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大叶桃花心木中的柠檬苦素成分

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摘要: 为研究大叶桃花木(*Swietenia macrophylla*)的柠檬苦素类成分,采用柱层析的方法从大叶桃花心木的枝叶中分离得七个柠檬苦素分别为swiamacronoid A(1)、mahonin(2)、methyl angolensate(3)、methyl 6-hydroxyangolensate(4)、methyl 6-acetoxyangolensate(5)、swietmanin(6)、deacetylsecomahoganin(7)。其中化合物1为一个新的evodulone型的柠檬苦素,化合物7为首次从该种中分得。

关键词: 大叶桃花心木; 楝科; 柠檬苦素; 天然产物

中图分类号: Q946.91; R284.1

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Limonoids from the Twigs and Leaves of *Swietenia macrophylla*

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Abstract: To explore structural diversity of limonoids from *Swietenia macrophylla*, one new evodulone-type limonoid swiamacronoid A(1) along with another six known limonoids, namely mahonin B(2), methyl angolensate C(3), methyl 6-hydroxyangolensate D(4), methyl 6-acetoxyangolensate E(5), swietmanin F(6) and deacetylsecomahoganin G(7), were isolated from the 95% ethanol extract of leaves and twigs of *S. macrophylla* with different chromatographic methods. Among them, compound 7 was obtained from this plant for the first time. Their structures were elucidated by extensive spectroscopic techniques, including 1D, 2D-NMR spectroscopy, mass spectrometry and IR. We report herein the isolation and structural elucidation of these limonoids.

Key words: *Swietenia macrophylla*; Meliaceae; limonoids; natural products

Introduction

Limonoids are a kind of structurally complicated compounds with variety of potentially useful biological properties. They are mainly elaborated by families of Meliaceae, Rutaceae, Simaroubaceae, and Cneoraceae, and about 1300 limonoids with more than 35 carbon skeletons had been isolated^[1-2]. Their unique structural features have attracted much attention for biogenetic research^[1-6].

Swietenia is a genus of family Meliaceae which grows mainly in Southeast Asia, Malaysia and India. Many of them have been used as traditional medicines^[7-9] for the treatment of hypertension, diabetes, and malaria.

Chemical investigation on the genus of *Swietenia* have led to the isolation of many structurally diverse limonoids^[10,11]. These compounds have a range of biological activities such as antibacterial, antimalarial, anticancer etc. As a part of an ongoing program to explore structural diversity and to screen bioactive natural products, we isolated seven limonoids from the twigs

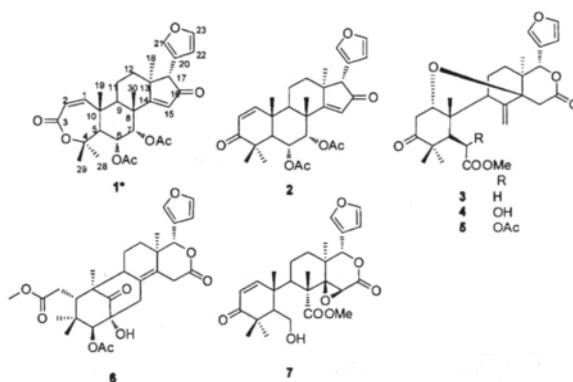


Fig. 1 Chemical structures of compounds 1-7

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and leaves of *S. macrophylla*. Herein ,we reported the details of the isolation and structural elucidation of these compounds.

Experimental

General

Optical rotations were measured with a JASCO P-1020 digital polarimeter. UV spectra were determined on a Shimadzu UV-2401 PC spectrophotometer. IR spectra were detected on a Bruker Tensor-27 infrared spectrometer with a KBr disk. CD spectra were obtained on a JASCO J-810 spectro-photometer. Brucker HCT/E squire and Waters Autospec Premier P776 spectrum were respectively used for measuring ESI-MS and HR-EI-MS spectra. 1D-NMR and 2D-NMR spectra were recorded on a Bruker AM-400 and Bruker DRX-500 spectrometer ,using TMS as an internal standard. Column chromatography was performed on silica gel(100–200 ,200–300 and 300–400 mesh ,Qingdao Marine Chemical Inc.) ,MCI gel CHP 20P(75–150 μm ,Mitsubishi Chemical Corporation ,Tokyo) ,Sephadex LH-20(40–70 μm ,Amersham Pharmacia Biotech AB ,Uppsala ,Sweden) ,and Chromatorex RP-C₁₈ gel (20–45 μm ,Merck ,Darmstadt ,Germany) .

Plant material

The twigs and leaves of *S. macrophylla* were collected from Hainan Province ,P. R. China in August ,2012 ,which were identified by Mr. Chen Y ,Kunming Institute of Botany ,Chinese Academy of Sciences(CAS) . The voucher specimen(No. H201207291) was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China ,Kunming Institute of Botany ,CAS.

Extraction and isolation

The leaves and twigs of *S. macrophylla*(5. 5 kg) were extracted with 95% EtOH three times. The EtOH distillate was concentrated in vacuum to obtain a crude residue ,which was partitioned with PE(petroleum ether) ,EtOAc ,and *n*-BuOH ,successively. The combined PE fraction and EtOAc fraction(300 g) was submitted to column chromatography(CC) over normal silica gel(100–200 mesh) using PE/ EtOAc 50: 1 ,and finally cleaned by 100% MeOH give six fractions A-F.

Fr. D(26 g) was then separated over a MCI to give six fractions(D1–D6) . Compounds **3**(22 mg) ,**4**(66 mg) and **5**(46 mg) were obtained from Fr. D5(3 g) by normal silica gel(300–400 mesh) eluted by PE/Acetone = 2: 1. Fr. D4(1 g) was further subjected to repeated normal silica gel and Sephadex LH-20 to yield compounds **1**(9 mg) ,**2**(10 mg) ,**6**(7 mg) ,and **7**(22 mg) .

Structural identification

Swimacronoid A(1) : white amorphous powder; ESI-MS *m/z* 547 [M + Na]⁺; HR-EI-MS *m/z* 524.2417(C₃₀H₃₆O₈ ,calcd for 524.2410) ; [α]D₂₀–72.0(*c* 0.15 ,MeOH) ; IR(KBr) ν_{max} 3438 ,2949 ,1748 ,1705 ,1630 ,1240 and 1223 cm^{–1}; UV(MeOH) λ_{max} 343 nm(0.88) ,201 nm(30.02) ; ¹H and ¹³C NMR data were shown in Table 1.

In addition to the easily distinguishable resonances for two acetyl(δ_{H} 1.99 ,2.02 ,each 3H ,s) groups ,the ¹H NMR spectrum also indicated the presence of five tertiary methyls(δ_{H} 1.04 ,1.45 ,1.47 ,1.48 ,1.54 ,each 3H ,s) ,one cis-disubstituted double bonds(δ_{H} 6.67 ,d ,*J* = 11.6 δ_{H} 5.98 ,d ,*J* = 12.0 ,each 1H) ,and one β-substituted furan ring(δ_{H} 6.26 ,7.48 ,and 7.43 ,each 1H ,s) . The ¹³C NMR spectrum displayed 30 carbon resonances ,which were classified by DEPT and HSQC experiments as seven methyls ,two sp³ methylenes ,five sp³ methines(two oxygenated) ,four sp³ quaternary carbons ,two ester ,one ketone conjugated to a trisubstituted double bond(δ_{H} 5.93 δ_{C} 123.1) ,and one ester or lactone(δ_{C} 167.8) conjugated to the disubstituted double bond(δ_{H} 5.98 and 6.68 ,AB system) . Apart from the eight degrees of unsaturation occupied by four carbonyls and four double bonds ,the remaining five degrees of unsaturation require 1 to contain a pentacyclic core ring system. The aforementioned data implied that **1** was an evodulone-type limonoid.

Table 1 ¹H(400 MHz) and ¹³C(100 MHz) NMR Data for **1** in CDCl₃(δ in ppm *J* in Hz)

Position	¹ H NMR	¹³ C NMR	HMBC
1	6.67(d , <i>J</i> = 12.0)	159.2(d)	5.9 ,10.19
2	5.98(d , <i>J</i> = 12.0)	124.3(d)	3.10

3		167.8(s)	
4		85.0(s)	
5	2.66(d , $J = 12.1$)	53.1(d)	4 6 ,10 ,19 28 29
6	5.35(dd , $J = 12.1$ 2.6)	69.1(d)	5 7 β -Ac
7	5.56(d , $J = 2.6$)	72.7(d)	5 8 9 7-Ac
8		43.1(s)	
9	2.57(m)	39.6(d)	1 ,19 30
10		43.8(s)	
11	1.93(m)	16.7(t)	9 ,12 ,13
12	2.18(s)	30.6(t)	14 ,18
13		47.5(s)	
14		189.9(s)	
15	5.93(s)	123.1(d)	8 ,13 ,14 ,16 ,17
16		204.9(s)	
17	3.46(s)	61.0(d)	13 ,16 ,18 20 21 22
18	1.04(s)	28.0(q)	13 ,14 ,17
19	1.45(s)	15.3(q)	1 5 9
20		118.1(s)	
21	7.43(s)	141.7(d)	20
22	6.26(s)	111.0(d)	20 21
23	7.47(s)	142.9(d)	20 22 ,
28	1.54(s)	34.7(q)	4 5 29
29	1.48(s)	24.5(q)	4 5 28
30	1.47(s)	26.6(q)	7 8 9
6-OAc	2.02(s)	21.1(q) 169.9(s) ,	6
7-OAc	1.99(s)	20.8(q) 169.5(s) ,	7

The NMR spectra data of **1** were closely related to those of Munronoid E^[11], with the only difference being the presence of a β -furan ring group at C-17 in **1** instead of a γ -lactone in the latter. This structural variation was confirmed by HMBC correlations of H-21(δ_H 7.43 s) to C-20(δ_C 118.1), C-22(111.0), C-23(142.9), and C-17(61.0) as well as H-22(δ_H 6.26 s) to C-20 and C-17. Peaks of H-6/C-6-OAc and H-7/C-7-OAc in HMBC spectra identified the two acetoxy groups located at C-6 and C-7, respectively. The planar structure of **1** was thus established as shown in Fig. 1.

The relative configuration of compound **1** was deduced from the ROESY correlations and the ^1H - ^1H vicinal coupling constants. As shown in Fig. 2B, ROESY correlations of Me-19/Me-30/H-6, Me-30/H-17, indicated

that they were cofacial and were arbitrarily assigned as β -configuration. the ^1H - ^1H vicinal coupling constants of $^{16}\text{O}^{15}\text{O}$ $J = 12.1$ Hz and $^{16}\text{O}^{17}\text{O}$ $J = 2.6$ Hz requiring a *trans* relationship between H-5 and H-6, and *cis* relationship between H-6 and H-7, thus H-5 and H-7 were assigned as α -orientation and β -orientation respectively. In addition, the ROESY cross-peaks of H-5/H-9 and H-9/Me-18 revealed their *a*-orientation. Consequently, the relative configuration of compound **1** was achieved as shown in Fig. 2B. According to the naming conventions and published papers, compound **1** was named as swimacronoid A which consisted of three parts: swi- is from the genus name, *Swietenia*; -macro- is from the species name *macrophylla*, and -nioid means the compound is terpenoid.

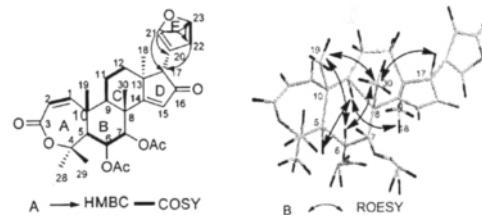


Fig. 2 ^1H - ^1H COSY(**Bold**) Key HMBC correlations(**A**) and Key ROESY correlations(**B**) of compound **1**

Mahonin^[13](2) White amorphous powder; ESI-MS m/z 531 [M + Na]⁺; molecular formula $C_{30}H_{36}O_7$; ^1H NMR(CDCl_3 400 MHz): 7.13(1H ,d , $J = 10.2$ Hz ,H-4) 5.96(1H ,d , $J = 10.2$ Hz ,H-2) 5.47(1H ,dd , $J = 12.5$ 2.5 Hz ,H-6) 5.56(1H ,d , $J = 2.5$ Hz ,H-7) ,5.88(1H ,s ,H-15) ,3.43(1H ,s ,H-17) ,1.03(3H ,s ,H-18) ,1.24(3H ,s ,H-19) ,7.45(1H ,s ,H-21) ,6.27(1H ,s ,H-22) ,7.47(1H ,s ,H-23) ,1.27(3H ,s ,H-28) ,1.20(3H ,s ,H-29) ,1.44(3H ,s ,H-30) 2.05(3H ,s ,Ac) ,2.00(3H ,s ,Ac); ^{13}C NMR(CDCl_3 100 MHz): 155.9(C-4) ,126.7(C-2) 204.1(C-3) 44.9(C-4) 36.8(C-5) 69.2(C-6) 73.3(C-7) 44.7(C-8) 47.9(C-9) ,40.7(C-10) ,15.8(C-11) 30.0(C-12) 47.8(C-13) ,190.8(C-14) ,123.5(C-15) ,204.7(C-16) ,60.8(C-17) ,26.7(C-18) ,21.3(C-19) ,118.2(C-20) ,141.7(C-21) ,111.1(C-22) ,142.8(C-23) 31.8(C-28) ,20.8(C-29) ,25.7(C-30) ,20.7(Ac) ,20.4(Ac) ,170.2(Ac) ,169.6(Ac) .

Methyl 6-hydroxyangolensate^[14] (3) White amorphous powder; ESI-MS *m/z* 493 [M + Na]⁺; formula C₂₇H₃₄O₈; ¹H NMR (CDCl₃, 400 MHz): 5.64 (1H, s, H-17) δ, 90 (3H, s, H-18), 1.00 (3H, s, H-19), 7.50 (1H, s, H-21), 6.45 (1H, s, H-22), 7.54 (1H, s, H-23), 1.01 (3H, s, H-28), 1.21 (3H, s, H-29), 5.02 (1H, s, H-30), 5.21 (1H, s, H-30), 3.70 (3H, s, -OCH₃); ¹³C NMR (CDCl₃, 100 MHz): 79.1 (C-1), 40.5 (C-2), 216.1 (C-3), 49.3 (C-4), 44.5 (C-5), 34.7 (C-6), 175.8 (C-7), 147.3 (C-8), 51.2 (C-9), 45.2 (C-10), 25.0 (C-11), 30.8 (C-12), 41.2 (C-13), 81.7 (C-14), 33.6 (C-15), 172.8 (C-16), 81.4 (C-17), 14.4 (C-18), 21.8 (C-19), 122.4 (C-20), 142.2 (C-21), 110.9 (C-22), 144.3 (C-23), 21.9 (C-28), 25.9 (C-29), 112.5 (C-30), 52.5 (-OCH₃).

Methyl angolensate^[14] (4) White amorphous powder; ESI-MS *m/z* 509 [M + Na]⁺; C₂₇H₃₄O₇; ¹H NMR (CDCl₃, 500 MHz): 3.54 (1H, dd, *J* = 5.0, 2.5 Hz, H-1), 4.38 (1H, s, H-6), 5.60 (1H, s, H-17), 0.84 (3H, s, H-18), 1.01 (3H, s, H-19), 7.36 (1H, d, *J* = 0.8 Hz, H-21), 6.33 (1H, s, H-22), 7.40 (1H, s, H-23), 1.35 (3H, s, H-28), 1.43 (3H, s, H-29), 5.17 (1H, s, H-30), 4.89 (1H, s, H-30), 3.80 (3H, s, -OCH₃); ¹³C NMR (CDCl₃, 125 MHz): 78.3 (C-1), 39.1 (C-2), 212.8 (C-3), 48.7 (C-4), 47.4 (C-5), 72.2 (C-6), 176.6 (C-7), 145.7 (C-8), 50.7 (C-9), 44.5 (C-10), 23.9 (C-11), 28.5 (C-12), 41.2 (C-13), 80.3 (C-14), 33.6 (C-15), 170.6 (C-16), 79.5 (C-17), 13.7 (C-18), 23.2 (C-19), 120.6 (C-20), 140.8 (C-21), 109.8 (C-22), 142.7 (C-23), 23.6 (C-28), 24.7 (C-29), 111.6 (C-30), 53.2 (-OCH₃).

Methyl 6-acetoxyangolensate^[14] (5) White amorphous powder; ESI-MS *m/z* 551 [M + Na]⁺; formula C₂₉H₃₆O₉; ¹H NMR (CDCl₃, 400 MHz): 3.54 (1H, dd, *J* = 5.0, 2.5 Hz, H-1), 4.85 (1H, s, H-6), 5.56 (1H, s, H-17), 0.81 (3H, s, H-18), 1.01 (3H, s, H-19), 7.32 (1H, d, *J* = 1.5 Hz, H-21), 6.30 (1H, s, H-22), 7.37 (1H, s, H-23), 1.05 (3H, s, H-28), 1.41 (3H, s, H-29), 5.39 (1H, s, H-30), 5.12 (1H, s, H-30), 3.70 (3H, s, -OCH₃), 2.15 (3H, s, -Ac); ¹³C NMR (CDCl₃, 100 MHz): 78.1 (C-1), 39.1 (C-2), 211.9 (C-3), 48.9 (C-4), 46.5 (C-5), 72.3 (C-6), 170.9 (C-7), 145.3 (C-8), 50.7 (C-9), 44.4 (C-10), 23.8 (C-11),

28.6 (C-12), 41.2 (C-13), 80.4 (C-14), 33.5 (C-15), 170.3 (C-16), 79.6 (C-17), 13.7 (C-18), 22.6 (C-19), 120.5 (C-20), 140.7 (C-21), 109.7 (C-22), 142.8 (C-23), 23.6 (C-28), 24.7 (C-29), 111.8 (C-30), 53.0 (-OCH₃), 170.6 (6-OAc), 21.0 (6-OAc).

Swietmanin^[14] (6) White amorphous powder; ESI-MS *m/z* 551 [M + Na]⁺; formula C₂₉H₃₆O₉; ¹H NMR (CDCl₃, 400 MHz): 5.06 (1H, s, H-2), 5.69 (1H, s, H-17), 1.07 (3H, s, H-18), 1.25 (3H, s, H-19), 7.5 (1H, s, H-21), 6.47 (1H, s, H-22), 7.41 (1H, s, H-23), 0.76 (3H, s, H-28), 0.69 (3H, s, H-29), 3.71 (1H, s, -OMe); ¹³C NMR (CDCl₃, 100 MHz): 217.4 (C-1), 78.0 (C-2), 85.6 (C-3), 38.9 (C-4), 40.8 (C-5), 33.4 (C-6), 174.0 (C-7), 125.7 (C-8), 52.0 (C-9), 52.0 (C-10), 18.7 (C-11), 29.1 (C-12), 38.2 (C-13), 133.0 (C-14), 33.2 (C-15), 170.0 (C-16), 80.5 (C-17), 18.0 (C-18), 16.8 (C-19), 120.5 (C-20), 141.8 (C-21), 109.9 (C-22), 142.9 (C-23), 22.6 (C-28), 19.8 (C-29), 44.1 (C-30), 52.2 (-OMe), 21.3 (3-Ac), 169.7 (3-Ac).

Deacetylsecomahoganin^[15] (7) White amorphous powder; ESI-MS *m/z* 509 [M + Na]⁺; formula C₂₇H₃₄O₈; ¹H NMR (CDCl₃, 400 MHz): 6.65 (1H, d, *J* = 10.4 Hz, H-1), 5.90 (1H, d, *J* = 10.5 Hz, H-2), 4.07 (1H, m, H-6), 3.91 (1H, m, H-6), 5.40 (1H, s, H-17), 1.20 (3H, s, H-18), 1.16 (3H, s, H-19), 7.36 (1H, s, H-21), 6.31 (1H, s, H-22), 7.36 (1H, s, H-23), 1.23 (3H, s, H-30), 3.77 (-OMe); ¹³C NMR (CDCl₃, 100 MHz): 153.9 (C-1), 127.8 (C-2), 204.9 (C-3), 46.4 (C-4), 52.9 (C-5), 62.5 (C-6), 177.8 (C-7), 44.6 (C-8), 44.6 (C-9), 52.2 (C-10), 23.1 (C-11), 33.9 (C-12), 39.3 (C-13), 69.6 (C-14), 52.8 (C-15), 168.2 (C-16), 79.8 (C-17), 20.9 (C-18), 19.7 (C-19), 121.3 (C-20), 142.4 (C-21), 111.3 (C-22), 144.5 (C-23), 25.8 (C-28), 24.7 (C-29), 16.7 (C-30), 54.8 (-OMe).

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(C-4', C-4''), 120.1 (C-6', 6''), 116.9 (C-5', 5''), 111.4 (C-2', 2''), 86.8 (C-2, 6), 72.4 (C-4, 8) 56.4 (2 × OCH₃) 55.2 (C-1, 5)。以上数据与文献^[8]报道的松脂素数据一致。

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