Limonoids and Sesquiterpenoids from *Amoora tsangii*

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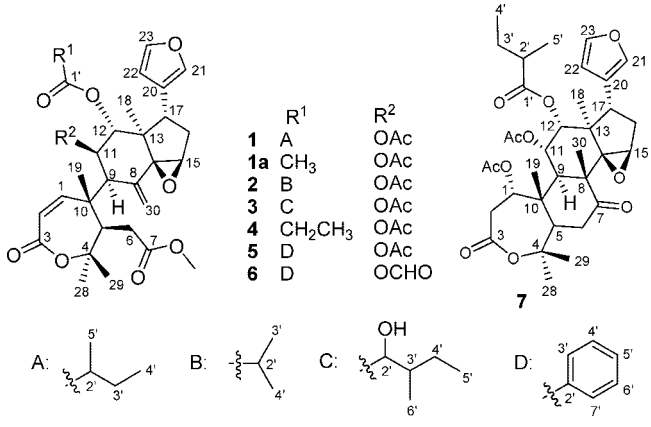
Seven new limonoids, amotsangins A−G (**1**−**7**), two known limonoids, and four known sesquiterpenoids were isolated from the twigs and leaves of *Amoora tsangii*. Their structures were elucidated primarily on the basis of spectroscopic data.

Chemical investigations of the Meliaceae family for structurally diverse and biologically significant limonoids have been attractive programs of natural products[1] and synthetic chemistry.[2] In recent years, a number of new limonoids have been isolated from the Meliaceae family by several research groups.[3–5] The genus *Amoora* (Meliaceae) comprises about 25 species distributed in China, India, and Malaysia, of which eight species and one variant grow in China. Hitherto, only one limonoid was reported from this genus.[6] *Amoora tsangii* (Merr.) X. M. Chen, an economically important timber tree, is native to Hainan Island of China. It was previously misidentified as *Aglaia tsangii* Merr.[7] and revised lately as *Amoora tsangii*.[8] The stem bark of this plant has applications in folklore medicine as a vermicide.[7] Chemical studies on this plant have not been reported previously.

As a part of our continuous effort to search for novel compounds from plants of the Meliaceae family, seven new limonoids, namely, amotsangins A−G (**1**–**7**), two known limonoids, DM-3[9] and DM-4,[9] and four known sesquiterpenoids, 10-hydroxy-15-oxo-α-cadinol,[10] 11β-hydroxy-1β,8α-aromadendrene,[11] octahydro-4-hydroxy-3α-methyl-7-methylene-α-(1-methylethyl)-1*H*-indene-1-methanol,[10] and eudesm-4(15)-ene-1β,6α-diol,[10] were isolated from the twigs and leaves of *A. tsangii*. Herein, we report the isolation and structural elucidation of these new limonoids.



Results and Discussion

Amotsangin A (**1**) was obtained as a white, amorphous powder. Its molecular formula was determined by the HREIMS ion at *m/z* 612.2947 $[M]^+$ as $C_{34}H_{44}O_{10}$ (calcd 612.2934), indicating the presence of 13 degrees of unsaturation. Its ESIMS ions (in positive mode) at 635.4 $[M + Na]^+$ and 1247.7 $[2\ M + Na]^+$ further secured the molecular formula. The strong IR absorptions at 1747, 1728, and 1699 cm^{-1} showed the presence of carbonyl groups. In addition to the easily distinguishable resonances for an acetyl (δ_H 2.10, 3H, s) and a methoxy (δ_H 3.71, 3H, s) group, the ^1H NMR spectrum also indicated the presence of four tertiary methyls (δ_H 0.95, 1.00, 1.28, and 1.55, each 3H, s), one secondary methyl (δ_H 0.76, 3H, d, $J = 8.6$ Hz), one primary methyl (δ_H 0.79, 3H, t, $J = 7.5$ Hz), and one β-substituted furan ring (δ_H 6.17, 7.11, and 7.27, each 1H, s). The ^{13}C NMR spectrum displayed 34 carbon resonances, which were classified by DEPT and HSQC experiments as eight methyls, three sp^3 methylenes, seven sp^3 methines (three oxygenated), four sp^3 quaternary carbons, four ester carbonyls, an exocyclic double bond (C-8: δ_C 136.7; CH_2-30: δ_C 120.8, δ_H 5.34, 5.22), two disubstituted double bonds, and one trisubstituted double bond. The aforementioned NMR data implied that **1** was a ring B-*seco* limonoid with a typical $\Delta^{8(30)}$ double bond.[12]

Comparison of the ^1H and ^{13}C NMR data of **1** (Tables 1 and 2) with those of nymania-3 (**1a**)[13] indicated that their structures are closely related, just differing in the nature of the acyloxy group at C-12. The presence of a 2-methylbutanoyloxy group was readily identified by the ^1H and ^{13}C NMR data (Tables 1 and 2) and confirmed by the relevant HMBC correlations within this moiety (Figure 1a). The key correlations between H-12 and C-1′ further confirmed the location of the 2-methylbutanoyloxy moiety at C-12. The complete planar structure of **1** was further verified by the analysis of its HMBC spectrum. The correlations from two olefinic protons (δ_H 5.34, and 5.22, each 1H, s) to C-8, C-9, and C-14 revealed the exocyclic $\Delta^{8(30)}$ double bond, typical of a B-*seco* limonoid.[14] The presence of a 14,15-epoxide was implied by the chemical shifts of C-14 at δ_C 71.0 and C-15 at δ_C 59.4 and was supported by the mutual HMBC correlations of H_2-16/C-15, H-17/C-15, Me-18/C-14, H-9/C-14, and H_2-30/C-14. The HMBC correlations H-1/C-3, C-5, and C-10; H-2/C-3 and C-10; Me-19/C-1; and a rare ^4J correlation Me-28/C-3 indicated that an α,β-unsaturated lactone was formed between C-3 and C-4. The sole methoxy group (δ_H 3.71; δ_C 52.3) was placed at C-7 (δ_C 173.5) from its cross-peak with this carbon. The HMBC correlation from H-11 to the carbonyl of the OAc allowed the attachment of the acetoxy group at C-11.

The relative configuration of the limonoid core was mainly established by a ROESY experiment (Figure 1b), in which the correlations Me-18/H-11, Me-18/H-16α, H-11/H-9, and Me-28/H-5 indicated that they were cofacial and were arbitrarily assigned an α-orientation. The ROESY cross-peaks of H-17 and Me-29, with H-12 and Me-19, respectively, revealed that H-17, H-12, and Me-19 were assigned a β-orientation. The large coupling constant ($J_{11,12}$ = 10.8 Hz) showed a 1,2-diaxial relationship between H-11 and H-12, consistent with the previous α- and β-assignments for these two protons.[5a,f] The ROESY correlations of H-6a (δ 2.29)/Me-19 and H-6b (δ 2.18)/Me-28 indicated that CH_2-6 was approximately equatorial toward the β-face. The chemical shifts of C-14 and C-15 of **1** were nearly identical to those of nymania-3 (**1a**),[13] suggesting that the 14,15-epoxide was β-oriented, and this was confirmed by

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Table 1. ^{1}H NMR Data (400 MHz, $CDCl_3$) for Compounds **1**–**7**

	1	**2**	**3**	**4**
proton	δ_H (*J* in Hz)	δ_H (*J* in Hz)	δ_H (*J* in Hz)	δ_H (*J* in Hz)
1	6.92, d (13.2)	6.93, d (12.9)	6.95, d (13.1)	6.93, d (12.9)
2	6.25, d (13.2)	6.26, d (12.9)	6.28, d (13.1)	6.27, d (12.9)
5	3.27, d (9.2)	3.29, d (9.2)	3.31, d (8.8)	3.33, d (9.1)
6a	2.29, d (16.6)	2.29, d (16.8)	2.30, d (17.2)	2.28, d (17.3)
6b	2.18, dd (16.6, 9.2)	2.18, dd (16.8, 9.2)	2.20, dd (17.2, 8.8)	2.18, dd (17.3, 9.1)
9	3.06, d (7.3)	3.07, d (7.3)	3.08, d (7.1)	3.07, d (7.3)
11	5.62, dd, (10.8, 7.3)	5.62, dd (10.9, 7.3)	5.69, dd (11.0, 7.1)	5.60, dd (10.8, 7.3)
12	5.84, d, (10.8)	5.83, d (10.9)	6.00, d (11.0)	5.86, d (10.8)
15	3.86, s	3.86, s	3.86, s	3.88, s
16*β*	2.22, dd (14.0, 6.9)	2.22, dd (13.8, 7.0)	2.27, dd (14.0, 7.1)	2.22, dd (13.3, 7.0)
16α	1.81, dd (14.0, 10.9)	1.81, dd (13.8, 11.1)	1.84, dd (14.0, 11.0)	1.83, dd (13.3, 10.4)
17	3.07, dd (10.9, 6.9)	3.00, dd (11.1, 7.0)	3.06, dd (11.0, 7.1)	3.04, dd (10.4, 7.0)
18	0.95, s	0.95, s	0.97, s	0.93, s
19	1.00, s	1.00, s	1.02, s	1.01, s
21	7.11, s	7.11, s	7.12, s	7.11, s
22	6.17, s	6.17, s	6.17, s	6.15, s
23	7.27, s	7.28, s	7.33, s	7.30, s
28	1.28, s	1.29, s	1.30, s	1.29, s
29	1.55, s	1.55, s	1.58, s	1.56, s
30a	5.34, s	5.34, s	5.37, s	5.35, s
30b	5.22, s	5.22, s	5.25, s	5.23, s
OMe	3.71, s	3.71, s	3.73, s	3.72, s
OAc	2.10, s	2.09, s	2.14, s	2.10, s
2′	1.94, m	2.17, m	3.45, s	1.96, m
3′a	1.41, m	0.85, d (7.1)	1.41, m	0.93, t (7.6)
3′b	1.17, m			
4′	0.79, t (7.5)	0.82, d (7.1)	1.40, m	
			1.23, m	
5′	0.76, d (8.6)		0.82, t (7.1)	
6′			0.69, d (6.6)	

	5	**6**	**7**
proton	δ_H (*J* in Hz)	δ_H (*J* in Hz)	δ_H (*J* in Hz)
1	7.00, d (13.1)	6.96, d (12.9)	5.11, d (7.0)
2	6.35, d (13.1)	6.34, d (12.9)	3.28, dd (15.9, 7.0)
			3.19, d (15.9)
5	3.35, d (8.9)	3.32, d (8.4)	2.61, d (8.4)
6a	2.32, d (16.6)	2.32, d (16.6)	2.83, d (14.8)
6b	2.20, dd (16.6, 8.9)	2.23, dd (16.6, 8.4)	2.61, dd (14.8, 8.4)
9	3.13, d (7.3)	3.19, d (7.5)	2.96, s
11	5.77, d (10.8, 7.3)	5.89, dd (10.6, 7.5)	4.98, s
12	6.10, d (10.8)	6.13, d (10.6)	5.19, s
15	3.91, s	3.92, s	3.71, s
16*β*	2.26, dd (13.6, 6.9)	2.28, dd (14.0, 7.0)	2.24, dd (13.1, 6.8)
16α	1.86, dd (13.6, 11.2)	1.86, dd (14.0, 10.7)	2.04, dd (13.1, 11.3)
17	3.13, dd (11.2, 6.9)	3.14, dd (10.7, 7.0)	2.90, dd (11.3, 6.8)
18	1.00, s	1.02, s	0.96, s
19	1.04, s	1.06, s	1.46, s
21	7.00, s	6.98, s	7.09, s
22	6.05, s	6.05, s	6.14, s
23	7.01, s	6.98, s	7.28, s
28	1.28, s	1.28, s	1.47, s
29	1.57, s	1.56, s	1.56, s
30a	5.39, s	5.41, s	1.43, s
30b	5.26, s	5.28, s	
OMe	3.70, s	3.71, s	
OAc	1.89, s		2.05, s
			2.16, s
2′			2.09, m
3′a	7.75, dd (8.1, 1.4)	7.74, dd (8.1, 1.3)	1.40, m
3′b			1.17, m
4′	7.33, dd (8.1, 7.4)	7.32, dd (8.1, 7.6)	0.73, t (7.5)
5′	7.48, tt, (7.4, 1.4)	7.47, tt, (7.6, 1.4)	1.05, d (6.9)
6′	7.33, dd (8.1, 7.4)	7.32, dd (8.1, 7.6)	
7′	7.75, dd (8.1, 1.4)	7.74, dd (8.1, 1.3)	
OCHO		7.98 (s)	

the ROESY correlation between H-15 and H-30a, which was also observed in the structural elucidation of a known compound, 11-*epi*-21-hydroxytoonacilide, with a *β*-oriented 14,15-epoxide moiety.[12] The structure of **1** was thus elucidated.

Comparison of the NMR and MS data of amotsangins B−E (**2**–**5**) with those of **1** showed that these compounds differed in the nature of the C-12 acyloxy groups (Experimental Section and Tables 1 and 2). The presence of a methylpropanoyloxy group in **2** was

Table 2. ^{13}C NMR Data (100 MHz, $CDCl_3$) for Compounds **1–7**

position	1	2	3	4	5	6	7
1	148.5	148.5	148.4	148.5	148.5	148.2	70.9
2	122.0	122.0	122.2	122.0	122.1	122.6	34.8
3	166.5	166.5	166.5	166.6	166.5	166.9	169.3
4	83.5	83.5	83.7	83.5	83.5	83.5	84.2
5	50.0	50.0	50.0	49.9	50.0	50.6	50.9
6	34.9	34.9	34.9	34.9	35.0	35.0	38.6
7	173.5	173.5	173.4	173.5	173.4	173.5	207.1
8	136.7	136.7	136.5	136.6	136.8	136.6	45.1
9	53.2	53.2	53.5	53.2	53.3	53.3	44.0
10	46.2	46.2	46.3	46.2	46.3	46.2	44.4
11	70.9	71.0	70.4	71.0	71.1	71.1	75.5
12	73.6	73.7	72.9	74.0	75.1	74.7	80.6
13	45.5	45.4	45.6	45.1	45.4	45.5	45.1
14	71.0	71.0	71.0	71.0	71.2	71.1	67.8
15	59.4	59.4	59.5	59.5	59.7	59.7	56.2
16	34.0	33.8	34.0	33.5	33.3	33.5	33.5
17	37.6	37.6	37.7	37.7	38.0	37.9	41.5
18	13.6	13.6	13.6	13.5	13.6	13.7	14.8
19	22.6	22.6	22.8	22.6	22.4	22.4	17.0
20	122.1	122.1	121.9	121.1	122.1	122.6	121.9
21	140.5	140.4	140.5	140.3	140.3	140.4	141.1
22	111.3	111.2	111.0	111.1	111.0	111.0	111.7
23	142.3	142.4	142.7	142.4	142.3	142.3	142.3
28	30.2	30.2	30.2	30.2	30.2	30.2	23.2
29	22.3	22.4	22.3	22.3	22.7	22.9	33.8
30	120.8	120.9	121.1	120.9	121.0	121.2	21.2
OMe	52.3	52.3	52.3	52.3	52.3	52.3	
OAc	20.6	20.5	20.8	20.3	20.2		20.9
	170.4	170.3	170.3	170.3	170.4		168.5
							21.2
							169.1
1′	174.8	175.3	175.0	173.0	165.6	165.5	174.9
2′	41.1	33.9	75.3	27.4	129.7	129.5	40.8
3′	25.9	18.2	37.8	8.7	129.5	129.6	26.1
4′	11.7	18.4	26.2		128.2	128.2	11.4
5′	15.3		11.6		132.8	132.9	15.5
6′			13.0		128.2	128.2	
7′					129.5	129.6	
OCHO						160.1	

evidenced by the 1D NMR data [C-1′: δ_C 175.3; CH-2′: δ_C 33.9, δ_H 2.17 (m); CH_3-3′: δ_C 18.2, δ_H 0.85 (3H, d, J = 7.1 Hz); CH_3-4′: δ_C 18.4, δ_H 0.82 (3H, d, J = 7.1 Hz)]. In the same way, the acyloxy groups at C-12 of **3**−**5** were determined as follows: a 2-hydroxy-3-methylpentanoyloxy for **3** [C-1′: δ_C 175.0; CH-2′: δ_C 75.3, δ_H 3.45 (s); CH-3′: δ_C 37.8, δ_H 1.41 (m); CH_2-4′: δ_C 26.2, δ_H 1.40 (m), 1.23 (m); CH_3-5′: δ_C 11.6, δ_H 0.82 (3H, t, J = 7.1 Hz); CH_3-6′: δ_C 13.0, δ_H 0.69 (3H, d, J = 6.6 Hz)],[15] a propanoyloxy for **4** [C-1′: δ_C 173.0; CH_2-2′: δ_C 27.4, δ_H 1.96 (m); CH_3-3′: δ_C 8.7, δ_H 0.93 (3H, t, J = 7.6 Hz)], and a benzoyloxy for **5** [C-1′: δ_C 165.6; C-2′: δ_C 129.7; CH-3′, 7′: δ_C 129.5, δ_H 7.75 (1H, dd, J = 8.1, 1.4 Hz); CH-4′, 6′: δ_C 128.2, δ_H 7.33 (1H, dd, J = 8.1, 7.4 Hz); CH-5′: δ_C 132.8, δ_H 7.48 (1H, tt, J = 7.4, 1.4 Hz)]. The attachment of the acyloxy groups to C-12 of compounds **2**−**5** was confirmed by key HMBC correlations between H-12 and C-1′ of each acyloxy group (Supporting Information), respectively. Thus the structures of amotsangins B−E were assigned as **2–5**, respectively.

Amotsangin F (**6**) gave a molecular formula of $C_{35}H_{38}O_{10}$, as deduced from HREIMS at m/z 618.2482 (calcd for $C_{35}H_{38}O_{10}$, 618.2465). The ^1H and ^{13}C NMR data of amotsangin F (**6**) showed high similarity to those of **5**, except that the acetoxy group was replaced by a formyloxy group (δ_H 7.98; δ_C 160.1). To confirm this, compound **6** was treated with aqueous $NaHCO_3$ (5%, 0.5 mL) in MeOH (3 mL) at room temperature for 30 min. The mixture was then reacted with Ac_2O in dried pyridine overnight to give a crude product, whose HPLC-ESIMS showed a major peak at 2.27 min with a pseudomolecular ion at m/z 633 $[M + H]^+$ corresponding to the molecular formula of compound **5** (Supporting Information S5, S6). After preparative TLC purification, the ESIMS spectrum and HPLC retention time (by coinjection) of the major compound were consistent with those of compound **5** (Supporting Information S7−S9). The structure of **6** was therefore determined.

Amotsangin G (**7**) gave a molecular formula of $C_{35}H_{46}O_{11}$ with 13 degrees of unsaturation, as determined by HREIMS at m/z 642.3033 $[M]^+$ (calcd 642.3040). The ESIMS in the positive mode showed pseudomolecular ions at 643.4 $[M + H]^+$ and 665.3 $[M + Na]^+$ supporting this assignment. The IR absorptions at 1755 and 1720 cm^{-1} revealed the presence of carbonyl groups. The ^{13}C NMR of **7** displayed 35 signals, which were further classified by DEPT and HSQC spectra as nine methyls, four methylenes, 11 methines, and 11 quaternary carbons. The presence of five tertiary methyls (δ_H 0.96, 1.43, 1.46, 1.47, and 1.56, each 3H, s), two acetyls (δ_H 2.05, 2.16; δ_C 20.9, 21.2, 168.5, and 169.1), one 2-methylbutanoyloxy group [δ_H 0.73 (3H, t, J = 7.5 Hz), 1.05 (3H, d, J = 6.9 Hz), 1.17 (m), 1.40 (m), and 2.09 (m); δ_C174.9, 40.8, 26.1, 15.5, and 11.4], and a β-substituted furan ring (δ_H 6.14, 7.09, 7.28; δ_C 111.7, 122.9, 141.1, and 142.3) were indicated by the ^1H and ^{13}C NMR data. The aforementioned data suggested that compound **7** was also a limonoid.[16]

The planar structure of **7** was constructed by extensive analysis of its 1D and 2D NMR spectra. In the HMBC spectrum (Figure 2a), H-5, H_2-6, H-9, and Me-30 showed correlations with the ketone carbonyl at δ_C 207.1, indicating that compound **7** had an intact B ring with a ketone group at C-7. An oxygenated methine (δ_H 4.98, δ_C 75.5) bearing an acetoxy group was assigned to C-11 on the basis of the HMBC correlations from H-11 to C-8, C-9, C-10, and the carbonyl carbon of OAc at δ_C 169.1. The HMBC correlation between H-12 at δ_H 5.19 and the carbonyl signal at δ_C 174.9 of the 2-methylbutanoyloxy group facilitated placement of this group at C-12 (δ_C 80.6). The HMBC correlation from the methyl protons of the remaining acetoxy group to C-1 at δ_C 70.9 allowed the attachment of OAc to C-1, which also showed HMBC correlations with H_2-2 and Me-19. The presence of a 14,15-epoxide was assigned on the basis of the chemical shifts [δ_H 3.86, H-15; δ_C 59.4 (C-15) and 71.0 (C-14)], which was supported by the HMBC correlations of H_2-16 with C-15 and C-14, and 18-Me and 30-Me with C-14. One ester carbonyl at δ 169.3 and one oxygenated quaternary carbon at δ 84.2 were assigned to C-3 and C-4, respectively, by the mutual HMBC correlations from H_2-2 and H-1 to C-3, and from Me-28 (and 29) to C-4, indicating that a lactone existed between C-3 and C-4, which was confirmed by a weak ^4J HMBC correlation between Me-28 and C-3.

The relative configuration of **7** was determined by a ROESY experiment (Figure 2b). The ROESY correlations of Me-19/H-1, Me-19/H-2β, Me-19/Me-29, Me-19/H-6β, H-6β/Me-30, and Me-29/H-2β indicated that these methyl groups and protons were cofacial and were randomly assigned as the β-orientation. Subsequently, the ROESY correlations of H-5/Me-28, Me-28/H-6α, H-5/H-9, H-9/H-11, and H-9/Me-18 revealed that Me-18, H-5, H-9, and Me-28 were in an α-orientation; the ROESY correlations of H-17/H-12 and H-17/H-16β indicated that H-12 and H-17 were β-oriented. The 14,15-epoxide was assigned as β-oriented on the basis of the chemical shifts of H-15, C-14, and C-15, which were nearly identical to those of **1**−**6**. This assignment was further supported by the similarity of the chemical shifts of C-14 and C-15 with those of a known compound, 11β,12α-diacetoxy-1-deoxo-14β,15β-epoxy-3β-hydroxy-2-oxo-neotecleanin.[17]

Six known compounds, DM-3,[8] DM-4,[8] 10-hydroxy-15-oxo-α-cadinol,[9] 11β-hydroxy-1β,8α-aromadendrene,[10] octahydro-4-hydroxy-3α-methyl-7-methylene-α-(1-methylethyl)-1*H*-indene-1-methanol,[9] and eudesm-4(15)-ene-1β,6α-diol,[9] were identified by comparison of their spectroscopic data with literature data.

Experimental Section

General Experimental Procedures. Optical rotations were determined on a Perkin-Elmer 341 polarimeter. UV spectra were recorded

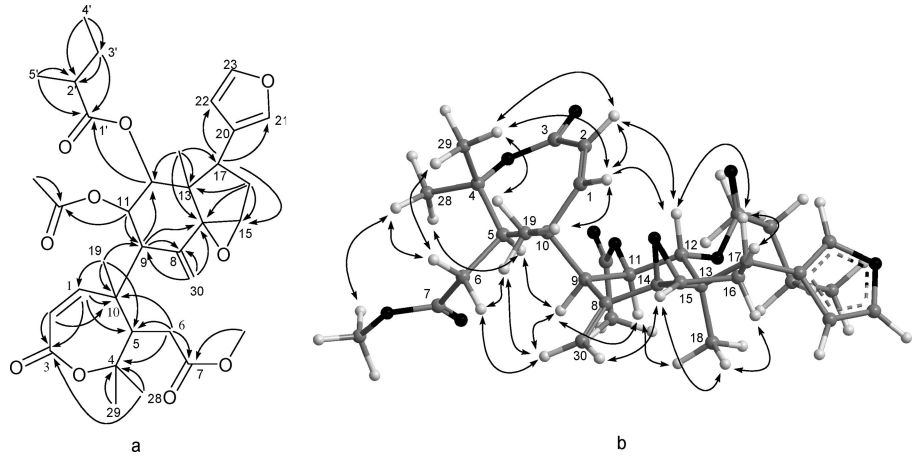

Figure 1. (a) Selected HMBC (H→C) correlations of **1**; (b) key ROESY (H↔H) correlations of **1**.

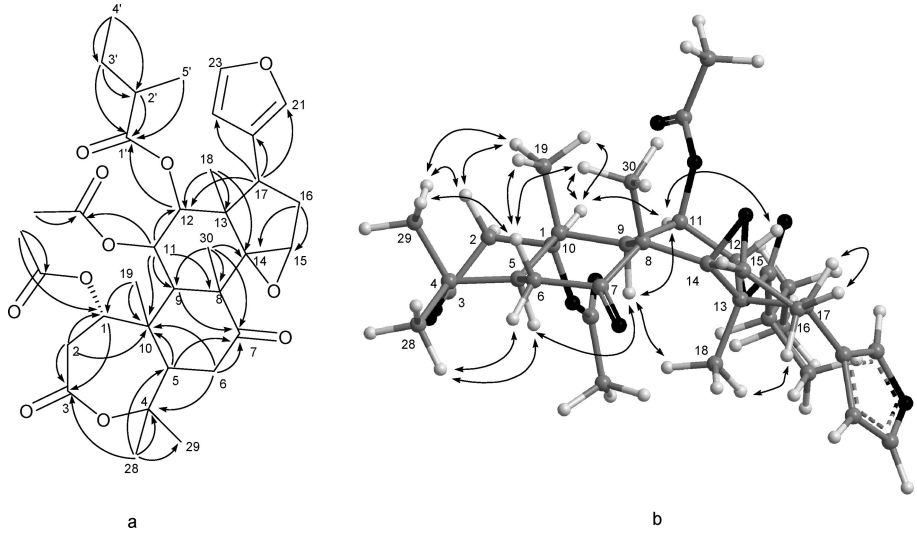

Figure 2. (a) Selected HMBC (H→C) correlations of **7**; (b) key ROESY (H↔H) correlations of **7**.

on a Shimadzu UV-2550 spectrophotometer. 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, and ESIMS was obtained on an Esquire 3000plus (Bruker Daltonics). Si gel (200–300 mesh) and Si gel H (Qingdao Haiyang Chemical Co. Ltd.), C18 reverse-phased Si gel (150–200 mesh, Merck), MCI gel (CHP20P, 75–150 μm, Mitsubishi Chemical Industries Ltd.), and Sephadex LH-20 gel (Amersham Biosciences) were used for column chromatography. Precoated Si gel GF254 plates (Qingdao Marine Chemical Plant, Qingdao, China) were used for TLC. All solvents used were of analytical grade (Shanghai Chemical Plant, Shanghai, China).

HPLC-MS was carried out on an Agilent Lcmsd vl mass spectrometer with an Agilent 1100 Series HPLC system, and the HPLC column was a XTerra MS reversed-phase C18 Si gel (2.1 × 50 mm, 5.0 μm). The mobile phase was 10–95% CH_3CN in H_2O (10 mmol of NH_4HCO_3) with a flow rate of 1.1 mL/min, and the column chamber was kept at ca. 50 °C for analysis of all compounds.

Plant Material. The twigs and leaves of *Amoora tsangii* were collected from Hainan Island of China in February 2004 and authenticated by Prof. Shi-Man Huang, Department of Biology, Hannan University of China. A voucher specimen has been deposited in Shanghai Institute of Materia Medica, Chinese Academy of Sciences (accession number AMTA-tzzf-02Y).

Extraction and Isolation. The air-dried powder of twigs and leaves of *A. tsangii* (9 kg) was extracted three times with 95% EtOH at room temperature to provide an extract (800 g), which was partitioned between EtOAc and H_2O to give an EtOAc-soluble fraction (165 g). Fractionation of the EtOAc-soluble fraction on a column of MCI gel (MeOH/H_2O, 40/60 → 90/10, v/v) afforded three fractions, 1–3. Fraction 2 (28 g) was chromatographed on a Si gel column eluted with a mixture of petroleum ether/acetone (25:1 to 100% acetone, v/v) in gradient to give seven major fractions, 2a−2g. Fraction 2a (283 mg) was separated on a Si gel column (petroleum ether/EtOAc, 2:1, v/v) to obtain a major compound, which was purified by column chromatography (RP-18 Si gel; MeOH/H_2O, 75/25, v/v) to give 11β-hydroxy-1β,8α-aromadendrene (9 mg). Fraction 2b (2.3 g) was subjected to Si gel column chromatography (petroleum ether/acetone, 10:1, v/v) to give two major subfractions, each of which was purified successively on a reversed-phase Si gel column (MeOH/H_2O, 70/30, v/v) and Si gel column (petroleum ether/EtOAc, 2:1, v/v) to obtain **1** (40 mg) and eudesm-4(15)-ene-1β,6α-diol (7 mg), respectively. Fraction 2d (2.5 g) was separated on a Si gel column (petroleum ether/EtOAc, 2:1, v/v) to afford three major fractions, 2d1 (140 mg), 2d2 (430 mg), and 2d3 (300 mg). Fractions 2d1–2d3 were respectively purified by column chromatography over a reversed-phase Si gel column (MeOH/H_2O, 70/30, v/v) and then a Si gel column (petroleum ether/2-propanol, 10:1, v/v) to afford **2** (14 mg), **3** (6 mg), and **4** (9 mg). Fraction 2e (1.2 g) was separated by column chromatography over a Si gel column (petroleum ether/2-propanol, 10:1, v/v) to give three major subfractions, and each of them was then purified on a reversed-phase RP-18 Si gel column (MeOH/H_2O, 70/30, v/v) to yield **6** (4 mg), **5** (9 mg), and **7** (229 mg), respectively. Fraction 2f (330 mg) was subjected to a Si gel column (petroleum ether/EtOAc, 2:1, v/v) to give two subfractions, 2f1 and 2f2. Fraction 2f1 was separated by an RP-18 reversed-phase Si gel column (MeOH/H_2O, 70/30, v/v) to give two major compounds, each of which was then chromatographed on a column of Sephadex LH-20 (MeOH) to give DM-3 (6 mg) and DM-4 (9 mg), respectively. Fraction 2f2 was dealt with in the same way as fraction 2f1 to obtain two

compounds, 10-hydroxy-15-oxo-α-cadinol (5 mg) and octahydro-4-hydroxy-3α-methyl-7-methylene-α-(1-methylethyl)-1*H*-indene-1-methanol (5 mg).

Amotsangin A (1): white powder; $[\alpha]^{21}_D$ +108.0 (*c* 0.15, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 215.8 (3.14), 203.4 (3.13), 201.0 (3.13) nm; IR (KBr) υ_{max} 3435 (w br, water), 3128, 2958, 2933, 1747, 1728, 1699, 1460, 1373, 1219, 1124, 1038, 824, 606 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 100 MHz) see Table 2; positive-ion ESIMS *m/z*635.4 $[M + Na]^+$, 1247.7 $[2\ M + Na]^+$; EIMS *m/z* 612 (2), 552 (2), 387 (4), 225 (100), 207 (36), 135 (31), 107 (35), 57 (60); HREIMS *m/z* 612.2947 (calcd for $C_{34}H_{44}O_{10}$, 612.2934).

Amotsangin B (2): white powder; $[\alpha]^{21}_D$ +110.0 (*c* 0.11, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 215.0 (3.24), 198.6 (3.23) nm; IR (KBr) υ_{max} 3446 (water), 2974, 1747, 1734, 1699, 1373, 1221, 1126, 1040, 824, 604 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 100 MHz) see Table 2; positive-ion ESIMS *m/z* 621.3 $[M + Na]^+$, 1219.5 $[2\ M + Na]^+$; EIMS *m/z* 598 (1), 582 (16), 421 (60), 225 (100), 207 (42), 135 (42), 107 (55), 57 (42); HREIMS *m/z* 598.2796 (calcd for $C_{33}H_{42}O_{10}$, 598.2778).

Amotsangin C (3): white powder; $[\alpha]^{21}_D$ +131.0 (*c* 0.10, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 215.2 (3.06), 198.2 (3.06) nm; IR (KBr) υ_{max} 3444 (OH), 2962, 2933, 1745, 1701, 1373, 1277, 1252, 1221, 1128, 1039, 604 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 100 MHz) see Table 2; positive-ion ESIMS *m/z* 643.4 $[M + H]^+$, 1307.7 $[2\ M + Na]^+$; negative-ion ESIMS *m/z* 687.6 $[M + HCOOH - H]^-$; EIMS *m/z* 642 (5), 582 (4), 540 (8), 421 (60), 225 (100), 207 (41), 135 (35), 107 (59), 57 (16); HREIMS *m/z*642.3050 (calcd for $C_{35}H_{46}O_{11}$, 642.3040).

Amotsangin D (4): white powder; $[\alpha]^{21}_D$ +125.0 (*c* 0.12, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 216.0 (3.15), 200.4 (3.13), 198.8 (3.14) nm; IR (KBr) υ_{max} 3446 (water), 2987, 2955, 1749, 1701, 1371, 1223, 1128, 1026, 604 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 100 MHz) see Table 2; positive-ion ESIMS *m/z* 585.2 $[M + H]^+$, 1191.5 $[2\ M + Na]^+$; EIMS *m/z* 584 (7), 451 (12), 225 (100), 207 (37), 135 (36), 107 (49), 97 (36), 57 (52); HREIMS *m/z*584.2620 (calcd for $C_{32}H_{40}O_{10}$, 584.2621).

Amotsangin E (5): white powder; $[\alpha]^{21}_D$ +100.0 (*c* 0.11, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 224.8 (3.23), 199.4 (3.40) nm; IR (KBr) υ_{max} 3446 (water), 2955, 2989, 1749, 1728, 1701, 1373, 1275, 1219, 1128, 1028, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 100 MHz) see Table 2; positive-ion ESIMS *m/z* 655.2 $[M + Na]^+$, 1288.3 $[2\ M + Na + H]^+$; EIMS *m/z* 632 (1), 417 (6), 225 (10), 105 (100), 77 (15); HREIMS *m/z* 632.2605 (calcd for $C_{36}H_{40}O_{10}$, 632.2621).

Amotsangin F (6): white powder; $[\alpha]^{21}_D$ +29.0 (*c* 0.11, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 226.2 (3.14), 199.4 (3.36) nm; IR (KBr) υ_{max} 3433 (moderate to strong, water), 2926, 2852, 1734, 1450, 1383, 1273, 1121, 1028, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 100 MHz) see Table 2; positive-ion ESIMS *m/z* 641.3 $[M + Na]^+$, 1259.5 $[2\ M + Na]^+$; negative-ion ESIMS *m/z* 663.5 $[M + HCOOH - H]^-$; EIMS *m/z* 618 (1), 417 (4), 225 (11), 105 (100), 77 (16); HREIMS *m/z* 618.2482 (calcd for $C_{35}H_{38}O_{10}$, 618.2465).

Chemical Transformation of 6 to 5. Compound **6** (1 mg) was dissolved in 3 mL of MeOH, and then 0.5 mL of aqueous $NaHCO_3$ (5%, wt/v) was added. The mixture was stirred for 30 min at room temperature. Water (2 mL) was then added, and the mixture was extracted with EtOAc (3 × 1 mL) to obtain the crude product. After the removal of the EtOAc 0.4 mL of dried pyridine and 0.4 mL of Ac_2O were added, and the mixture was then kept overnight at room temperature. After workup, the residue was purified by TLC ($CHCl_3$/MeOH, 20:1, v/v) to yield **5** (0.33 mg, 32.6%).

Amotsangin G (7): white powder; $[\alpha]^{21}_D$ −17.0 (*c* 0.13, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 211.0 (2.71), 197.4 (2.65) nm; IR (KBr) ν_{max} 3445 (moderate br, water), 2976, 1755, 1720, 1462, 1373, 1229, 1119, 1026, 604 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) see Table 1; ^{13}C NMR ($CDCl_3$, 100 MHz) see Table 2; positive-ion ESIMS *m/z*643.4 $[M + H]^+$, 665.3 $[M + Na]^+$; EIMS *m/z* 642 (40), 582 (35), 481 (76), 421 (100), 225 (100), 107 (26), 85 (29), 57 (100); HREIMS *m/z* 642.3033 (calcd for $C_{35}H_{46}O_{11}$, 642.3040).

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Supporting Information Available: Selected HMBC correlations of amotsangins B−E (**2**–**5**); HPLC-ESIMS monitoring of the transformation of compound **6** to **5**; IR, EIMS, and ^1H and ^{13}C NMR spectra of amotsangins A−G (**1**–**7**); 2D NMR spectra of amotsangins A−E (**1**–**5**) and amotsangin G (**7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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