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Chemical constituents from stems and leaves of *Micromelum integerrimum*

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Abstract: A new benzene derivative microintegerrin C (**1**) and a new norsesquiterpenoid microintegerrin D (**2**), along with six known compounds (**3**−**8**), were isolated and identified from stems and leaves of *Micromelum integerrimum* by various chromatographies such as silica gel, Sephadex LH-20, RP-18 column chromatography and HPLC. Their structures were mainly identified based on the spectral data analysis such as 1D-, 2D-NMR and HR-EI-MS. All known compounds were isolated from this plant for the first time.

Key words: *Micromelum integerrimum*; Rutaceae; benzene derivative; norsesquiterpenoid; microintegerrins C-D

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小芸木茎和叶中化学成分研究

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摘要: 通过硅胶、凝胶、RP-18 和 HPLC 等一系列色谱方法对小芸木茎和叶中化学成分进行研究, 得到 8 个化合物, 包括两个新化合物 (**1**、**2**) 和 6 个已知化合物 (**3**～**8**)。通过一维、二维核磁共振以及高分辨质谱等波谱数据对这些化合物进行结构鉴定, 其中化合物 microintegerrin C (**1**) 为一个新的苯环衍生物, 化合物 microintegerrin D (**2**) 为一个新的降倍半萜, 化合物 **3**～**8** 为首次从该植物中分离得到。

关键词: 小芸木; 芸香科; 苯环衍生物; 降倍半萜; microintegerrins C-D

Micromelum integerrimum (Buch.-Ham. ex DC.) Wight & Arn. ex M. Roem. (Rutaceae) is distributed mainly in China[1]. The leaves and barks have been used for the treatment of cold and trauma, and the roots for stomach pain[1]. Previous chemical investigations on this genus afforded a number of structurally interesting coumarins, alkaloids and other compounds[2−7]. Although coumarins, alkaloids and phenylpropanoids have also been isolated from *M. integerrimum*, some coumarins showed cytotoxicity[3−5, 8]. As part of our continuous investigation on the chemical and biological constituents of *M. integerrimum*, chemical investigation

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on the stems and leaves of *M. integerrimum* leads to the isolation of two new compounds (**1**, **2**) and six known compounds (**3**−**8**).

Results and discussion

Two new compounds, a benzene derivative (**1**) and a norsesquiterpenoid (**2**), together with six known compounds (**3**−**8**) were isolated and determined as microintegerrin C (**1**), microintegerrin D (**2**), 2-methoxy-4-(2-propenyl)-phenyl-*β*-*D*-glucoside (**3**)[9], erigeside Ⅱ (**4**)[10], acantrifoside E (**5**)[11], benzyl-*β*-*D*-glucoside (**6**)[12], 5,7-dihydroxyl-3,8,4'-trimethoxylflavone (**7**)[13] and kaempferol 3-*O*-*β*-*D*-glucoside (**8**)[14] (Figure 1), based on the spectral data analysis such as 1D-, 2D-NMR and HR-EI-MS.

Compound **1** was isolated as yellow oil. The molecular formula of $C_{20}H_{26}O_9$ was determined on the basis of its HR-EI-MS molecular ion peak (*m/z* 410.156 7 $[M]^+$), in combination with an analysis of the ^{13}C NMR spectrum (DEPT), corresponding to eight degrees of unsaturation. The IR spectrum showed absorption bands of hydroxyl (3 405 cm^{-1}) and carbonyl groups (1 680 cm^{-1}). The ^{13}C NMR spectrum (Table 1) displayed 20 carbon signals: two CH_3 (δ_C 18.5, 14.5), three CH_2 (δ_C 74.6, 62.8, 62.5), eleven CH (δ_C 134.4, 130.6, 130.6, 129.7, 129.7, 122.3, 103.3, 78.2, 78.1, 75.2, 71.7) and four C (δ_C 170.0, 168.1, 139.6, 131.6). The ^1H NMR, COSY and HMBC spectra (Table 1, Figure 2) displayed the following moiety signals: one mono-substituted benzoyl [δ_C 168.1, 134.4, 131.6, 130.6, 130.6, 129.7, 129.7; δ_H 8.01 (2H, dd, *J* = 7.8, 1.2 Hz), 7.60 (1H, m), 7.48 (2H, t, *J* = 7.8 Hz)], one glucosyl [δ_C 103.3, 78.2, 78.1, 75.2, 71.7, 62.8; δ_H 4.28 (1H, d, *J* = 7.8 Hz), 3.86 (1H, dd, *J* = 12.0, 1.8 Hz), 3.66 (1H, dd, *J* = 12.0, 5.4 Hz), 3.35 (1H, t, *J* = 9.0 Hz), 3.25 (3H, overlapped)], one acetyl [δ_C 170.0, 18.5; δ_H 2.21 (3H, s)], and one [-$OCH_2C(CH_3)$=$CHCH_2O$-] unit [δ_C 139.6, 122.3, 74.6, 62.5, 14.5; δ_H 5.83 (1H, dt, *J* = 7.2, 1.2 Hz), 4.90 (2H, d, *J* = 7.2 Hz), 4.31 (1H, d, *J* = 12.6 Hz), 4.11 (1H, d, *J* = 12.6 Hz), 1.84 (3H, s)]. The *β*-configuration of the glucose was determined from the coupling constant (7.8 Hz) of the anomeric proton signal in the ^1H NMR spectrum[15]. Further analysis of the HMBC spectrum (Figure 2) revealed the following connections: the correlation of H-6''/C-7'' indicated that the acetyl was linked to C-6'' of the *β*-*D*-glucopyranosyl unit; the correlation of H-1/C-1'' indicated that the *β*-*D*-glucopyranosyl moiety was linked to C-1; the correlation of H-4/C-7' indicated that the [-$OCH_2C(CH_3)$=$CHCH_2O$-] unit was linked to C-7'. Thus, the structure of **1** is elucidated and named as microintegerrin C (Figure 1).

Compound **2** was obtained as yellow oil. The HR-EI-MS revealed an ion peak at *m/z* 412.207 0 $[M]^+$, corresponding to the molecular formula $C_{21}H_{32}O_8$ (Calcd. 412.209 7). Comparison of the 1D- and 2D-

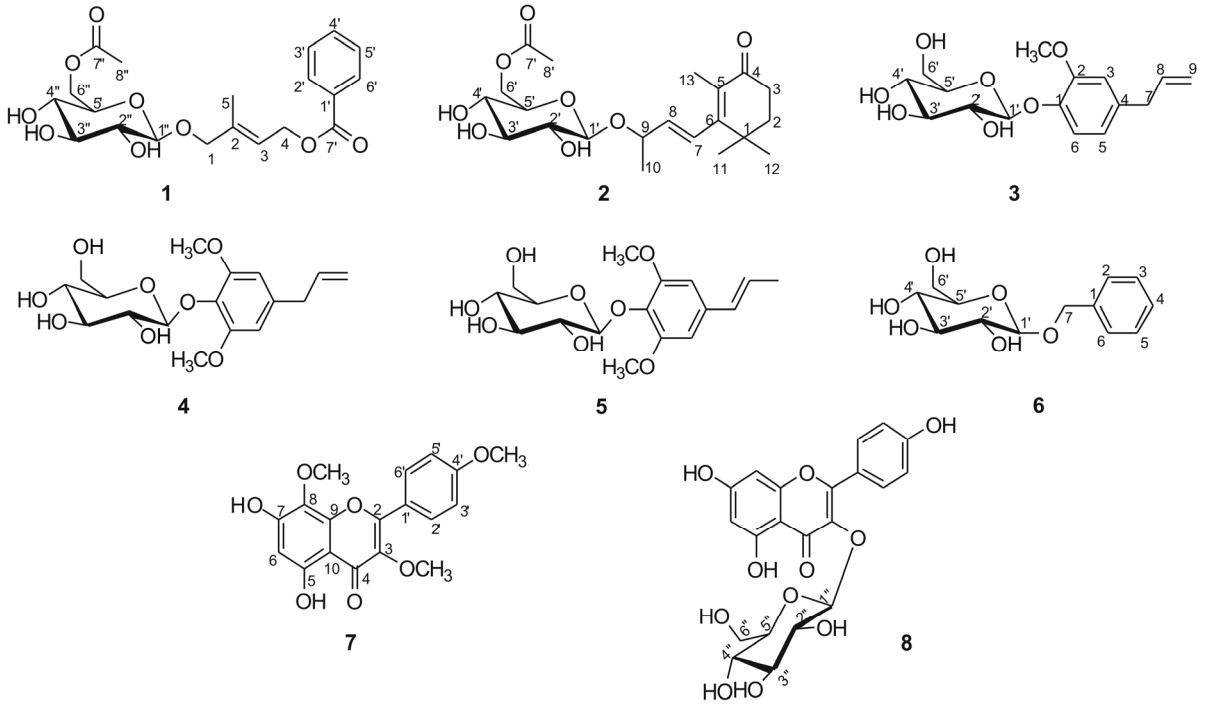

Figure 1 Structures of compounds **1**−**8**

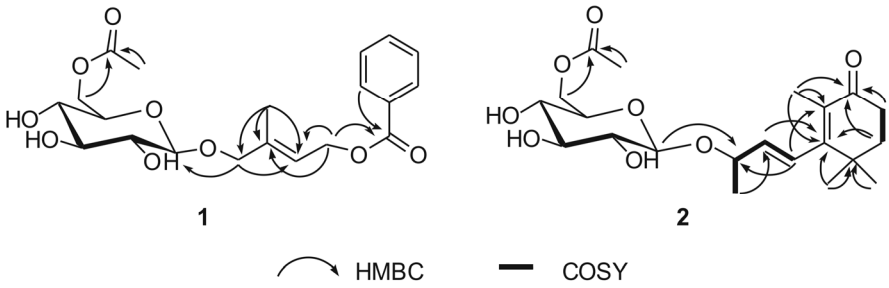

Figure 2 Key HMBC correlations of compounds **1** and **2**

Table 1 ^{1}H, ^{13}C NMR data of **1** and **2** at 600 and 150 MHz, in CD_3OD, respectively (*J* in Hz)

No.	1		2	
	δ_H	δ_C	δ_H	δ_C
1	4.31 (1H, d, 12.6)	74.6 (t)		36.7 (s)
	4.11 (1H, d, 12.6)			
2		139.6 (s)	1.87 (2H, t, 6.7)	38.3 (t)
3	5.83 (1H, dt, 7.2, 1.2)	122.3 (d)	2.50 (2H, t, 6.7)	35.3 (t)
4	4.90 (2H, d, 7.2)	62.5 (t)		201.9 (s)
5	1.84 (3H, s)	14.5 (q)		130.8 (s)
6				163.8 (s)
7			6.41 (1H, d, 16.2)	129.8 (d)
8			5.61 (1H, dd, 16.2, 7.4)	139.4 (d)
9			4.60 (1H, m)	75.3 (d)
10			1.35 (3H, d, 6.5)	22.3 (q)
11			1.19 (3H, s)	27.9 (q)
12			1.20 (3H, s)	27.8 (q)
13			1.80 (3H, s)	13.9 (q)
1'		131.6 (s)	4.38 (1H, d, 7.8)	101.5 (d)
2'	8.01 (1H, dd, 7.8, 1.2)	130.6 (d)	3.25 (1H, overlapped)	75.1 (d)
3'	7.48 (1H, t, 7.8)	129.7 (d)	3.25 (1H, overlapped)	78.3 (d)
4'	7.60 (1H, m)	134.4 (d)	3.25 (1H, overlapped)	71.8 (d)
5'	7.48 (1H, t, 7.8)	129.7 (d)	3.25 (1H, overlapped)	78.3 (d)
6'	8.01 (1H, dd, 7.8, 1.2)	130.6 (d)	3.89 (1H, dd, 11.9, 2.1)	63.0 (t)
			3.66 (1H, dd, 11.9, 6.1)	
7'		168.1 (s)		170.0 (s)
8'			2.21 (3H, s)	18.5 (q)
1"	4.28 (1H, d, 7.8)	103.3 (d)		
2"	3.25 (1H, overlapped)	75.2 (d)		
3"	3.35 (1H, t, 9.0)	78.2 (d)		
4"	3.25 (1H, overlapped)	71.7 (d)		
5"	3.25 (1H, overlapped)	78.1 (d)		
6"	3.86 (1H, dd, 12.0, 1.8)	62.8 (t)		
	3.66 (1H, dd, 12.0, 5.4)			
7"		170.0 (s)		
8"	2.21 (3H, s)	18.5 (q)		

NMR data of **2** with those of 4-oxo-*β*-ionol *β-D*-glucopyranoside[15] suggested their structures were closely related, except for an additional acetyl group [δ_C 170.0, 18.5; δ_H 2.21 (3H, s)]. In the HMBC spectrum (Figure 2), the correlation of H-6'a/C-7' indicated the acetyl was connected with C-6' of the *β-D*-glucopyranose. Therefore, compound **2** was elucidated and named as microintegerrin D (Figure 1).

Experimental

General experiment procedures Optical rotations were measured with a Horiba SEPA-300 polarimeter. UV spectra were recorded using a Shimadzu UV-2401A spectrophometer. CD spectra were recorded on a Chirascan Circular Dichroism spectrometer. IR spectra were obtained on a Tensor 27 spectrometer with KBr pellets. 1D and 2D NMR spectra were performed on the Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), Bruker AVANCE III-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or AV-600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) spectrometer with TMS as the internal standard. Mass spectra were measured on a VG Auto Spec-3000 or API-Qstar-Pulsar instrument. Column chromatography was performed using silica gel (100−200 and 200−300 mesh, Qingdao marine Chemical Inc., China), Sephadex LH-20 (Amersham Biosciences, Sweden), MCI (CHP-20P, Mitsubishi, Japan) or Lichroprep RP-18 (40−63 mm, Merck, Darmstadt, Germany). Fractions were monitored by TLC (GF254, Qingdao Marine Chemical Inc., China). Spots were first visualized under UV light (254 and 365 nm), followed by spraying with 5% H_2SO_4 in EtOH and then heating. Analytical or semi-preparative HPLC was performed on Agilent 1100 with Eclipse XDB-C18 (Agilnent, 9.4 mm×250 mm). Preparative HPLC was performed on an Agilent 1100 apparatus with a diode-array detector and a Sun Fire^{TM} Pre C_{18} OBD^{TM} (Waters, 19 mm×250 mm, 5 μm) column.

Plant material The stems and leaves of *M. integerrimum* were collected in Xishuangbanna, Yunnan Province, China, in September 2011, and authenticated by Prof. Hua Peng, Kunming Institute of Botany, Chinese Academy of Sciences, where a voucher specimen (KUN No. 0182256) was deposited.

Extraction and isolation Air-dried stems and leaves of *M. integerrimum* (29.0 kg) were extracted with methanol at 70 ℃ under reflux for four times. The extract was concentrated in vacuum to give a residue (4.5 kg), which was suspended in water, and then partitioned successively with petroleum ether, EtOAc, and *n*-BuOH. The EtOAc extract (530.0 g) and *n*-BuOH extract (600.0 g) were subjected separately to silica gel (100−200 mesh) column, and eluted with $CHCl_3$−MeOH gradient (1∶0, 30∶1, 15∶1, 9∶1, 8∶2, 7∶3, 1∶1, 0∶1, *v*/*v*) to give 26 fractions (Fr. A1 to Fr. A26) and 19 fractions (Fr. B1 to Fr. B19) separately, monitored by TLC. Fr. A18 (21.0 g) was further separated to obtain **2** (20.6 mg), **3** (64.8 mg) and **6** (49.4 mg) by MPLC and preparative HPLC with the eluent of MeOH/H_2O and CH_3CN/H_2O. Fr. A24 (10.0 g) was subjected to silica gel column (200−300 mesh) and eluted with a CH_3Cl/MeOH gradient to afford 6 fractions (Fr. A24-1 to Fr. A24-6). Fr. A24-3 and Fr. A24-6 were chromatographed through sephadex LH-20 eluted with MeOH and semi-preparative HPLC with the eluent of CH_3CN/H_2O to yield **1** (5.9 mg) and **8** (16.0 mg). Fr. B3 (30.0 g) was further purified by means of MPLC on RP-18 eluting with MeOH/H_2O, followed by semi-preparative HPLC with the eluent of CH_3CN/H_2O to give the pure **7** (696.1 mg). Fr. B7 was further chromatographed through MCI column with the eluent of MeOH/H_2O, semi-preparative and preparative HPLC with the eluent of CH_3CN/H_2O to yield **4** (0.6 mg) and **5** (183.6 mg).

Microintegerrin C (1) Yellow oil; $C_{20}H_{26}O_9$; $[\alpha]_D^{17.9}$ −22.4 (*c* 0.16, MeOH); positive ESI-MS *m/z* : 449 $[M+K]^+$; HR-EI-MS: *m/z* 410.156 7 $[M]^+$ (Cacld. For $C_{20}H_{26}O_9$: 410.157 7); IR (KBr): 3 405, 2 924, 1 680, 1 452, 1 430, 1 384, 1 278, 1 205, 1 137, 1 074, 1 027, 839, 802 and 720 cm^{-1}; UV (MeOH) λ_{max} (log ε): 201 (4.2), 226 (4.0), and 273 (3.4) nm; CD (MeOH): 218 ($\Delta\varepsilon$ −0.01) nm; ^1H and ^{13}C NMR spectral data, see Table 1.

Microintegerrin D (2) Yellow oil; $C_{21}H_{32}O_8$; $[\alpha]_D^{23.3}$ −30.8 (*c* 0.21, MeOH); EI-MS *m/z*: 412 $[M]^+$; HR-EI-MS *m/z* 412.207 0 $[M]^+$ (Calcd. for $C_{21}H_{32}O_8$: 412.209 7); IR (KBr): 3 383, 2 969, 2 934, 1 677, 1 514, 1 429, 1 383, 1 204, 1 187, 1 138, 1 076, 1 037, 840, 802 and 723 cm^{-1}; UV (MeOH) λ_{max} (log ε): 203 (3.9), 261 (3.5) nm; CD (MeOH): 265 ($\Delta\varepsilon$ −0.50) nm; ^1H and ^{13}C NMR spectral data, see Table 1.

2-Methoxy-4-(2-propenyl)-phenyl-*β*-*D*-glucopyranoside (3) White solid; $C_{16}H_{22}O_7$; positive ESI-MS *m/z* 349 $[M+Na]^+$; ^1H NMR (CD_3OD, 600 MHz) δ: 7.08 (1H, d, *J* = 7.8 Hz, H-6), 6.83 (1H, d, *J* = 1.8 Hz, H-3), 6.72 (1H, dd, *J* = 7.8, 1.8 Hz, H-5), 5.95 (1H, m, H-8), 5.06 (1H, dd, *J* = 16.8, 1.8 Hz, H-9b), 5.03 (1H, dd, *J* = 9.6, 1.8 Hz, H-9a), 4.86 (1H, d, *J* = 7.8 Hz, H-1'), 3.87 (1H, d, *J* = 10.8 Hz, H-6'a), 3.84 (3H, s, 2-OCH_3), 3.69 (1H, m, H-6'b), 3.31−3.50 (6H, m, H-2'-5', 7); ^{13}C NMR (CD_3OD, 150 MHz) δ: 150.8 (C, C-2), 146.4 (C, C-1), 139.2 (CH, C-8), 136.5 (C, C-4), 122.2 (CH, C-5), 118.2 (CH, C-6), 116.0 (CH_2, C-9), 114.1 (CH, C-3), 103.1 (CH, C-1'), 78.3 (CH, C-3'), 77.9 (CH, C-5'), 75.0 (CH, C-2'), 71.4 (CH, C-4'), 62.6 (CH_2, C-6'), 56.8 (3-OCH_3), 40.9 (CH_2, C-7).

ErigesideⅡ (4) Needle (CH_3CN-H_2O); $C_{17}H_{24}O_8$; positive ESI-MS *m/z* 379 $[M+Na]^+$, 735 $[2M+Na]^+$; ^1H NMR ($CDCl_3$, 500 MHz) δ: 6.41 (2H, s, H-3, 5), 5.89 (1H, m, H-8), 5.08 (2H, m, H-9), 4.53 (1H, d, *J* = 7.7 Hz, H-1'), 3.81 (6H, s, OCH_3×2), 3.25−3.74 (6H, m, H-2'-6'); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 152.4 (C, C-2, 6), 137.5 (C, C-1), 136.7 (CH, C-8), 130.4 (C, C-4), 116.3 (CH_2, C-9), 105.7 (CH, C-3, 5), 103.0 (CH, C-1'), 76.2 (CH, C-3'), 76.1 (CH, C-5'), 74.1 (CH, C-2') , 69.5 (CH, C-4'), 61.6 (CH_2, C-6'), 56.2 (CH_3, OCH_3×2), 40.4 (CH_2, C-7).

Acantrifoside E (5) White powder; $C_{17}H_{24}O_8$; positive ESI-MS *m/z* 379 $[M+Na]^+$, 735 $[2M+Na]^+$; ^1H NMR (DMSO-d_6, 500 MHz) δ: 6.66 (2H, s, H-3, 5), 6.31 (1H, d, *J* = 16.1 Hz, H-7), 6.23 (1H, m, H-8), 4.87 (1H, d, *J* = 7.1 Hz, H-1'), 3.74 (6H, s, 2-OCH_3, 6-OCH_3), 3.00−3.56 (6H, m, H-2'-6'), 1.81 (3H, d, *J* = 6.2 Hz, H-9); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 152.7 (C, C-2, 6), 133.5 (C, C-1), 133.2 (C, C-4), 130.7 (CH, C-7), 125.0 (CH, C-8), 104.0 (CH, C-3, 5), 102.6 (CH, C-1'), 77.2 (CH, C-3'), 76.5 (CH, C-5'), 74.2 (CH, C-2'), 69.9 (CH, H-4'), 60.9 (CH_2, C-6'), 56.3 (CH_3, 3, 5-OCH_3), 18.2 (CH_3, C-9).

Benzyl *β*-*D*-glucopyranoside (6) White solid; $C_{13}H_{18}O_6$; positive ESI-MS *m/z* 293 $[M+Na]^+$, 563 $[2M+Na]^+$; ^1H NMR (CD_3OD, 400 MHz) δ: 7.44 (2H, d, *J* = 7.2 Hz, H-2, 6), 7.35 (2H, t, *J* = 7.2 Hz, H-3, 5), 7.29 (1H, t, *J* = 7.2 Hz, H-4), 4.95 (1H, d, *J* = 12.0 Hz, H-7b), 4.69 (1H, d, *J* = 12.0 Hz, H-7a), 4.38 (1H, d, *J* = 7.7 Hz, H-1'), 3.92 (1H, d, *J* = 11.9 Hz, H-6'a), 3.72 (1H, dd, *J* = 11.9, 5.3 Hz, H-6'b), 3.26−3.38 (4H, m, H-2'-5'); ^{13}C NMR (CD_3OD, 100 MHz) δ: 139.1 (C, C-1), 129.3 (CH, C-3, 5), 129.2 (CH, C-2, 6), 128.7 (CH, C-4), 103.3 (CH, C-1'), 78.1 (CH, C-3') , 78.0 (CH, C-5'), 75.1 (CH, C-2'), 71.7 (CH_2, C-7), 71.7 (CH, C-4'), 62.8 (CH_2, C-6').

5, 7-Dihydroxyl-3, 8, 4'-trimethoxylflavone (7) Yellow needle ($CHCl_3$-MeOH); $C_{18}H_{16}O_7$; positive ESI-MS *m/z* 711 $[2M+Na]^+$; ^1H NMR ($CDCl_3$, 400 MHz) δ: 12.45 (1H, s, OH), 8.13 (2H, d, J = 8.8 Hz, H-2', 6'), 7.06 (2H, d, J = 8.8 Hz, H-3', 5'), 6.43 (1H, s, H-6), 4.10 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 3.87 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.9 (C, C-4), 161.7 (C, C-4'), 157.3 (C, C-7), 155.6 (C, C-5), 155.1 (C, C-3), 148.0 (C, C-9), 138.7 (C, C-2), 130.0 (CH, C-2', 6'), 126.8 (C, C-8), 122.7 (C, C-1'), 114.2 (CH, C-3', 5'), 105.5 (C, C-10), 98.5 (CH, C-6), 61.9 (C, 3-OCH_3), 60.2 (C, 8-OCH_3), 55.4 (C, 4'-OCH_3),

Kaempferol 3-*O*-*β*-*D*-glucopyranoside (8) Yellow needle (MeOH); $C_{21}H_{20}O_{11}$: negative ESI-MS *m/z* 447 $[M-H]^+$, 895$[2M-H]^+$; ^1H NMR (DMSO-d_6, 500 MHz) δ: 12.62 (1H, s, OH), 10.97 (1H, s, OH), 10.26 (1H, s, OH), 8.04 (2H, d, J = 8.7 Hz, H-2', H-6'), 6.88 (2H, d, J = 8.7 Hz, H-3', H-5'), 6.44 (1H, s, H-8), 6.21 (1H, s, H-6), 5.46 (1H, d, J = 7.5 Hz, H-1''), 3.08−3.57 (6H, m, H-2''-6''); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 177.5 (C, C-4), 164.1 (C, C-7), 161.2 (C, C-5), 160.0 (C, C-4'), 156.4 (C, C-2), 156.2 (C, C-9), 133.1 (C, C-3), 130.9 (CH, C-2', 6'), 120.9 (C, C-1'), 115.1 (CH, C-3', 5'), 104.0 (C, C-10), 100.8 (CH, C-1''), 98.7 (CH, C-6), 93.6 (CH, C-8), 77.5 (CH, C-3''), 76.4 (CH, C-5''), 74.2 (CH, C-2''), 69.9 (CH, C-4''), 60.8 (CH_2, C-6').

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