Mesendanins A−J, Limonoids from the Leaves and Twigs of *Melia toosendan*

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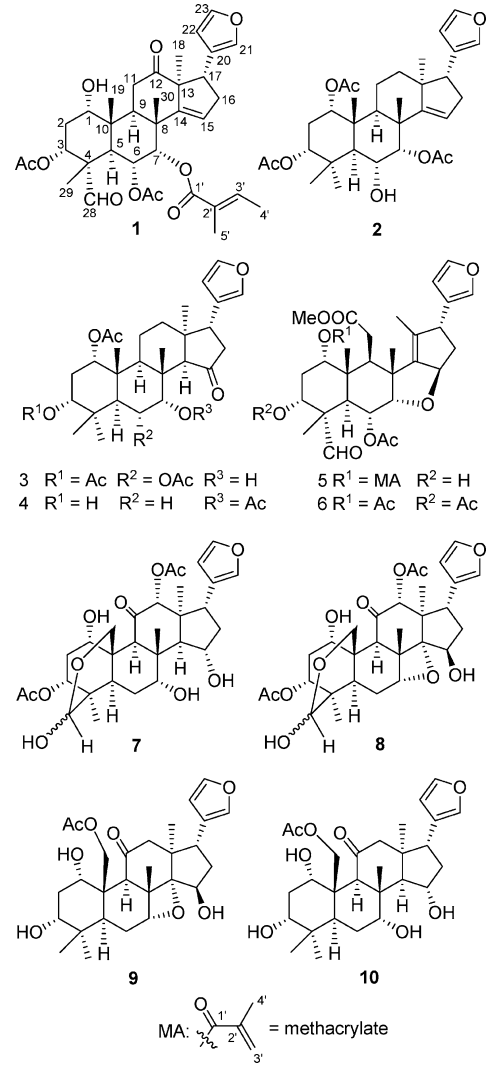
Ten new limonoids, namely, mesendanins A−J (**1**−**10**), together with 14 known compounds, have been isolated from the leaves and twigs of *Melia toosendan*. Their structures were established on the basis of spectroscopic data analysis.

Limonoids are a class of highly oxygenated nortriterpenoids with complex and diverse structures and are typical metabolites of plants in the family Meliaceae.[1] Previous chemical investigations on *Melia* species have led to the isolation of a series of limonoids and other triterpenes,[2] of which some exhibit insect antifeedant and/or cytotoxic activities.[2a−d,g] The plant *Melia toosendan* Sieb. et Zucc. (Meliaceae) grows mainly in southwest mainland China,[3] and the chemical constituents of this species have been extensively investigated previously.[2a−f] As part of our continuing chemical investigations on the constituents of plants of the family Meliaceae, 10 new limonoids (**1**−**10**) and 14 known compounds have been isolated from the leaves and twigs of *M. toosendan*, collected from Yunnan Province. We report herein the details of the isolation and structure elucidation of these new compounds.

Results and Discussion

Compound **1**, a white, amorphous powder, gave a molecular formula of $C_{35}H_{44}O_{10}$, as established on the basis of HRESIMS, with 14 degrees of unsaturation. The IR absorption bands showed the presence of hydroxy (3446 cm^{-1}) and carbonyl (1751 and 1713 cm^{-1}) groups. The NMR data (Tables 1 and 2) exhibited resonances assignable to an aldehyde group (δ_H 9.40, s; δ_C 203.5), a keto carbonyl (δ_C 213.0), a tiglyl group, and two acetyl groups (δ_H 2.05 and 1.84, s, each 3H), together with a typical β-substituted furan ring and a trisubstituted double bond (δ_H 5.56, t, J = 2.4 Hz; δ_C 153.9 and 123.1). These functionalities accounted for 10 out of the 14 degrees of unsaturation present, and the remaining four thus required a tetracyclic core for **1**. The aforementioned data suggested that **1** is a limonoid based on a sendanal carbon skeleton, as isolated from the title plant previously,[4] with the differences from previously known analogues being due to the substitution patterns of their functional groups. In the HMBC spectrum (Figure 1A) of **1**, the keto carbonyl was placed at C-12 from the correlations from H-11, H-17, and Me-18 to C-12. Two acetoxy groups were attached to C-3 and C-6 on the basis of HMBC correlations from H-3 and H-6 to each corresponding carbonyl of the acetyls, respectively. The presence of a tigloyloxy group was confirmed and located at C-7 from the HMBC correlations of H-7/C-1′, H-3′/C-1′, and Me-5′/C-1′. The aldehyde group was located at C-4 as a result of the HMBC correlations between H-28/C-4, H-28/C-29, and H-5/C-28. The carbon resonance at δ_C 70.2 was assigned to C-1, a carbon bearing a hydroxy group, due to the HMBC correlations of H-2α/C-1, H-3/C-1, H-5/C-1, H-9/C-1, Me-19/C-1, H-1/C-3, H-1/C-5, and H-1/C-10. This inference was supported by the ^{1}H NMR chemical shift of H-1 at δ_H 3.57 (m).

The relative configuration of **1** was assigned from the ROESY spectrum and also by comparing its NMR data with those of sendanal.[4] From the ROESY spectrum (Figure 1B), H-6 and H-7 were assigned with a β-configuration as a result of the correlations between H-6/Me-19, H-6/Me-29, H-6/Me-30, H-7/H-15, and H-7/Me-30. The other stereocenters of **1** were identical to those of sendanal. Therefore, the structure of **1** (mesendanin A) was assigned as depicted.



Compound **2** was found to possess a molecular formula of $C_{32}H_{44}O_8$, from the sodiated molecular ion at m/z 579.2932 [M + Na]$^+$ in the HRESIMS. The IR absorption bands showed the presence of hydroxy (3446 cm^{-1}) and carbonyl (1751 and 1713 cm^{-1}) groups. The NMR data of **2** indicated a close similarity to analogous data for 14,15-deoxyhavanensin triacetate,[5] with the only difference being due to the presence of an additional hydroxy group at C-6 (δ_C 68.8), which was fixed by the HMBC correlations of H-5/C-6, H-7/C-6, H-6/C-5, and H-6/C-7 (Figure S1, Supporting

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Table 1. ^{1}H NMR Spectroscopic Data of Compounds **1**−**5**[a]

	1	**2**	**3**	**4**	**5**
position	(mult., *J* in Hz)	(mult., *J* in Hz)	(mult., *J* in Hz)	(mult., *J* in Hz)	(mult., *J* in Hz)
1	3.57 (m)	4.55 (t, 3.5)	4.76 (t, 3.2)	5.03 (brs)	5.06 (t, 2.8)
2α	2.02 (dt, 16.4, 2.7)	1.95 (dt, 16.3, 3.5)	1.96 (dt, 16.6, 3.2)	1.93 (m)	2.06 (m)
2*β*	2.29 (m)	2.24 (dt, 16.3, 3.5)	2.22 (dt, 16.6, 3.2)	2.29 (dt, 16.3, 3.1)	2.22 (m)
3	5.03 (t, 2.7)	4.70 (t, 3.5)	4.62 (t, 3.2)	3.37 (brs)	3.75 (brs)
5	3.45 (d, 12.1)	2.27 (d, 11.5)	2.74 (d, 12.0)	2.02 (d, 2.6)	3.66 (d, 11.8)
6α	5.40 (dd, 12.1, 2.2)	4.37 (ddd, 11.5, 5.8, 2.5)	5.57 (dd, 12.0, 1.8)	1.79 (m)	5.28 (dd, 11.8, 2.7)
6*β*				1.89 (m)	
7	5.62 (d, 2.2)	5.32 (d, 2.5)	3.73 (d, 1.8)	4.89 (brs)	4.01 (d, 2.7)
9	3.54 (m)	2.53 (dd, 11.5, 7.1)	1.77 (brd, 10.3)	1.59 (m)	2.83 (dd, 8.5, 2.9)
11α	2.33 (d, 18.7)	1.29 (m)	1.23 (m, 2H)	1.50 (m, 2H)	2.29 (d, 8.2)
11*β*	2.66 (dd, 18.7, 5.9)	1.52 (m)			2.33 (d, 8.5)
12α		1.80 (m)	1.04 (m)	1.00 (m)	
12*β*		1.54 (m)	1.91 (m)	1.94 (m)	
14			2.92 (s)	2.42 (s)	
15	5.56 (t, 2.4)	5.40 (dd, 3.2, 1.5)			5.46 (m)
16α	2.43 (m, 2H)	2.41 (dd, 10.8, 1.5)	2.50 (brd, 9.9, 2H)	2.47 (brd, 10.3, 2H)	2.08 (m)
16*β*		2.37 (dd, 7.5, 3.2)			2.24 (m)
17	3.46 (m)	2.78 (dd, 10.8, 7.5)	3.43 (t, 9.9)	3.44 (t, 10.3)	3.63 (brs)
18	1.06 (s, 3H)	0.79 (s, 3H)	0.76 (s, 3H)	0.74 (s, 3H)	1.63 (d, 1.5, 3H)
19	1.07 (s, 3H)	1.05 (s, 3H)	1.05 (s, 3H)	0.96 (s, 3H)	1.07 (s, 3H)
21	7.31 (s)	7.23 (t, 0.7)	7.24 (s)	7.24 (s)	7.23 (s)
22	6.52 (s)	6.26 (dd, 1.7, 0.7)	6.25 (d, 0.9)	6.25 (s)	6.27 (t, 1.3)
23	7.40 (t, 1.5)	7.38 (t, 1.7)	7.38 (t, 1.6)	7.38 (t, 1.4)	7.32 (t, 1.3)
28	9.40 (s)	1.12 (s, 3H)	1.00 (s, 3H)	0.93 (s, 3H)	9.71 (s)
29	1.07 (s, 3H)	1.11 (s, 3H)	0.95 (s, 3H)	0.83 (s, 3H)	0.98 (s, 3H)
30	1.24 (s, 3H)	1.23 (s, 3H)	1.14 (s, 3H)	1.09 (s, 3H)	1.40 (s, 3H)
OAc-1		2.02 (s, 3H)	2.03 (s, 3H)	2.13 (s, 3H)	
OAc-3	2.05 (s, 3H)	2.03 (s, 3H)	2.05 (s, 3H)		
OAc-6	1.84 (s, 3H)		2.11 (s, 3H)		1.96 (s, 3H)
OAc-7		2.09 (s, 3H)		2.11 (s, 3H)	
OMe					3.24 (s, 3H)
3′	6.95 (m)				a 5.67 (s)
					b 6.18 (s)
4′	1.83 (d, 8.4, 3H)				2.05 (s, 3H)
5′	1.90 (s, 3H)				

[a] Data were measured in $CDCl_3$ at 400 MHz.

Information). As a result, the H-6 signal shifted downfield to δ_H 4.37 (ddd, J = 11.5, 5.8, 2.5 Hz). The relative configuration of **2** was established by a ROESY experiment (Figure S1, Supporting Information), in which OH-6 was assigned as α-oriented by the correlations of H-6/Me-19, Me-29, and Me-30, while the other stereocenters of **2** (mesendanin B) were determined as identical to those of 14,15-deoxyhavanensin triacetate, on the basis of their ROESY spectra and their similar NMR patterns. Thus, compound **2** was determined as 6α-hydroxy-14,15-deoxyhavanensin triacetate.

Compound **3** (mesendanin C) showed a molecular formula of $C_{32}H_{44}O_9$ by HRESIMS. On comparing the NMR data (Tables 1 and 2) of **3** with those of **2**, it was evident that they share similar structures, with the major differences being the presence of a keto group (δ_C 221.3) and the absence of a Δ^{14} double bond in **3**. The keto group was assigned to C-15 by the HMBC correlations of H-14/C-15 and H_2-16/C-15. Three acetoxy groups were located at C-1, C-3, and C-6 on the basis of HMBC correlations from H-1, H-3, and H-6 to each corresponding carbonyl of the acetyls, respectively. The only hydroxy group present was attached to C-7 according to the HMBC correlations of H-7/C-5, C-6, C-8, and C-9, H-6/C-7, H-14/C-7, and Me-30/C-7 (Figure S1, Supporting Information). The relative configuration of **3** was assigned as being identical with that of **2** by comparing their NMR data and the coupling patterns of the relevant protons (Tables 1 and 2).

Compound **4** (mesendanin D, $C_{30}H_{42}O_7$) showed one less acetoxy group (58 mass units) than **3**. The NMR data (Tables 1 and 2) of **4** displayed many similarities to those of **3**, with the differences being due to the acetylation patterns. Two acetoxy groups were located at C-1 and C-7 from the HMBC correlations between H-1/H-7 and each corresponding acetyl carbonyl, respectively. When compared with compound **3**, the H-3 signal was shifted upfield to δ_H 3.37 (brs), suggesting that a hydroxy group is located at C-3 (δ_C 75.9). This was confirmed by the HMBC correlations of H-1/C-3, H-2α/C-3, Me-28/C-3, and Me-29/C-3 (Figure S1, Supporting Information). The relative configuration of **4** was assigned as depicted by the ROESY spectrum (Figure S1, Supporting Information) and on comparing the NMR data with those of **3**.

Compound **5** (mesendanin E) gave a molecular formula of $C_{33}H_{42}O_{10}$, as established on the basis of the HRESIMS at *m*/*z* 621.2680 $[M + Na]^+$ (calcd for $C_{33}H_{42}O_{10}Na$, 621.2676). Comparison of the NMR data of **5** (Tables 1 and 2) with those of salannal[6] indicated that they are structural analogues, and the only difference was the presence of a methacrylate group [δ_H (5.67, s, 1H; 6.18, s, 1H; 2.05, s, 3H) and δ_C (165.6, 135.8, 126.6, and 18.4)] at C-1 of **5** instead of the tigloyloxy group at C-1 of salannal. This was confirmed by the HMBC correlations of H-1/C-1′, H_2-3′/C-1′, and Me-4′/C-1′ (Figure S2, Supporting Information). The relative configuration of **5** was determined as being the same as that of salannal by a ROESY experiment (Figure S2, Supporting Information). Thus, compound **5** was assigned as 1-methacrylsalannal.

The IR spectrum of **6** (mesendanin F, $C_{33}H_{42}O_{11}$) displayed absorption bands at 3458 (OH) and 1736 (ester carbonyl) cm^{-1}. Its NMR data (Tables 2 and 3) showed many similarities to those of 3-*O*-acetylohchinolal,[2b] but differences occurred in their acylation patterns. The presence of an additional acetoxy group (δ_H 2.01, s, 3H; δ_C 169.1) at C-1 of **6** was assigned, replacing the tigloyloxy group of 3-*O*-acetylohchinolal. This was confirmed by the key HMBC correlation observed between H-1 and the carbonyl of OAc-1 (Figure S2, Supporting Information). The relative configuration of **6** was determined as being the same as that of 3-*O*-acetylohchinolal by a ROESY experiment (Figure S2, Supporting Information). Thus, compound **6** was assigned as 1,3-diacetylsalannal.

Compound **7** (mesendanin G), a white, amorphous powder, was obtained as a mixture of C-29 epimers, with the ratio of epimers

Table 2. ^{13}C NMR Spectroscopic Data of Compounds **1**−**10**

carbon	**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]	**7**[b]	**8**[b]	**9**[b]	**10**[b]
1	70.2	72.6	71.9	74.2	72.6	70.4	71.4	70.3	69.9	71.0
2	28.1	25.8	25.8	28.3	28.3	25.5	37.6	37.9	31.1	31.3
3	76.5	77.4	77.5	75.9	74.8	75.1	75.2	75.1	78.5	78.4
4	47.4	36.5	36.1	37.3	48.9	47.5	41.4	42.0	38.9	39.0
5	35.6	43.2	39.3	35.6	34.9	35.8	30.0	33.4	39.9	36.0
6	69.0	68.8	70.9	21.6	68.8	69.0	23.6	24.1	25.1	25.1
7	73.9	80.3	73.4	73.4	85.8	85.8	72.5	84.3	83.9	73.3
8	42.7	42.8	41.6	40.6	46.9	47.0	40.1	45.4	47.9	42.8
9	37.4	35.1	42.5	44.5	39.5	39.3	52.5	53.6	56.9	54.6
10	41.5	41.5	42.4	40.8	41.9	41.4	44.4	40.8	46.4	51.4
11	34.4	15.9	16.7	16.8	30.1	29.8	208.2	205.6	210.2	215.9
12	213.0	32.8	34.3	34.4	172.5	172.9	83.5	81.7	53.6	53.9
13	61.3	47.2	41.9	41.9	136.1	135.6	45.1	51.2	47.5	43.2
14	153.9	158.7	61.0	61.4	145.8	145.9	62.8	98.9	99.7	62.5
15	123.1	119.6	221.3	219.2	87.5	87.5	72.3	76.7	77.5	72.4
16	33.9	34.2	43.3	43.1	41.0	41.0	41.5	39.8	38.6	40.1
17	42.6	51.3	37.6	37.4	49.5	49.5	46.9	44.5	46.6	47.4
18	18.8	20.1	27.5	27.9	13.0	12.8	23.9	16.7	22.3	28.3
19	17.0	17.1	17.9	16.6	16.8	17.0	64.8	65.7	63.3	64.8
20	124.4	124.5	122.7	122.7	126.8	126.9	125.3	126.7	126.5	125.2
21	140.8	139.6	140.1	140.1	138.8	139.0	141.6	141.9	141.4	141.3
22	112.4	111.0	110.7	110.7	110.6	110.7	112.7	113.1	112.6	112.0
23	142.4	142.6	142.9	142.9	143.0	143.0	144.1	144.4	144.7	144.6
28	203.5	30.3	30.5	28.2	206.9	204.4	20.6	19.2	29.1	29.5
29	13.7	22.1	22.2	21.7	13.8	13.9	97.7	97.1/97.8	21.9	22.6
30	26.0	27.4	18.3	18.1	17.0	17.0	23.1	18.7	18.2	20.3
OAc-1		170.0	170.0	169.2		169.1				
		21.2	21.2	21.4		20.9				
OAc-3	168.1	170.2	170.3			170.2	173.2	173.4		
	20.8	21.2	21.2			21.3	21.9	21.9		
OAc-6	169.7		169.8		170.3	170.4				
	20.5		21.9		20.9	20.9				
OAc-7		171.9		169.6						
		21.3		21.2						
OAc-12							172.8	172.6		
							21.2	21.4		
OAc-19									173.8	172.8
									21.7	21.1
OMe					51.6	51.7				
1′	166.6				165.6					
2′	128.2				135.8					
3′	138.0				126.6					
4′	14.6				18.4					
5′	12.1									

[a] Data were measured in $CDCl_3$ at 400 MHz. [b] Data were measured in CD_3OD at 400 MHz.

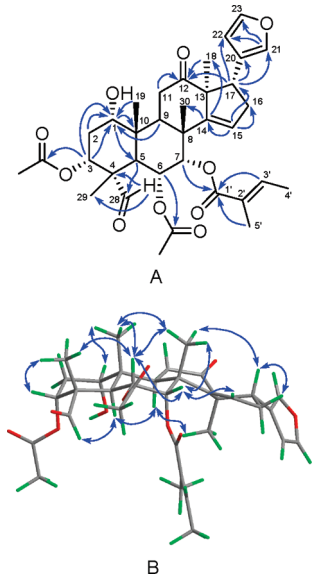

Figure 1. Selected HMBC (H→C) and ROESY (H↔H) correlations of **1**.

being about 5:2, as determined by the peak area from the HPLC. Its molecular formula was determined to be $C_{30}H_{40}O_{11}$, on the basis of HRESIMS. The NMR data of **7** (Tables 2 and 3) showed close similarities to those of iso-chuanliansu,[7] with differences being due to the presence of an additional hydroxy group with the concomitant absence of a keto group, suggesting that **7** is a reduced product of iso-chuanliansu. The hydroxy group was located at C-15 from the chemical shifts of H-15 at δ_H 4.70 (1H, m) and C-15 at δ_C 72.3 and the HMBC correlations of H-15/C-8, H-15/C-14, H-14/C-15, and H_2-16/C-15 (Figure 2A). The relative configuration of **7** was established by a ROESY experiment (Figure 2B), in which key correlations of H-15/H-7, H-15/H-17, and H-15/H-30 revealed that OH-15 is α-oriented. Therefore, the structure of **7** was assigned as 15α-hydroxy-iso-chuanliansu.

Compound **8** (mesendanin H) was also obtained as a mixture of C-29 epimers, with the ratio of epimers being about 5:2, again as determined by peak area in the HPLC. It gave a molecular formula of $C_{30}H_{38}O_{11}$, as determined by HRESIMS. The NMR data (Tables 2 and 3) of **8** resembled closely those of 7,14-epoxyazedarachin B[8] except for the presence of an additional acetoxy group and the absence of the isobutyrate group. The acetoxy group was placed at C-12 from HMBC correlation between H-12 and the carbonyl carbon of OAc-12 (Figure S2, Supporting Information). The relative configuration of **8** was assigned by the ROESY spectrum and is consistent with that of 7,14-epoxyazedarachin B (Figure S2, Supporting Information). Thus, the structure of **8** was assigned as 7,14-epoxychuanliansu.

Table 3. ^{1}H NMR Spectroscopic Data of Compounds **6**−**10**

	6[a]	**7**[b]	**8**[b]	**9**[b]	**10**[b]
position	(mult., *J* in Hz)	(mult., *J* in Hz)	(mult., *J* in Hz)	(mult., *J* in Hz)	(mult., *J* in Hz)
1	4.80 (m)	4.71 (m)	4.60 (m)	4.56 (brs)	4.52 (t, 2.7)
2α	2.17 (m, 2H)	1.84 (brd, 15.7)	1.80 (m)	1.91 (m)	1.93 (m)
2*β*		2.72 (m)	2.71 (m)	2.31 (m)	2.33 (m)
3	4.80 (m)	5.19 (brd, 4.1)	5.19 (brd, 4.1)	3.48 (brs)	3.42 (t, 2.7)
5	3.65 (d, 12.2)	2.75 (m)	2.67 (m)	2.40 (m)	2.50 (dd, 13.5, 2.8)
6α	5.22 (dd, 12.2, 2.7)	2.13 (m)	1.83 (m, 2H)	1.84 (m)	1.76 (dt, 14.4, 2.8)
6*β*		1.75 (m)		1.77 (m)	1.97 (m)
7	4.03 (d, 2.7)	3.78 (brs)	5.01 (t, 2.4)	4.96 (brs)	3.77 (t, 2.8)
9	2.88 (dd, 8.3, 2.7)	3.34 (s)	4.60 (s)	4.34 (s)	2.70 (s)
11	2.24 (m, 2H)				
12α		5.52 (s)	5.28 (s)	2.35 (m, 2H)	2.06 (d, 13.8)
12*β*					3.05 (d, 13.8)
14		2.54 (d, 7.4)			2.11 (m)
15	5.58 (m)	4.70 (m)	4.80 (m)	4.77 (m)	4.43 (m)
16α	2.09 (m)	2.09 (m)	1.90 (m, 2H)	1.91 (m, 2H)	2.29 (m)
16*β*	2.28 (m)	2.17 (m)			2.11 (m)
17	3.65 (brs)	2.89 (dd, 13.6, 5.3)	3.30 (m)	3.21 (dd, 10.9, 5.6)	2.92 (dd, 14.0, 5.5)
18	1.63 (d, 1.3, 3H)	1.03 (s, 3H)	1.11 (s, 3H)	0.95 (s, 3H)	0.78 (s, 3H)
19a	1.04 (s, 3H)	3.87 (d, 12.1)	3.79 (dd, 11.7, 1.3)	3.80 (d, 12.4)	4.74 (d, 12.5)
19b		4.14 (d, 12.1)	4.07 (d, 11.7)	4.76 (d, 12.4)	4.07 (d, 12.5)
21	7.27 (s)	7.22 (s)	7.21 (s)	7.28 (s)	7.32 (s)
22	6.33 (d, 1.2)	6.25 (s)	6.22 (t, 0.8)	6.28 (s)	6.31 (d, 1.0)
23	7.34 (t, 1.2)	7.40 (s)	7.41 (s)	7.43 (s)	7.42 (t, 1.6)
28	9.62 (s)	0.84 (s, 3H)	0.81 (s, 3H)	0.95 (s, 3H)	0.99 (s, 3H)
29	1.04 (s, 3H)	4.86 (s)/4.65 (s)	4.83 (s)/4.65 (s)	0.84 (s, 3H)	0.82 (s, 3H)
30	1.39 (s, 3H)	1.26 (s, 3H)	1.36 (s, 3H)	1.36 (s, 3H)	1.37 (s, 3H)
OAc-1	2.01 (s, 3H)				
OAc-3	2.13 (s, 3H)	2.05 (s, 3H)	2.04 (s, 3H)		
OAc-6	1.96 (s, 3H)				
OAc-12		1.90 (s, 3H)	2.13 (s, 3H)		
OAc-19				2.00 (s, 3H)	1.96 (s, 3H)
OMe	3.31 (s, 3H)				

[a] Data were measured in $CDCl_3$ at 400 MHz. [b] Data were measured in CD_3OD at 400 MHz.

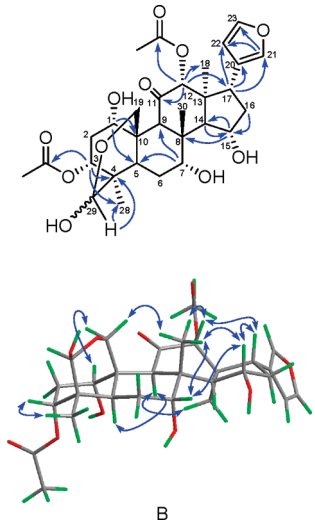

Figure 2. Selected HMBC (H→C) and ROESY (H↔H) correlations of **7**.

Compound **8** possesses an oxetane ring, which has been reported only once among the limonoids.[8]

As depicted in Figure 3, the biogenetic formation of compound **8** may be correlated with the coexisting chuanliansu, which could undergo an intramolecular nucleophilic attack of the C-7 hydroxy group at the C-14 position of the epoxide ring to give **8**.[8] The configuration of the oxetane ring and of the OH-15 group of **8** are coincident with the product of this proposed biosynthesis, further supporting its structural assignment.

Compound **9** (mesendanin I), a white, amorphous powder, was determined to have a molecular formula of $C_{28}H_{38}O_8$ by HRESIMS, exhibiting 10 degrees of unsaturation. Analysis of its NMR data

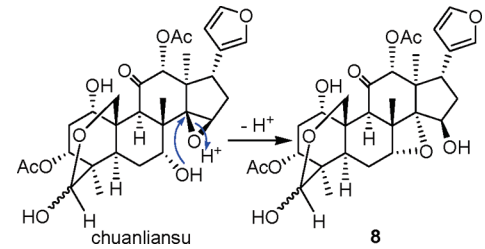

Figure 3. Plausible biosynthetic pathway for **8**.

(Tables 2 and 3) revealed that **9** shares a high structural similarity to **8**. The major difference is due to the presence of Me-28, with the concomitant absence of the C-28 hemiacetal group of **8**. In the HMBC spectrum (Figure 4A), the only acetoxy group could be attached to C-19 from the key correlation between H_2-19 and the carbonyl carbon of OAc-19, and three hydroxy groups were assigned to C-1, C-3, and C-15 from the chemical shifts of H-1, H-3, and H-15 (or C-1, C-3, and C-15) and the HMBC correlations of H-3/C-1, H_2-19/C-1, H-1/C-5, Me-28/C-3, Me-29/C-3, H-1/C-3, H-3/C-4 and C-5, H-16/C-15, H-17/C-15, and H-15/C-17. The relative configuration of **9** was established as shown on the basis of the ROESY spectrum (Figure 4B).

Compound **10** gave a molecular formula of $C_{28}H_{40}O_8$, as assigned by HRESIMS, requiring nine degrees of unsaturation. Detailed analysis of its NMR data (Tables 2 and 3) showed many similarities to **9**, suggesting that their structures are closely related. The differences found were the absence of an oxetane ring and with there being opposite stereochemistry at C-15 as compared with **9**. A keto group and an acetoxy group could be located at C-11 and C-19, from the HMBC correlations from H-9 and H-12 to C-11 (δ_C 215.9) and from H_2-19 to the carbonyl of OAc-19, respectively. Four hydroxy groups were assigned to C-1, C-3, C-7, and C-15 from their chemical shifts and the HMBC spectrum. In the latter,

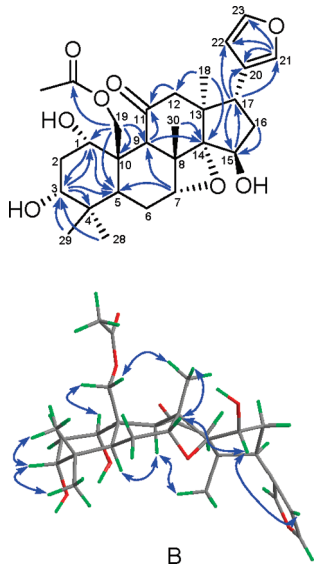

Figure 4. Selected HMBC (H→C) and ROESY (H↔H) correlations of **9**.

the key correlations from H-3 and H_2-19 to C-1 (δ_C 71.0) and from H-1 and Me-28 (29) to C-3 (δ_C 78.4) indicated the presence of hydroxy groups at C-1 and C-3, respectively. The HMBC correlations from H-5, H-9, and Me-30 to C-7 (δ_C 73.3) allowed the assignment of a hydroxy group at C-7, while the HMBC correlations from H-14, H-16, and H-17 to C-15 (δ_C 72.4) showed the presence of a OH-15 group (Figure S3, Supporting Information). The small *J* values of H-1, H-3, and H-7 revealed an equatorial orientation, and the hydroxy groups at C-1, C-3, and C-7 were thus assigned with α-configurations, as confirmed from the ROESY spectrum (Figure S3, Supporting Information). In the ROESY spectrum, H-15 showed correlations with H-7, H-17, and H-30, indicating that OH-15 is α-oriented. This was supported by the upfield shifted C-15 (Δ δ_C 5.1), as compared with compound **9**, due to the γ-gauche effects from H-14. Thus, the structure of **10** (mesendanin J) was elucidated as shown.

Fourteen known limonoids were also obtained and identified on the basis of their ^{1}H NMR, ^{13}C NMR, and EIMS data; these are amoorastabon,[9] chuanliansu,[7] 3-de-*O*-acetyl-3-*O*-[(*E*)-2-methylbut-2-enoyl]salannin,[10] 14,15-deoxyhavanensin-1,7-diacetate,[5] 1-desacetylnimbolinin B,[11] 12-hydroxyamoorastatone,[12] iso-chuanliansu,[7] isomeldenin,[13] 1-*O*-detigloyl-1-*O*-benzoylohchinolal,[2e] 12-*O*-methylvolkensin,[2c] salannal,[6] 1-tigloyl-3,20-diacetyl-11-methoxymeliacarpinin,[14] 3-tigloyl-1,20-acetyl-11-methoxymeliacarpinin,[14] and spirosendan.[15]

Experimental Section

General Experimental Procedures. Melting points were measured on an SGW X-4 melting instrument and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 polarimeter at room temperature. UV spectra were recorded on a Shimadzu UV-2550 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 577 IR spectrometer with KBr disks. NMR spectra were obtained on a Bruker AM-400 NMR spectrometer with TMS as internal standard. LRESIMS and HRESIMS were carried out on an Esquire 3000plus LC-MS instrument and a Bruker Daltonics micrOTOFQII mass spectrometer, respectively. All solvents used were of analytical grade (Shanghai Chemical Plant, Shanghai, People's Republic of China). Silica gel (300−400 mesh), C_{18} reversed-phase silica gel (250 mesh, Merck), and MCI gel (CHP20P, 75−150 μM, Mitsubishi Chemical Industries, Ltd.) were used for column chromatography, and precoated silica gel GF254 plates (Qingdao Marine Chemical Plant, Qingdao, People's Republic of China) were used for TLC.

Plant Material. The leaves and twigs of *Melia toosendan* were collected in June 2008, from Xishuangbanna, Mengla County, Yunnan Province, China, and were authenticated by Professor You-Kai Xu of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen (2008-Meltoo-1Y) has been deposited at the Shanghai Institute of Materia Medica.

Extraction and Isolation. The air-dried powdered leaves and twigs (5 kg) of *M. toosendan* were extracted with 95% EtOH (each 25 L, three days) at room temperature three times to give a dark green residue (340 g), which was then partitioned between EtOAc and water to give the EtOAc-soluble fraction E (200 g). Fraction E was subjected to passage over a MCI gel column eluted with MeOH−H_2O (3:7 to 9:1) to produce four fractions, F1−F4. F2 (20 g) was chromatographed over a silica gel column eluted with petroleum ether−acetone as a gradient (10:1 to 1:1) to afford four subfractions, F2a−F2d. F2c was subjected to separation over a reversed-phase C_{18} silica gel column, eluted with MeOH−H_2O (from 5:5 to 8:2), to give three major fractions, F2c1−F2c3. F2c1 was purified by silica gel column chromatography, eluted with $CHCl_3$−MeOH (100:1), to yield compound **7** (30 mg) and iso-chuanliansu (15 mg). F2c2 was purified by silica gel column chromatography, eluted with $CHCl_3$−MeOH (150:1), to yield **8** (10 mg) and chuanliansu (30 mg). F2c3 was separated initially by silica gel column chromatography, eluted with $CHCl_3$−MeOH (200:1), to obtain a major fraction, which was then purified using reversed-phase C_{18} silica gel column chromatography, eluted with MeOH−H_2O (6:4), to give **9** (13 mg), amoorastabon (10 mg), and 12-hydroxyamoorastatone (12 mg). Fraction F3 (22 g) was chromatographed on a silica gel column, eluted with petroleum ether−acetone in a gradient (20:1 to 1:1), to afford five subfractions (F3a−F3e). F3a was subjected to reversed-phase C_{18} silica gel column chromatography, eluted with MeOH−H_2O (6:4 to 9:1), to give two major fractions, F3a1 and F3a2. Both were separated in turn over a silica gel column, eluted with $CHCl_3$−MeOH (200:1). F3a1 gave **5** (10 mg), salannal (8 mg), and 1-*O*-detigloyl-1-*O*-benzoylohchinolal (13 mg), while F3a2 afforded **6** (15 mg) and 3-de-*O*-acetyl-3-*O*-[(*E*)-2-methylbut-2-enoyl]salannin (10 mg). Fraction F3b was subjected to reversed-phase C_{18} silica gel column chromatography, eluted with MeOH−H_2O (from 6:4 to 9:1), to obtain a major portion, which was purified by silica gel column chromatography, eluted with $CHCl_3$−MeOH (150:1), to give 12-*O*-methylvolkensin (7 mg) and 1-desacetylnimbolinin B (12 mg). F3c was subjected to reversed-phase C_{18} silica gel column chromatography, eluted with MeOH−H_2O (from 6:4 to 9:1), in turn, to give four major fractions, F3c1−F3c4. F3c1 and F3c3 were purified by silica gel column chromatography, eluted with $CHCl_3$−MeOH (200:1), and then by reversed-phase C_{18} silica gel column column chromatography, eluted with MeOH−H_2O (6:4). Fraction F3c1 gave **1** (8 mg) and 14,15-deoxyhavanensin-1,7-diacetate (7 mg), while F3c3 yielded **2** (12 mg) and isomeldenin (10 mg). F3e was subjected to reversed-phase C_{18} silica gel column chromatography, eluted with MeOH−H_2O (from 6:4 to 9:1), to give five major fractions, F3e1−F3e5. F3e1, F3e3, and F3e4 were purified by silica gel column chromatography, eluted with $CHCl_3$−MeOH (200:1), and then by reversed-phase C_{18} silica gel column chromatography, eluted with MeOH−H_2O (6:4), to give **3** (7 mg), **4** (10 mg), and**10** (15 mg), sequentially. F3e2 was separated by silica gel column chromatography, eluted with $CHCl_3$−MeOH (150:1), to afford spirosendan (5 mg), 3-tiglyl-1,20-acetyl-11-methoxymeliacarpinin (10 mg), and 1-tigloyl-3,20-diacetyl-11-methoxymeliacarpinin (11 mg).

Mesendanin A (1): white, amorphous powder; mp 130−132 °C; $[\alpha]^{22}_D$ −2.7 (*c* 0.30, MeOH); UV (MeOH) λ_{max} (log ε) 216 (4.18) nm; IR (KBr) ν_{max} 3446, 2978, 2931, 2850, 1751, 1713, 1651, 1375, 1256, 1225, 1032, 602 cm^{-1}; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; LRESIMS *m/z* 647.3 $[M + Na]^+$; HRESIMS *m/z* 647.2864 $[M + Na]^+$ (calcd for $C_{35}H_{44}O_{10}Na$, 647.2832).

Mesendanin B (2): white, amorphous powder; mp 88−90 °C; $[\alpha]^{22}_D$ −0.9 (*c* 0.33, MeOH); UV (MeOH) λ_{max} (log ε) 205 (4.08) nm; IR (KBr) ν_{max} 3448, 2937, 1732, 1450, 1375, 1261, 1051, 874, 600 cm^{-1}; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; LRESIMS *m/z* 579.3 $[M + Na]^+$; HRESIMS *m/z* 579.2932 $[M + Na]^+$ (calcd for $C_{32}H_{44}O_8Na$, 579.2934).

Mesendanin C (3): white, amorphous powder; mp 88−90 °C; $[\alpha]^{22}_D$ 0 (*c* 0.43, MeOH); UV (MeOH) λ_{max} (log ε) 206 (3.75) nm; IR (KBr) ν_{max} 3448, 2953, 1728, 1632, 1460, 1375, 1242, 1165, 1051 cm^{-1}; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; LRESIMS *m/z* 595.4 $[M + Na]^+$, 1167.8 $[2M + Na]^+$; HRESIMS *m/z* 595.2850 $[M + Na]^+$ (calcd for $C_{32}H_{44}O_9Na$ 595.2883).

Mesendanin D (4): white, amorphous powder; mp 158−160 °C; $[\alpha]^{22}_D$ −34.0 (*c* 0.10, MeOH); UV (MeOH) λ_{max} (log ε) 205 (3.74)

nm; IR (KBr) ν_{max} 3448, 2958, 1732, 1379, 1248, 1030, 874 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; LRESIMS *m/z* 537.4 $[M + Na]^+$, 1051.8 $[2M + Na]^+$; HRESIMS *m/z* 537.2795 $[M + Na]^+$ (calcd for $C_{30}H_{42}O_7Na$, 537.2828).

Mesendanin E (5): colorless oil; mp 180−182 °C; $[\alpha]^{22}_D$ +105.0 (*c* 0.16, MeOH); UV (MeOH) λ_{max} (log ε) 206 (4.30) nm; IR (KBr) ν_{max} 3481, 2955, 2872, 1724, 1635, 1437, 1375, 1232, 1032, 964, 872, 602 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; LRESIMS *m/z* 621.3 $[M + Na]^+$, 1219.5 $[2M + Na]^+$; HRESIMS *m/z* 621.2680 $[M + Na]^+$ (calcd for $C_{33}H_{42}O_{10}Na$, 621.2676).

Mesendanin F (6): colorless oil; mp 96−98 °C; $[\alpha]^{22}_D$ +70.6 (*c* 0.42, MeOH); UV (MeOH) λ_{max} (log ε) 204 (4.10) nm; IR (KBr) ν_{max} 3458, 2935, 2870, 1736, 1437, 1375, 1229, 1153, 1051, 1032, 874, 602 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 2 and 3; LRESIMS *m/z* 637.3 $[M + Na]^+$, 1251.4 $[2M + Na]^+$; HRESIMS *m/z* 637.2633 $[M + Na]^+$ (calcd for $C_{33}H_{42}O_{11}Na$ 637.2625).

Mesendanin G (7): white, amorphous powder; mp 200−202 °C; $[\alpha]^{22}_D$ −23.0 (*c* 0.17, MeOH); UV (MeOH) λ_{max} (log ε) 210 (3.80) nm; IR (KBr) ν_{max} 3435, 2960, 2887, 1716, 1643, 1502, 1431, 1375, 1252, 1032, 874, 602 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 2 and 3; LRESIMS *m/z* 599.3 $[M + Na]^+$, 1175.6 $[2M + Na]^+$; HRESIMS *m/z* 599.2496 $[M + Na]^+$ (calcd for $C_{30}H_{40}O_{11}Na$, 599.2468).

Mesendanin H (8): white, amorphous powder; mp 198−200 °C; $[\alpha]^{22}_D$ 0.0 (*c* 0.27, MeOH); UV (MeOH) λ_{max} (log ε) 210 (3.75) nm; IR (KBr) ν_{max} 3446, 2941, 1728, 1637, 1504, 1460, 1429, 1375, 1242, 1040, 874, 602 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 2 and 3; LRESIMS *m/z* 597.4 $[M + Na]^+$, 1171.7 $[2M + Na]^+$; HRESIMS *m/z* 597.2352 $[M + Na]^+$ (calcd for $C_{30}H_{38}O_{11}Na$, 597.2312).

Mesendanin I (9): white, amorphous powder; mp 210−212 °C; $[\alpha]^{22}_D$ −87.9 (*c* 0.45, MeOH); UV (MeOH) λ_{max} (log ε) 210 (3.76) nm; IR (KBr) ν_{max} 3489, 3415, 3124, 2964, 2868, 1732, 1701, 1502, 1435, 1379, 1244, 1084, 874, 604 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 2 and 3; LRESIMS *m/z* 1027.7 $[2M + Na]^+$; HRESIMS *m/z* 525.2501 $[M + Na]^+$ (calcd for $C_{28}H_{38}O_8Na$, 525.2464).

Mesendanin J (10): white, amorphous powder; mp 200−202 °C; $[\alpha]^{22}_D$ −22.0 (*c* 0.44, MeOH); UV (MeOH) λ_{max} (log ε) 206 (3.71) nm; IR (KBr) ν_{max} 3438, 2960, 2879, 1743, 1686, 1392, 1236, 1070, 874, 602 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 2 and 3; LRESIMS *m/z* 527.3 $[M + Na]^+$, 1031.7 $[2M + Na]^+$; HRESIMS *m/z* 527.2642 $[M + Na]^+$ (calcd for $C_{28}H_{40}O_8Na$, 527.2621).

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Supporting Information Available: Selected HMBC and ROESY correlations of **2**−**6**, **8**, and **10**, IR, MS, HRESIMS, and 1D and 2D NMR spectra of **1**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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