔ H) of **6**.

nan A (Li and Kuo, 2000), ficusesquilignan B (Li and Kuo, 2000), 2α,3α,4β-trihydroxypregnan-16-one (Pupo et al., 1997), 2β,3β, 4β-trihydroxypregnan-16-one (Pupo et al., 1997), and 2α,3α,19α, 23-tetrahydroxyurs-12-en-28-oic acid (Seto et al., 1984) were identified by spectroscopic analysis.

3. Conclusion

The structural types of limonoids in the Meliaceae family, in combination with their biosynthetic pathways on the biogenetic map, serve as biomarks for chemotaxonomic analysis (Da Silva et al., 1984). A series of limonoids isolated from the genus *Dysoxylum* (Jogia and Andersen, 1987; Luo et al., 2002) favored the affiliation of *Dysoxylum* to the subfamily of Melioideae. In our study, three degraded limonoids, dysodensiols A–C (**1**–**3**) that were likely biotransformed from a common precursor of a B-*seco*-limonoid, were isolated from *D. densiflorum*, supporting that the genus *Dysoxylum* should preferably be included in the subfamily of the Melioideae (Chen et al., 1997).

4. Experimental

4.1. General

Optical rotations were measured on a Perkin–Elmer 341 polarimeter (Na filter, $\gamma = 589$ nm). UV spectra were obtained on a Shimadzu UV-2550 spectrophotometer, whereas IR spectra were recorded on a Perkin–Elmer 577 spectrometer with KBr disks. NMR spectra were measured on a Bruker AM-400 spectrometer. EIMS and HREIMS (70 eV) were carried out on a Finnigan MAT 95 mass spectrometer. All solvents used were of analytical grade (Shanghai Chemical Reagents Company Ltd.). Silica gel (200–300 mesh), silica gel H (Qingdao Haiyang Chemical Co. Ltd., People's Republic of China), C18 reversed-phase silica gel (150–200 mesh, Merck), and MCI gel (CHP20P, 75–150 μm, Mitsubishi Chemical Industries Ltd., Japan) were used for column chromatography. Precoated thin-layer chromatography (TLC) plates with silica gel GF_{254} (Qingdao Haiyang Chemical Co. Ltd., People's Republic of China) were used for TLC.

4.2. Plant material

The plant material of *D. densiflorum* was collected from Xishuangbanna Tropical Botanical Garden, Mengla County, China, and was authenticated by Professor You-Kai Xu of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen (accession number DD-2006-1Y) has been deposited in the Shanghai Institute of Materia Medica.

4.3. Extraction and isolation

The air dried powder of twigs and leaves of *D. densiflorum* (4.6 kg) was percolated with 95% EtOH–H_2O (95:5, v/v) three times. After removal of the solvent under reduced pressure, the EtOH extract (220 g) was partitioned between H_2O and EtOAc to give an EtOAc-soluble fraction (52 g), which was subjected to MCI cc to obtain fractions 1 (MeOH/H_2O, 50:50) and 2 (MeOH/H_2O, 60:40 → 70:30). Fraction 1 was separated on a silica gel column (petroleum ether/EtOAc, 1:1; $CHCl_3$/MeOH, 20:1) and then a reversed-phase silica gel column (MeOH/H_2O, 45:55 → 50:50) to yield *allo*-aromadendrane-10β,13,14-triol (120 mg). Fraction 2 was subjected to a silica gel column eluted with petroleum ether/acetone (from 20:1 to 0:1) to afford three major fractions 2a–2c. Fraction 2a (1.7 g) was separated on a silica gel column (petroleum ether/EtOAc, 6:1) and then a RP-18 silica gel column (MeOH/H_2O, 60:40 → 80:20) to give subfractions 2a1–2a5. Recrystallization of 2a1 from MeOH afforded **3** (91 mg). The purification of subfractions from 2a2 to 2a5, by using a silica gel column, gave chromolaevane dione (7 mg), eudesm-4(15)-ene-1β,6α-diol (31 mg), aphanamol I (30 mg), and **6a** (92 mg), respectively. Fraction 2b (1.0 g) was separated on a silica gel column (petroleum ether/EtOAc, 6:1) and then a RP-18 silica gel column (MeOH/H_2O, 60:40 → 70:30) to give subfractions 2b1–2b2. Purification of subfraction 2b1 using a silica gel column (petroleum ether/EtOAc, 3:1) gave **2** (21 mg). Purification of subfraction 2b2 using a silica gel column ($CHCl_3$/MeOH, 100:1; petroleum ether/EtOAc, 3:1) gave alismoxide (9 mg). A similar purification procedure on fraction 2c (4.7 g) yielded ethyl 3-(3,4-dihydroxyphenyl)prop-2-enoate (32 mg), **1** (12 mg), **4** (11 mg), **4a** (18 mg), **5** (8 mg), clovandiol (2 mg), 20S,24S-epoxy-7β,25-dihydroxy-3,4-secodammar-4(28)-en-3-oic acid (9 mg), **6** (95 mg), **5a** (9 mg), 2α,3α,19α-trihydroxyurs-12-en-28-oic acid (41 mg), ficusesquilignan A (25 mg), ficusesquilignan B (13 mg), 2α,3α,4β-trihydroxypregnan-16-one (40 mg), 2β,3β,4β-trihydroxypregnan-16-one (24 mg), and 2α,3α,19α,23-tetrahydroxyurs-12-en-28-oic acid (9 mg).

4.4. Dysodensiol A (*1*)

White amorphous powder; $[\alpha]_D^{20}$ −37.0 (*c* 0.1500, $CHCl_3$); IR (KBr, disc) ν_{max} (cm^{-1}): 3466, 2928, 2956, 1718, 1284, 1169, 1036, 878, 808; for ^1H and ^{13}C NMR spectroscopic data, see Table 1; EIMS *m/z* (rel. int.): 278 $[M]^+$ (20), 250 (11), 232 (12), 221 (47), 203 (37), 161 (30), 155 (99), 137 (98), 107 (88), 95 (100); HREIMS *m/z*: 278.1149 $[M]^+$ (calcd for $C_{15}H_{18}O_5$, 278.1154).

4.5. Dysodensiol B (*2*)

White amorphous powder; $[\alpha]_D^{20}$ −31.0 (*c* 0.1550, $CHCl_3$); IR (KBr, disc) ν_{max} (cm^{-1}): 3485, 2928, 1716, 1421, 1288, 1171, 1026, 818, 604; for ^1H and ^{13}C NMR spectroscopic data, see Table 1; EIMS *m/z* (rel. int.): 278 $[M]^+$ (5), 250 (19), 235 (9), 221 (48), 203 (28), 161 (19), 155 (61), 137 (64), 107 (90), 95 (100); HREIMS *m/z*: 278.1156 $[M]^+$ (calcd for $C_{15}H_{18}O_5$, 278.1154).

4.6. Dysodensiol C (*3*)

Colorless crystal; $[\alpha]_D^{20}$ −29.0 (*c* 0.2450, $CHCl_3$); IR (KBr, disc) ν_{max} (cm^{-1}): 3124, 2980, 1711, 1740, 1352, 1284, 1028, 810, 592; for ^1H and ^{13}C NMR spectroscopic data, see Table 1; EIMS *m/z* (rel. int.): 276 $[M]^+$ (15), 248 (9), 219 (53), 203 (7), 161 (40), 153 (87), 137 (18), 123 (75), 109 (60), 95 (100); HREIMS *m/z*: 276.0994 $[M]^+$ (calcd for $C_{15}H_{16}O_5$, 276.0998).

4.7. Dysodensiol D (*4*)

White amorphous powder; $[\alpha]_D^{20}$ +5.0 (*c* 0.4800, $CHCl_3$); UV (MeOH) λ_{max} ($\log\varepsilon$), nm: 209 (3.69); IR (KBr, disc) ν_{max} (cm^{-1}): 3425, 2958, 2870, 1687, 1639, 1387, 1277, 1111, 1086, 924; for ^1H and ^{13}C NMR spectroscopic data, see Table 2; EIMS *m/z* (rel. int.): 234 $[M-H_2O]^+$ (38), 219 (5), 191 (100), 173 (10), 145 (24), 123 (9), 105 (19), 91 (21); HREIMS *m/z*: 234.1611 $[M-H_2O]^+$ (calcd for $C_{15}H_{22}O_2$, 234.1620).

4.8. Dysodensiol E (*5*)

White amorphous powder; $[\alpha]_D^{20}$ −40.0 (*c* 0.0550, MeOH); UV (MeOH) λ_{max} ($\log\varepsilon$), nm: 215 (3.91); IR (KBr, disc) ν_{max} (cm^{-1}): 3423, 2956, 2870, 1696, 1630, 1277, 1198, 1034; for ^1H and ^{13}C NMR spectroscopic data, see Table 2; EIMS *m/z* (rel. int.): 252 $[M]^+$ (1), 234 (25), 219 (18), 209 (28), 191 (100), 173 (12), 153

(20), 145 (21), 123 (33), 81 (36); HREIMS *m/z*: 252.1729 $[M]^+$ (calcd for $C_{15}H_{24}O_3$, 252.1725).

4.9. Dysodensiol F (**6**)

White amorphous powder; $[\alpha]_D^{20}$ +149.0 (*c* 0.1850, $CHCl_3$); IR (KBr, disc) ν_{max} (cm^{-1}): 3558, 3448, 2954, 2881, 1722, 1456, 1375, 1090, 1043, 887; for ^1H and ^{13}C NMR spectroscopic data, see Table 2; EIMS *m/z* (rel. int.): 252 $[M]^+$ (15), 234 (51), 221 (92), 203 (100), 175 (38), 161 (46), 147 (66), 133 (36), 107 (70), 81 (47); HREIMS *m/z*: 252.1736 $[M]^+$ (calcd for $C_{15}H_{24}O_3$, 252.1725).

Acknowledgments

Financial support of the Key Project of National Natural Science Foundation (Grant No. 30630072) and Shanghai Municipal Scientific Foundation (Grant No. 06DZ22028) of P.R. China are gratefully acknowledged. We thank Professor Y.-K. Xu of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences for the identification of the plant material.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.phytochem.2008.09.017.

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