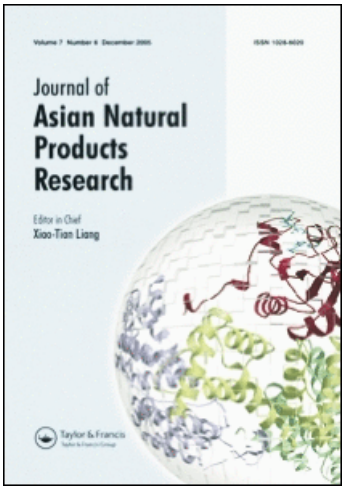

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A new *meta*-homoisoflavane from the fresh stems of *dracaena cochinchinensis*

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Note

A new *meta*-homoisoflavane from the fresh stems of *dracaena cochinchinensis*

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A new *meta*-homoisoflavane, 10,11-dihydroxydracaenone C (**1**), together with 7,4′-dihydroxyflavone (**2**), 7,4′-dihydroxyflavane (**3**), 4,4′-dihydroxy-2-methoxychalcone (**4**), 4,4′-dihydroxy-2-methoxydihydrochalcone (**5**), 7,4′-dihydrohomoisoflavanone (**6**), 7,4′-homoisoflavane (**7**), lophenol (**8**), β-sitosterol (**9**), stigma-5, 22-diene-3-ol (**10**), 1-(4′-*O*-β-D-glucopyranosyl)benzyl-ethan-2-ol (**11**), 3,4-dihydoxy-1-allylbenezene-4-*O*-α-L-rhamnopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside (**12**), 1-hydroxy-3,4,5-trimethoxybenzene-1-*O*-α-L-apiopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside (**13**), and tachioside (**14**) have been isolated from the fresh stems of *Dracaena cochinchinensis*. Their structures have been established by spectroscopic analysis, especially by 2D NMR. This is the first time compounds **11**, **13**, **14** have been isolated from *Dracaena*.

Keywords: 10,11-Dihydroxydracaenone C; *Dracaena cochinchinensis*; Agavaceae; Flavonoids; Phenolic glycosides; Sterols

1. Introduction

Dracaena cochinchinensis S. C. Chen is a tree of the family Agavaceae, growing in Southwest China, Myanmar, and Laos. In China, the red resin of this plant, named "longxuejie", was used as dragon's blood by local people to treat hurts and inflammation [1]. Chemical studies revealed that the resin contains phenolic compounds, steroids, and aliphatic acids [2–6]. Steroidal saponins had also been isolated from the fruits of *D. cochinchinensis* [7]. In a systematic chemical investigation on the resin and the original plants of dragon's blood we had reported two new C-22 steroidal lactone glycosides (dracaenoside A and B) and two new pregnane glycosides (dracaenoside C and D) from the fresh stems of this plant [8,9]. We report here the isolation and identification of a new *meta*-homoisoflavane,

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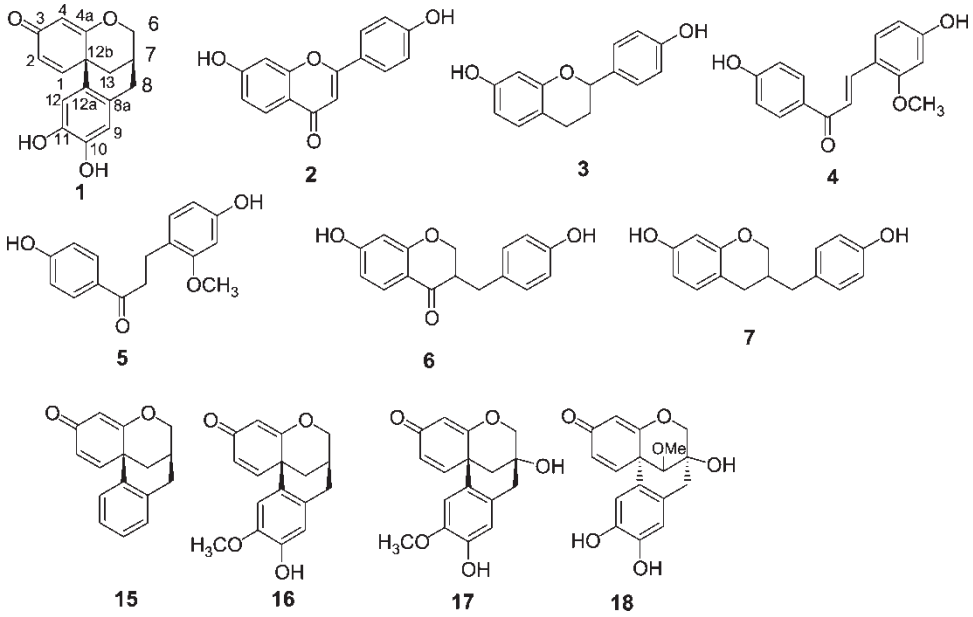

Figure 1. Structures of compounds **1**–**7** and **15**–**18**.

10,11-dihydroxydracaenon C (**1**), and 13 known compounds, including flavonoids (**2**–**7**, figure 1), sterols (**8**–**10**) and phenolic glycosides (**11**–**14**) from the fresh stems of this plant.

2. Results and discussion

Compound **1** was obtained as white crystals, mp >300°C, $[\alpha]_D^{21}$ -436.9 in MeOH. Negative HR-ESIMS gave a quasi-molecular peak at *m/z* 269.0812 ($[M - H]^-$, calcd. 269.0813) corresponding to a molecular formula of $C_{16}H_{14}O_4$, which indicates ten degrees of unsaturation. The absorptions at 3340, 1646, 1594 and 1521 cm^{-1} in the IR spectrum reveal the presence of a hydroxyl group, a carbonyl group and a benzene ring.

The ^{13}C NMR spectrum of **1** shows signals for all 16 carbon atoms, including one signal for a carbonyl group (δ_C 187.87), six quaternary carbons with three linked to an oxygen atom, six tertiary carbon atoms and three methylene carbon atoms (table 1). Detailed analysis of the ^1H NMR spectra of **1** reveals 5 protons bound to sp^2-type carbon atoms, including two singlets at δ 6.55, 6.31, an ABX spin system for another three protons at δ 6.80 (d, $J = 9.79$ Hz), 6.33 (dd, $J = 9.79, 1.69$ Hz) and 5.40 (d, $J = 1.69$ Hz), and 7 protons bound to sp^3-type carbon atoms (one CH, three CH_2) (table I)—consistent with the basic skeleton of draceanone (**15**) isolated earlier from *Dracaena loureiri* [10]. Long-range correlations observed in HMBC spectrum revealed the connection between these substructures. The signal at δ_H 2.36 (H-7) is correlated to three carbon atoms (CH_2) at δ 77.2 (C-6), 32.0 (C-13), and 33.8 (C-8) (C-ring). HMBC correlations from δ 6.80 to δ_C 128.7 (C-2), 42.1 (C-12b), 6.33 (H-2) to δ_C 128.7 (C-2), 42.1 (C-12b), and 5.40 (H-1) to δ 32.0 (C-7), 187.9 (C-3), 178.1 (C-4a), and 127.0 (C-12a) indicate the substructure of the A-ring. The protons at δ_H 3.12, 2.13 (H-8) show cross peaks with sp^2-type carbon atoms at δ_C 125.2 (C-8a), 116.1 (C-9), 127.0 (C-12a) (B-ring), while the singlet signal δ_H 6.31 (H-12) is correlated with 125.2

Table 1. ^{13}C (90.8 MHz) and ^{1}H (360 MHz) NMR data of compounds **1** and **16**.

	***1** in CD_3OD*			***16** in DMSO-d_6*		
Position	δ_C	δ_H *(ppm)*	*J (Hz)*	δ_C	δ_H *(ppm)*	*J (Hz)*
1	150.4	6.80, d	9.79	150.1	6.86, d	9.8
2	128.7	6.33, dd	9.79, 1.69	128.9	6.36, dd	9.8, 1.6
3	187.9			187.6		
4	107.2	5.40, d	1.69	107.6	5.45, d	1.6
4a	178.1			177.6		
6	77.2	ax, 4.12, dd	2.40, 11.08	77.3	ax, 4.13, dd	2.5, 10.9
		eq, 4.30, d	11.08		eq, 4.34, d	10.9
7	28.2	2.36, m		28.0	2.39, m	
8	33.8	ax, 3.12, dd eq,	17.04, 6.20 17.20	33.8	ax, 3.13, dd eq,	16.1, 6.3 16.1
		2.83, d			2.89, d	
8a	125.2			129.1		
9	116.1	6.55, s		116.1	6.63, s	
10	145.2			146.4		
11	143.4			145.8		
12	112.9	6.31, s		109.8	6.34, s	
12a	127.0			125.1		
12b	42.1			42.3		
13	32.0	ax, 1.97, dd	2.90, 12.44	32.3	ax, 2.04, dd	2.9, 12.6
		eq, 2.13, d	12.44		eq, 2.17, d	12.6
OCH_3				55.7	3.59	

(C-8a), 42.1 (C-12b). Other C-H connectivities provide evidence for the assignment of the ^{13}C NMR resonance of **1** (figure 2).

The NMR character of **1** is very similar to **16**. Neither **16** nor **17** have been isolated from *Dracaena loureiri* [10]. The stereochemistry of **1** was deduced from the optical rotation data compared with that of **16** ($[\alpha]_D^{21}$ −411.3, *c* 0.025, in MeOH). Compound **18** (caesalpin J) has been isolated from *Caesalpinia sappan* and has a positive optical rotation ($[\alpha]_D^{21}$ +445.0, in MeOH) [11]. The structure of **18** was established by an X-ray crystallographic study of its triacetate [12]. On these evidences, the stereochemistry of **1** was deduced as shown in figure 2. The proposed formation mechanism of **1** is shown in figure 3. Thus, the structure of **1** was established, and named as 10,11-dihydroxydracaenone C.

Along with the new *meta*-homoisoflavane, 13 known compounds were also obtained. By comparing their spectral data with those reported in the literature, these compounds were

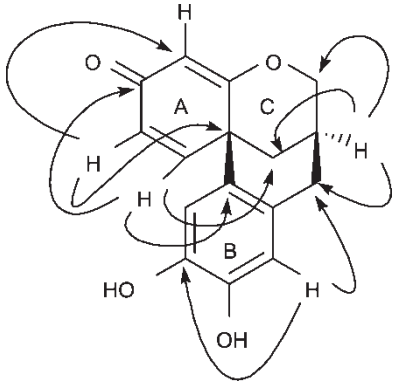

Figure 2. Selected HMBC correlations of **1**.

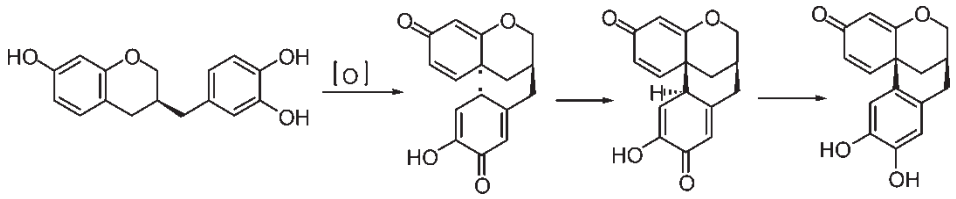

Figure 3. Postulated biogenesis of **1**.

identified as 7,4′-dihydroxyflavone (**2**) [13], 7,4′-dihydroxyflavane (**3**) [3,6], 4,4′-dihydroxy-2-methoxychalcone (**4**) [13], 4,4′-dihydroxy-2-methoxydihydrochalcone (**5**, loureirin C) [14], 7,4′-dihydrohomoisoflavanone (**6**) [15], 7,4′-homoisoflavane(**7**) [15], lophenol (**8**) [16], β-sitosterol (**9**) [16], stigma-5,22-diene-3-ol (**10**) [16], 1-(4′-*O*-β-D-glucopyranosyl)benzyl-ethan-2-ol (**11**) [17], 3,4-dihydoxy-1-allylbenezene-4-*O*-α-L-rhamnopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside (**12**) [4], 1-hydroxy-3,4,5-trimethoxybenzene-1-*O*-α-L-apiopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside (**13**) [18], and tachioside (**14**) [18]. This is the first study on the fresh stems of *D. cochinchinensis*. Compounds **11**, **13**, **14** were isolated from *Dracaena* plants for the first time.

3. Experimental

3.1 General experimental procedures

NMR spectra were run on Bruker AM-400 (for ^{1}H and ^{13}C NMR) and DRX-500 (for 2D NMR) instruments with TMS as internal standard; IR spectra were measured on a Bio-Rad FTS-135 spectrometer with KBr pellets. FAB-MS spectra were recorded on a VG Auto Spec-300 spectrometer. UV spectra were obtained on a Shimadzu double-beam 210A spectrophotometer. Silica gel (200–300 mesh and 10–40 μm), RP-18 (40–63 μm) and Sephadex LH-20 were used for column chromatography.

3.2 Plant material

Fresh stems of *Dracaena cochinchinensis* were collected at Xishuangbanna, Yunnan, China. A voucher specimen has been deposited in the State Key Laboratory of Phytochemistry and Plant Resources in west China, Kunming Institute of Botany, Chinese Academy of Sciences.

3.3 Extraction and isolation

Chipped fresh stems of *D. cochinchinensis* (25.0 kg) were extracted with hot MeOH. The MeOH extract was then condensed under reduced pressure, and the resultant viscous concentrate was partitioned between H_2O and EtOAc, n-BuOH successively. The EtOAc fraction (90 g) was submitted to repeated column chromatography on silica gel, and finally purified by column chromatography on Sephadex LH-20 to afford compounds **1** (30 mg), **2** (1.72 g), **3** (493 mg), **4** (889 mg), **5** (560 mg), **6** (393 mg), **7** (324 mg), **8** (28 mg), **9** (60 mg), **10** (36 mg). The n-butanol fraction was submitted to column chromatography on highly porous absorption resin (Diaion HP-20), eluting with H_2O and methanol. The methanol fraction

(150 g) was repeatedly column chromatographed (CC) over normal and reversed-phase silica gel to afford three fractions (Fr. I–III). Fr. I then was subjected to ODS CC and silica gel, eluting with H_2O–MeOH (gradient proportion), to afford compounds **11** (26 mg), **12** (49 mg), **13** (93 mg), **14** (33 mg).

3.3.1 10,11-Dihydroxydracaenone C (1). $C_{16}H_{14}O_4$, white needle, mp >300°C; $[\alpha]_D^{24}$ −436.90 (*c* 0.7, MeOH). UV λ_{max} (MeOH) (nm): 221.5, 240.3, 284.0; IR (KBr) ν_{max} (cm^{-1}): 3367 (br, OH), 2915 (CH), 2823, 1646 (C═O), 1594, 1579, 1521, 1456, 1406, 1252, 1200, 1176, 1111, 888, 864; EIMS *m/z* (%) 270 $[M]^+$ (100), 255 (5), 241 (7), 227 (13), 212 (16), 201 (12), 183 (10), 153 (10), 139 (14), 123 (17), 115 (16), 91 (7), 77 (14), 69 (13). Negative ion FAB-MS: *m/z* 269 $[M-1]^-$; negative ion HR-ESIMS: *m/z* 269.0812 $[M-1]^-$, calcd. for $C_{16}H_{14}O_4$, 269.0813; ^1H (400 MHz, CD_3OD) and ^{13}C (100 MHz, CD_3OD) NMR: see table I.

3.3.2 7,4′-Dihydroxyflavone (2). $C_{15}H_{10}O_4$, yellow powder; UV (MeOH) λ_{max} (nm): 237; IR (KBr) ν_{max} (cm^{-1}): 3433 (br, OH), 2933 (CH), 1652 (C═O), 1374, 1041, 887. Negative ion FAB-MS: *m/z* 254 $[M]^+$, 226; ^1H NMR (400 MHz, CD_3OD) δ (ppm): 6.69 (1H, s, H-3), 6.91 (2H, d, $J = 8.52$ Hz, H3′,5′), 6.94 (1H, dd, $J = 8.68, 2.0$ Hz, H-6), 6.90 (1H, d, $J = 2.0$ Hz, H-8), 7.85 (1H, d, $J = 8.68$ Hz, H-5), 7.89 (1H, d, $J = 8.52$ Hz, H2′,6′); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 162.5 (C-2), 104.5 (C-3), 176.3 (C-4), 116.1 (C-4a), 114.8 (C-5), 126.5 (C-6), 162.6 (C-7), 102.5 (C-8), 157.4 (C-8a), 121.8 (C-1′), 128.1 (C-2′, 6′), 115.9 (C-3′, 5′), 160.7 (C-4′).

3.3.3 7,4′-Dihydroxyflavane (3). $C_{15}H_{14}O_3$, colorless crystal; EI-MS: *m/z* 242 $[M]^+$ (98), 225 (17), 147 (15), 136 (25), 123 (80), 120 (100), 107 (70), 91 (40), 77 (16), 65 (32); UV (MeOH) λ_{max} (nm) (log ε): 209.8 (2.73), 224 (1.98), 282 (0.54); IR (KBr) ν_{max} (cm^{-1}): 3463 (br, OH), 3383, 1611, 1593, 1340, 1154, 1072, 999, 839; ^1H NMR (400 MHz, CD_3OD) δ (ppm): 6.24 (1H, s, H-8), 6.28 (1H, d, $J = 8.20$ Hz, H-6), 6.72 (1H, d, $J = 8.40$ Hz, H-3′, 5′), 6.89 (1H, d, $J = 8.20$ Hz, H-5), 7.12 (1H, d, $J = 8.40$ Hz, H-2′,6′), 4.80 (1H, dd, $J = 9.90, 1.65$ Hz, H-2), 2.73 (1H, m, H-3), 2.57 (1H, m, H-3), 1.99 (1H, m, H-4), 1.94 (1H, m, H-4); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 77.7 (C-2), 29.7 (C-3), 24.4 (C-4), 113.2 (C-4a), 129.8 (C-5), 108.1 (C-6), 156.3 (C-7), 103.2 (C-8), 155.6 (C-8a), 132.8 (C-1′), 127.5 (C-2′,6′), 115.6 (C-3′,5′), 156.0 (C-4′).

3.3.4 4,4′-Dihydroxy-2-methoxychalcone (4). $C_{16}H_{12}O_4$, yellow powder; EI-MS: *m/z* 268 $[M]^+$, 226; UV (MeOH) λ_{max} (nm): 204, 236; IR (KBr) ν_{max} (cm^{-1}): 3294 (br, OH), 2937 (CH), 1647, 1619, 1586, 1560, 1511, 1338, 1249, 1217, 1049, 824; ^1H NMR (400 MHz, CD_3OD) δ (ppm): 6.42 (1H, dd, $J = 8.45, 1.90$ Hz, H-5), 6.48 (1H, d, $J = 1.90$ Hz, H-2), 6.80 (1H, d, $J = 8.60$ Hz, H-3′,5′), 7.35 (1H, d, $J = 15.70$ Hz, H-α), 7.44 (1H, d, $J = 15.70$ Hz, H-β), 7.48 (1H, d, $J = 8.45$ Hz, H-6), 7.52 (1H, d, $J = 8.60$ Hz, H-2′,6′); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 141.1 (C-β), 123.6 (C-α), 188.7 (C═O), 125.6 (C-1), 131.8 (C-2, 6), 107.5 (C-3, 5), 160.1 (C-4), 119.9 (C-1′), 129.9 (C-2′, 6′), 115.5 (C-3′, 5′), 162.2 (C-4′), 55.3 (OMe).

3.3.5 4,4′-Dihydroxy-2-methoxydihydrochalcone (5, Loureirin C). $C_{16}H_{16}O_4$, colorless crystal; EI-MS: *m/z* 272 $[M]^+$ (65), 239 (11), 151 (17), 137 (100), 121 (89), 107 (28), 93 (30), 77 (15), 65 (29); IR (KBr) ν_{max} (cm^{-1}): 3406 (br, OH), 3139, 2949, 2824, 1654 (C═O), 1595, 1576, 1511, 1287, 1035, 983, 821. ^1H NMR (400 MHz, CD_3OD) δ (ppm): 7.82 (1H, d, $J = 9.45$ Hz, H-2′,6′), 6.80 (1H, d, $J = 9.45$ Hz, H-3′,5′), 6.88 (1H, d, $J = 8.0$ Hz, H-6), 6.37 (1H, d, $J = 2.75$ Hz, H-5), 6.27 (1H, dd, $J = 2.25, 8.0$ Hz, H-3), 3.07 (1H, t, $J = 7.30$ Hz, C-β), 2.82 (1H, t, $J = 7.30$ Hz, C-α), 3.72 (3H, OCH_3); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 39.1 (C-β), 26.8 (C-α), 201.7 (C═O), 130.0 (C-1), 159.6(C-2′), 99.7 (C-3), 158.1 (C-4), 107.6 (C-5), 131.3 (C-6), 121.3 (C-1′), 131.9 (C-2′,6′), 116.2 (C-3′,5′), 163.6 (C-4′), 55.5 (OMe).

3.3.6 7,4′-Dihydrohomoisoflavanone (6). $C_{16}H_{14}O_4$, white crystal; EI-MS *m/z* 270 $[M]^+$ (80), 253 (7), 33 (25), 107 (78), 85 (13), 73 (100), 60 (84); UV (MeOH) λ_{max} (nm) (log ε): 212.6 (2.42), 275.6 (1.43), 312.2 (0.76); IR (KBr) ν_{max} (cm^{-1}): 3411 (br, OH), 3129, 2927 (CH), 1653 (C═O), 1612, 1585, 1513, 1382, 1240, 1031, 855; ^1H NMR (400 MHz, CD_3OD) δ (ppm): 6.18 (1H, d, $J = 1.65$ Hz, H-8), 6.36 (1H, dd, $J = 8.75, 1.65$ Hz, H-6), 6.61 (2H, d, $J = 8.45$ Hz, H3′,5′), 6.91 (2H, d, $J = 8.45$ Hz, H-2′,6′), 7.69 (1H, d, $J = 8.75$ Hz, H-5), 4.15 (1H, dd, $J = 11.50, 4.15$ Hz, H-2), 3.97 (1H, dd, $J = 11.50, 7.70$ Hz, H-2), 2.93 (1H, dd, $J = 11.39, 4.60$ Hz, H-9), 2.47 (1H, dd, $J = 11.39, 4.60$ Hz, H-9), 2.61 (1H, m, H-3); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 70.7 (C-2), 48.9 (C-3), 195.1 (C-4), 114.6 (C-4a), 130.3 (C-5), 111.8 (C-6), 166.5 (C-7), 103.5 (C-8), 157.1 (C-8a), 33.0 (C-9), 130.4 (C-1′), 131.1 (C-2′,6′), 116.4 (C-3′,5′), 165.4 (C-4′).

3.3.7 7,4′-Homoisoflavane (7). $C_{16}H_{16}O_3$, colorless crystal; EI-MS *m/z* 256 $[M]^+$ (92), 161 (12), 148 (67), 133 (26), 123 (35), 107 (100), 73 (6), 55 (13); UV (MeOH) λ_{max} (nm) (log ε): 209 (2.56), 224 (1.77), 281 (0.54); IR (KBr) ν_{max} (cm^{-1}): 3587 (br, OH), 3287, 2916, 1600, 1512, 1237, 1151, 1029, 852; ^1H NMR (400 MHz, CD_3OD) δ (ppm): 6.27 (1H, d, $J = 3.65$ Hz, H-8), 6.77 (1H, dd, $J = 8.30, 3.65$ Hz, H-6), 6.73 (2H, d, $J = 8.15$ Hz, H3′,5′), 6.96 (2H, d, $J = 8.15$ Hz, H-2′,6′), 6.33 (1H, d, $J = 8.30$ Hz, H-5), 4.07 (1H, dd, $J = 10.60, 1.25$ Hz, H-2), 3.70 (1H, dd, $J = 10.60, 8.65$ Hz, H-2), 2.63 (1H, dd, $J = 15.70, 2.0$ Hz, H-9), 2.35 (1H, dd, $J = 15.70, 8.90$ Hz, H-9), 2.52 (1H, dd, $J = 13.30, 7.45$ Hz, H-4), 2.46 (1H, dd, $J = 13.30, 7.40$ Hz, H-4), 2.15 (1H, m, H-3); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 69.9 (C-2), 34.2 (C-3), 30.1 (C-4), 113.1 (C-4a), 130.3 (C-5), 108.7 (C-6), 155.3 (C-7), 102.8 (C-8), 154.8 (C-8a), 36.9 (C-9), 130.6 (C-1′), 129.9 (C-2′,6′), 115.2 (C-3′,5′), 154.5 (C-4′).

3.3.8 1-Hydroxy-3,4,5-trimethoxybenzene-1-*O*-α-L-apiopyranosyl-(1 → 6)-*O*-β-D-glucopyranoside (13). $C_{20}H_{30}O_{13}$, white powder; negative ion FAB-MS: *m/z* 478 $[M]^+$; IR (KBr) ν_{max} (cm^{-1}): 3396 (br, OH), 2932, 1601, 1505, 1462, 1229, 1127, 1063, 823; ^1H NMR (400 MHz, CD_3OD) δ (ppm): 6.49 (2H, s, H-2, 6), 4.91 (1H, d, $J = 7.55$ Hz), 5.03 (1H, d, $J = 3.0$ Hz), 3.94 (6H, s), 3.73 (3H, s); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 155.5 (C-1), 96.1 (C-2,6), 154.4 (C-3,5), 134.2 (C-4), 102.7 (glu-1), 74.4 (glu-2), 77.2 (glu-3), 71.0 (glu-4), 77.7 (glu-5), 68.6 (glu-6), 110.4 (api-1), 69.7 (api-2), 80.4 (api-3), 74.7 (api-4), 64.8 (api-5), 56.8 (OMe), 61.6 (OMe).

3.3.9 Tachioside (14). $C_{13}H_{18}O_8$, white powder, $[\alpha]_D^{22}$ −55.4 (MeOH, *c* 0.4); negative ion FAB-MS: *m/z* 301 $[M\text{-}H]^-$; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 6.81 (1H, d, $J = 2.0$ Hz, H-2), 6.69 (1H, d, $J = 8.60$ Hz, H-6), 6.59 (1H, dd, $J = 2.0, 8.6$ Hz, H-5), 4.74 (1H, d, $J = 7.30$, C-1′), 3.71 (3H, s, OCH_3). ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 142.9 (C-1), 149.2 (C-2), 103.8 (C-3), 152.8 (C-4), 110.0 (C-5), 116.0 (C-6), 103.7 (glu-1), 75.0 (glu-2), 78.1 (glu-3), 71.5 (glu-4), 78.0 (glu-5), 62.6 (glu-6).

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