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Compounds from the roots of *Jasminum sambac*

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Four new compounds (+)-jasminoids A (**1**), B (**2**), C (**3**), and D (**4**), together with seven known compounds, were isolated from the roots of *Jasminum sambac*. Their structures were identified using spectroscopic methods. This study provides a better understanding to the chemical composition of *J. sambac* roots that have been thought to be one ingredient of an ancient prescription 'Ma-Fei-San'.

Keywords: *Jasminum sambac*; jasminoids A–D; sesquiterpenoids; iridoids

1. Introduction

Jasminum sambac (Oleaceae) is an evergreen vine or shrub native to south and southeast Asia. It has been widely cultivated for its attractive and fragrant flowers. In China, the flower is processed and used for perfumes and the main ingredient in jasmine tea [1]. The root is a traditional Chinese medicine with anesthetic and analgesic effects and used for the treatment of insomnia, headache, decayed tooth, and injuries from falls [2]. Interestingly, the root is thought to be one important ingredient of Ma-Fei-San, i.e. the powder for anesthesia, which is an ancient prescription created by Tuo Hua and used for surgeries due to its significant anesthetic and analgesic effects, which aroused our great interest. Previous studies indicated the presence of lignans, terpenoids, and flavonoids [3,4]. The extract of the roots has been proved to have sedative effects in clinical trials [5]. However, the further study needs to be explored to get a better understanding of the chemical composition of *J. sambac* roots. In this paper, we report the isolation and structural elucidation of four new compounds.

2. Results and discussion

Compound **1** had the molecular formula $C_{15}H_{20}O_2$ derived from its HR-ESI-MS at *m/z* 231.1384 $[M-H]^-$, indicating six degrees of unsaturation. The IR spectrum showed the absorption bands for OH groups (3425 cm^{-1}) and a phenyl ring (1630 cm^{-1}). The ^{13}C NMR and DEPT spectra gave 15 carbon signals including two methyl, five methylene (one oxygenated methylene and one olefinic methylene), two methine, and six olefinic quaternary carbons, indicating that **1** is a sesquiterpenoid similar to cinalbicol [6]. The difference was that a methyl group in cinalbicol was replaced by a hydroxymethyl, corresponding to the chemical shift of C-13 (δ 65.8). This was also supported by the HMBC correlations of H-8/C-11, and H-12/C-7, C-13. The determination of configuration at C-4 is

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challengeable. There is only one chiral carbon in compound **1**, and the stereochemistry at C-4 was tentatively assigned as *S*-configuration by comparison of the specific rotation of **1** with that of cinalbicol. Thus, the structure of **1** was deduced as shown in Figure 1, with a trivial name (+)-jasminoid A.

Compound **2** had the molecular formula $C_{15}H_{20}O_3$ deduced from its HR-EI-MS at *m/z* 248.1406 $[M]^+$, requiring 6 degrees of unsaturation. The IR spectrum indicated the presence of OH (3425 cm^{-1}) and α,β-unsaturated ketone (1629 cm^{-1}) functionalities. Fifteen carbon signals in the ^{13}C NMR and DEPT spectra were attributed to two methyl, four methylene including one oxygenated methylene, two methine including an olefinic one, and six quaternary carbons (four olefinic ones, one carbonyl group, and one sp^3 quaternary carbon). These data suggested that **2** is an analog of **1**. Compared to **1**, compound **2** has a ketone group positioned at C-9 and a hydroxyl attached to C-6. This conclusion was supported by the HMBC correlations of H-1/C-10, C-9, H-8/C-6, C-7,C-9, C-10, C-11, H_3-14/C-6, and H-4/C-5, C-6 (Figure 1). ROESY correlation of H_3-14/H_3-15 established the relative configuration of **2** as shown in Figure 1. Therefore, the structure of **2** was determined and given a name jasminoid B.

Compound **3** was found to have the molecular formula $C_{17}H_{30}O_8$ from its HR-ESI-MS at *m/z* 361.1866 $[M-H]^-$. The ^{13}C NMR and DEPT spectra displayed 17 carbons, 11 of which were attributed to one methoxy group, one methyl, four methylene including two oxygenated ones, and five methine (one resonated at δ 100.9), the other six carbons were characteristic of a glucosyl moiety. $^1H-^1H$ COSY correlations of H-4/H-11, H-4/H-5/H-6/H-7/H-8/H-9, H-5/H-9, and H-8/H-10, in combination with HMBC correlations of H-3/C-1, revealed that **3** is an iridoidal derivative. HMBC correlation of a proton at δ 3.38 with a carbon at δ 100.9 positioned the methoxy group at C-1. Acid hydrolysis of **3** afforded a D-glucose identified by comparison with reference compound in terms of TLC and specific rotation. The anomeric proton at δ

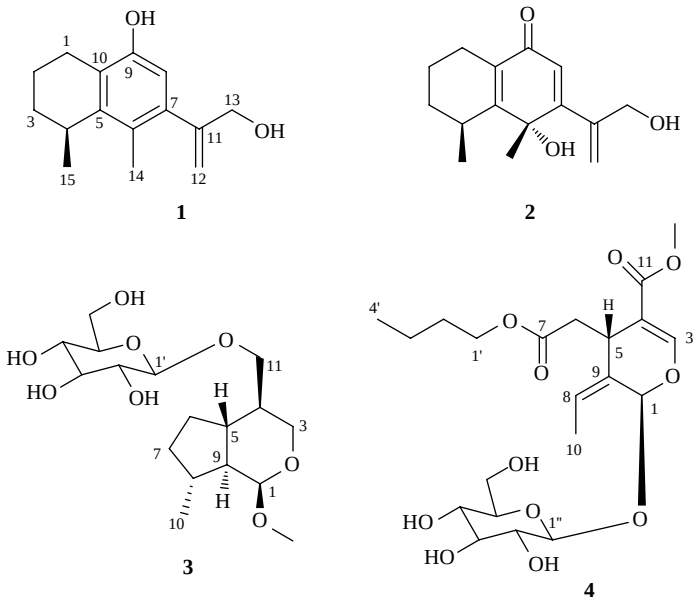

Figure 1. The structures of compounds **1**–**4**.

4.20 (d, 7.8 Hz) indicated a β-configuration glucose. HMBC correlation of H-1′/C-11 suggested the linkage of aglycone and glucose. The relative configuration of **3** was determined by the ROESY spectrum, which showed correlations of H_3-10/H-1, H-9, H-9/H-4, H-11/H-5, and H-1/H-8 indicative of α-form of H-1, H-4, and H-9, and β-form of H-5 and H-8. This is also in accordance with the observation of the split pattern of H-1 (d, 1.0) and H-9 (brdd, 8.7, 6.8). Hence, the structure of **3** was established as shown in Figure 1, with a trivial name jasminoid C.

Compound **4** had the molecular formula $C_{21}H_{32}O_{11}$ from the HR-EI-MS at *m/z* 460.1964 $[M]^+$, ^{13}C NMR, and DEPT spectra. The most NMR data of **4** were similar to those of compound **8**, which is a seco-iridoidal derivative. The difference was that one methyl ester in **8** was replaced by one butyl ester in **4**. This conclusion was readily confirmed by $^1H-^1H$ COSY correlations of H-1′/H-2′/H-3′/H-4′, and HMBC correlations of H-1′/C-7 (Figure 2). The glucosyl moiety was identified as D-glucose by acid hydrolysis of **4** followed by TLC comparison with reference compound and optical rotation determination. The glucose was attached to C-1 by the observed HMBC correlation of H-1″/C-1. The anomeric proton at δ 4.78 (d, 7.8) suggested a β-configuration glucose. ROESY correlation of H-1/H-6 indicated that they are spatially vicinal. Compound **4** was thus identified as shown in Figure 1, and named as jasminoid D.

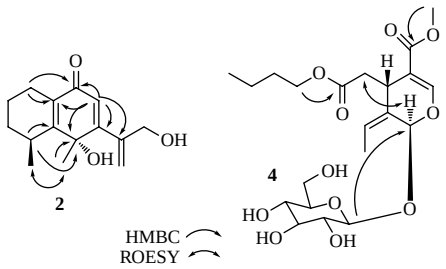

Figure 2. Selected HMBC (→) and COSY(—) correlations of **2** and **4**.

The known compounds were identified as (1*S**,5*S**,10a*R**)-1-[(8′*S**,8a′*R**)-8′,8a′-dimethyl-4′-oxo-1′,4′,6′,7′,8′,8a′-hexahydronaphthalen-2′-yl]-4-hydroxy-1,4,5,10a-tetramethyl-1,2,3,4,5,6,7,9,10,10a-decahydroanthracen-9-one (**5**) [7], tetraol (**6**) [8], oleside 7-(tetraol-(5″)-ester, 11-methyl ester (**7**) [8], oleside 7,11-methyl ester (**8**) [9], oleside 11-methyl ester (**9**) [10], α-asarone (**11**) [11], and 2,3-dihydroxypropyl-9-octadecenoate (**12**) [12], respectively, by comparison with the literature data.

3. Experimental

3.1 General experimental procedures

Optical rotations were measured with a Jasco-20C polarimeter (Jasco, Hachioji, Tokyo, Japan). IR spectra were obtained on a Bio-Rad FTS-135 (Bio-Rad, Richmond, Canada) with KBr pellets. UV spectra were measured on a Shimadzu UV-210A spectrophotometer (Shimadzu, Kyoto, Japan). NMR spectra were obtained on a Bruker DRX-500 MHz or a Bruker AV-400 MHz spectrometer (Bruker Corporation, Switzerland) with TMS as an internal standard. EI-MS spectra were determined using a VG Autospec-3000 spectrometer (VG, Manchester, England). ESI-MS and HR-ESI-MS spectra were determined using an API QSTAR Pulsar 1 spectrometer (Applied Biosystems/MDS Sciex, Foster City, CA, USA). Silica gel (200–300 mesh, Qingdao Marine Chemical Co. Ltd, Qingdao, China), RP-18 gel (40–63 μm; Daiso Co., Osaka, Japan), MCI gel CHP 20P (Mitsubishi, Tokyo, Japan), and Sephadex LH-20 (Amersham Biosciences, Uppsala, Sweden) were used for column chromatography (CC).

3.2 Plant material

The roots of *J. sambac* were collected from jasmine cultivation base of Nan-

ning, Guangxi Province of China, in July 2007. A voucher specimen (CHYX-0389) has been deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China of our institute.

3.3 Extraction and isolation

The air-dried and powdered roots of *J. sambac* (15 kg) were refluxed with 95% EtOH (3 × 50 liters). The extracts were combined and concentrated to give a crude extract (1.0 kg), which was suspended in H_2O and successively partitioned by petroleum ether, EtOAc, and *n*-BuOH. The latter two parts were combined (400 g) and were divided into four fractions by a gradient $CHCl_3$–MeOH. Fr. 2 (30 g) was passed through an MCI gel CHP 20P column eluting with gradient aqueous MeOH (60–90%) to give five fractions. Fr. 2.2 (4.6 g) was submitted to gel filtration over Sephadex LH-20 (MeOH) to yield a fraction (570 mg), which was purified by RP-18 gel (aqueous MeOH: 60–90%) followed by vacuum liquid chromatography (VLC) over silica gel ($CHCl_3$/MeOH, 30:1) to afford a mixture (300 mg). The final purification was carried out by preparative TLC ($CHCl_3$–Me_2CO, 20:1) followed by Sephadex LH-20 (MeOH) filtration, which afforded **5** (4 mg) and **11** (18 mg). Fr. 2.4 (6 g) was fractionated by RP-18 gel (60–90%) to yield two fractions. Fr. 2.4.1 (800 mg) was submitted to VLC over silica gel (petroleum ether/EtOAc, 6:1) to give a subfraction, which was purified by Sephadex LH-20 (MeOH) to afford **2** (5 mg). Fr. 2.4.2 (300 mg) was purified by the combination of RP-18, silica gel, and Sephadex LH-20 CC to yield **1** (16 mg). Fr. 3 (203 g) was divided into five parts over silica gel CC eluting with EtOAc–MeOH

Table 1. ^{1}H and ^{13}C NMR spectral data of **1** and **2** (δ in ppm, *J* in Hz).

	1[a]		**2**[b]	
No.	δ_H[c]	δ_C[c]	δ_H[d]	δ_C[d]
1a	2.81 (dd, 17.7, 6.1)	23.8 (CH_2)	2.40 (ddd, 18.6, 7.6, 1.8)	21.9 (CH_2)
1b	2.42 (dd, 17.7, 4.7)		2.24 (m)	
2a	1.83 (m)	17.2 (CH_2)	1.84 (m)	16.9 (CH_2)
2b	1.72 (overlap)		1.73 (m)	
3a	1.72 (overlap)	30.6 (CH_2)	1.69 (m)	31.4 (CH_2)
3b			1.58 (m)	
4	3.05 (m)	30.2 (CH)	3.08 (m)	29.2 (CH)
5		142.4 (qC)		166.4 (qC)
6		123.9 (qC)		72.1 (qC)
7		139.6 (qC)		165.5 (qC)
8	6.42 (s)	112.9 (CH)	6.05 (s)	125.7 (CH)
9		153.2 (qC)		188.4 (qC)
10		122.7 (qC)		130.8 (qC)
11		152.6 (qC)		148.2 (qC)
12a	5.43 (dd, 4.2, 1.9)	111.1 (CH_2)	5.53 (m)	117.5 (CH_2)
12b	4.83 (dd, 4.2, 1.9)		5.51 (m)	
13a	4.11 (brs)	65.8 (CH_2)	4.40 (d, 14.6)	65.5 (CH_2)
13b			4.25 (d, 14.6)	
14	2.12 (s)	14.7 (CH_3)	1.52 (s)	27.8 (CH_3)
15	1.14 (d, 7.0)	21.0 (CH_3)	1.28 (d, 7.0)	21.2 (CH_3)

[a] Acetone-d_6; [b] Methanol-d_4; [c] ^{1}H (400 MHz) and ^{13}C (100 MHz); [d] ^{1}H (600 MHz) and ^{13}C (150 MHz).

(5:1), of which, Fr. 3.1(13 g) was passed through an MCI gel CHP 20P column (aqueous MeOH, 40–90%) to give a subfraction (8 g), which was purified by Sephadex LH-20 (MeOH) and RP-18 CC (aqueous MeOH, 40–70%) to afford **6** (13 mg). Fr. 3.5 (82 g) was fractionated by MCI gel CHP 20P (40–90%) to give four subfractions. Fr. 3.5.4 (26 g) was fractionated by Sephadex LH-20 (MeOH) and RP-18 CC (aqueous MeOH, 40–55%) to give a mixture (90 mg), which was submitted to VLC (EtOAc–MeOH, 20:1) on silica gel to give **3** (22 mg). In the same manner, compounds **4** (15 mg) and **10** (6 mg) were purified from Fr. 3.5.5 (32 g). Fr. 4 was divided into three parts (Fr. 4.1–4.3) by silica gel CC (EtOAc–MeOH, 5:1). Fr. 4.1 (40 g) was fractionated into three portions (Fr. 4.1.1–4.1.3) by MCI gel CHP 20P (aqueous MeOH, 40–90%). Fr. 4.1.3 (13 g) was purified by a combination of Sephadex LH-20 (MeOH), RP-18 CC (aqueous MeOH, 40–80%) followed by VLC ($CHCl_3$/MeOH, 10:1) on silica gel to give **7** (10 mg). Fr. 4.3 (34 g) was submitted to MCI gel CHP 20P (aqueous MeOH, 40–90%) followed by a combination of RP-18, Sephadex LH-20 CC (MeOH) and VLC ($CHCl_3$/MeOH, 12:1) over silica gel to yield **8** (80 mg) and **9** (140 mg).

Table 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **3** and **4** (δ in ppm, J in Hz).

	3[a]		**4**[a]	
No.	δ_H	δ_C	δ_H	δ_C
1	4.56 (d, 1.0)	100.9 (CH)	5.90 (s)	95.1 (CH)
3a	3.76 (dd, 11.0, 4.6)	62.1 (CH_2)	7.50 (s)	155.1 (CH)
3b	3.57 (t, 11.0)			
4	1.78 (m)	38.1 (CH)		109.4 (qC)
5	2.02 (overlap)	37.3 (CH)	3.97 (overlap)	31.9 (CH)
6a	1.72 (m)	29.2 (CH_2)	2.69 (dd, 14.1, 4.5)	41.2 (CH_2)
6b	1.64 (m)		2.44 (dd, 14.1, 9.3)	
7a	2.02 (overlap)	32.7 (CH_2)		173.3 (qC)
7b	1.22 (m)			
8	2.02 (overlap)	34.9 (CH)	6.08 (q, 7.1)	124.7 (CH)
9	1.43 (brdd, 8.7, 6.8)	51.8 (CH)		130.6 (qC)
10	1.03 (d, 6.3)	20.2 (CH_3)	1.71 (dd, 7.1, 0.9)	14.1 (CH_3)
11a	3.98 (dd, 10.0, 3.5)	71.6 (CH_2)		168.7 (qC)
11b	3.27 (overlap)			
1′a	4.20 (d, 7.8)	105.1 (CH)	4.06 (m)	65.7 (CH_2)
1′b			3.97 (overlap)	
2′	3.18 (dd, 9.0, 7.8)	75.1 (CH)	1.58 (m)	31.7 (CH_2)
3′	3.38 (m)	78.0 (CH)	1.37 (m)	20.2 (CH_2)
4′	3.27 (overlap)	71.7 (CH)	0.92 (t, 7.4)	13.6 (CH_3)
5′	3.27 (overlap)	77.9 (CH)		
6′a	3.88 (dd, 11.8, 1.9)	62.7 (CH_2)		
6′b	3.69 (dd, 11.8, 5.4)			
1″			4.78 (d, 7.8)	100.8 (CH)
2″			3.28 (overlap)	74.8 (CH)
3″			3.28 (overlap)	78.4 (CH)
4″			3.28 (overlap)	71.5 (CH)
5″			3.37 (m)	77.9 (CH)
6″a			3.86 (dd, 11.9, 1.9)	62.8 (CH_2)
6″b			3.64 (dd, 11.9, 5.5)	
O-Me	3.38 (s)	55.2 (CH_3)	3.69 (s)	51.9 (CH_3)

[a] Methanol-d_4.

3.3.1 (+)-Jasminoid A (**1**)

White solids. $[\alpha]_D^{25} + 19.4$ ($c = 0.28$ MeOH); UV (MeOH) λ_{max} (log ε): 284 (2.62), 207 (3.67); IR (KBr) ν_{max} 3425, 2924, 2869, 1630, 1418, 1325, 1255, 1037 cm^{-1}; ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectral data, see Table 1. ESI-MS (negative): *m/z* 232 $[M-H]^-$; HR-ESI-MS (negative): *m/z* 231.1384 $[M-H]^-$ (calcd for $C_{15}H_{19}O_2$, 231.1385).

3.3.2 Jasminoid B (**2**)

White solids. $[\alpha]_D^{23} - 48.9$ ($c = 0.08$, MeOH); UV (MeOH) λ_{max} (log ε): 244 (3.11), 202 (3.21) nm; IR (KBr) ν_{max}: 3425, 2925, 1629, 1451, 1391, 1056 cm^{-1}. ^1H (600 MHz) and ^{13}C NMR (150 MHz) spectral data, see Table 1. EI-MS: *m/z* 248 $[M]^+$. HR-EI-MS: *m/z* 248.1406 $[M]^+$ (calcd for $C_{15}H_{20}O_3$, 248.1412).

3.3.3 Jasminoid C (**3**)

White solids. $[\alpha]_D^{25} - 18.7$ ($c = 0.39$, MeOH); UV (MeOH) λ_{max} (log ε): 276 (1.56), 207 (2.29) nm; IR (KBr) ν_{max}: 3432, 2951, 2923, 2871, 1630, 1461, 1378, 1066, 1045 cm^{-1}. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectral data, see Table 2. ESI-MS (negative): *m/z* = 361 $[M-H]^-$, HR-ESI-MS (negative): *m/z* 361.1866 $[M-H]^-$ (calcd for $C_{17}H_{29}O_8$, 361.1862).

3.3.4 Jasminoid D (**4**)

White solids. $[\alpha]_D^{23} - 192.8$ ($c = 0.32$, MeOH); UV (MeOH) λ_{max} (log ε): 236 (3.40), 200 (3.17) nm; IR (KBr) ν_{max}: 3449, 2959, 2925, 1708, 1691, 1632, 1305, 1161, 1077 cm^{-1}. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectral data, see Table 2. EI-MS: *m/z* 460 $[M]^+$, HR-EI-MS: *m/z* 460.1964 $[M]^+$ (calcd for $C_{21}H_{32}O_{11}$, 460.1945).

3.3.5 Acid hydrolysis of **4**

A solution of **4** (5 mg) in 2N HCl (6 ml) was heated in a H_2O bath at 70° for 6 h. After cooling, the mixture was neutralized with $NaHCO_3$ and extracted with EtOAc. The optical rotation determination of H_2O layer containing pure glucose suggested the D-form of glucose ($[\alpha]_D^{23} = +33.2$ ($c = 0.13$, H_2O)).

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Note

1. These authors contributed equally to this work.

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