Five New Biflavonoids from *Daphne aurantiaca*

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Five new biflavonoids, **1**–**5**, were isolated from the stem bark of *Daphne aurantiaca*. The structures were elucidated as 2,2″-bisteppogenin (**1**), 2,2″-bisteppogenin 7-*O*-*β*-glucopyranoside (**2**), 2‴-dehydroxy-2,2″-bisteppogenin (**3**), 2‴-dehydroxy-2,2″-bisteppogenin 7-*O*-*β*-glucopyranoside (**4**), and 7-methoxyneochamaejasmin B (**5**) on the basis of spectral analyses.

Introduction. – *Daphne aurantiaca* DIELS is a common evergreen shrub native to Yunnan and Sichuan provinces in China. Its stem bark is used for the treatment of injuries from falls and bruises in folk medicine [1]. In our previous study of *D. aurantiaca*, the occurrence of 17 terpenoids had been reported [2]. In the course of our study on the constituents of thymelaeaceous plants [2–5], five new biflavonoids, **1**–**5** (see *Fig. 1*), were isolated from the title plant. Here, we report the isolation and structure elucidation of the five new compounds.

Results and Discussion. – 2,2″-Bisteppogenin (**1**) was obtained as a brown oil (MeOH). The empirical molecular formula, $C_{30}H_{22}O_{12}$, was established by HR-ESI-MS (*m*/*z* 573.1034 ($[M-H]^-$)). The UV spectrum had two strong maxima in the short-wave region (at 226 and 294 nm) and an ill-defined maximum in the long-wave region (at 335 nm), which was similar to that of steppogenin (=2′,4′,5,7-tetrahydroxyflavanone) [6]. The assignments of the ^{1}H- and ^{13}C-NMR data (*Table 1*) were achieved by comparison with the data of steppogenin [7], and confirmed by COSY, HSQC, HMBC, and NOESY experiments.

The ^{13}C-NMR and DEPT spectra of **1** revealed 15 C-atom resonances, including those of seven CH groups and of eight quaternary C-atoms, which suggested that **1** would be a symmetric structure. In the ^{1}H-NMR spectrum, three aromatic H-atom signals in an *ABX* pattern (δ(H) 6.27 (*d*, $J=2.0$, H–C(3′)), 6.20 (*dd*, $J=8.4$, 2.0, H–C(5′)), and 6.61 (*d*, $J=8.4$, H–C(6′))) indicated a 1,2,4-trisubstituted aromatic ring [7], and other two aromatic H-atom signals (δ(H) 6.20 (*d*, $J=2.0$, H–C(6″)) and 5.79 (*d*, $J=2.0$, H–C(6″))) indicated a 1,3,4,5-tetrasubstituted aromatic ring. The NMR data of **1** (*Table 1*) revealed the presence of a CO group (δ(C) 198.9 (C(4))), an O-bearing CH_2 group (δ(C) (78.8, C(2)), and δ(H) 6.24 (br. *s*, H–C(2))), and a CH group (δ(C)

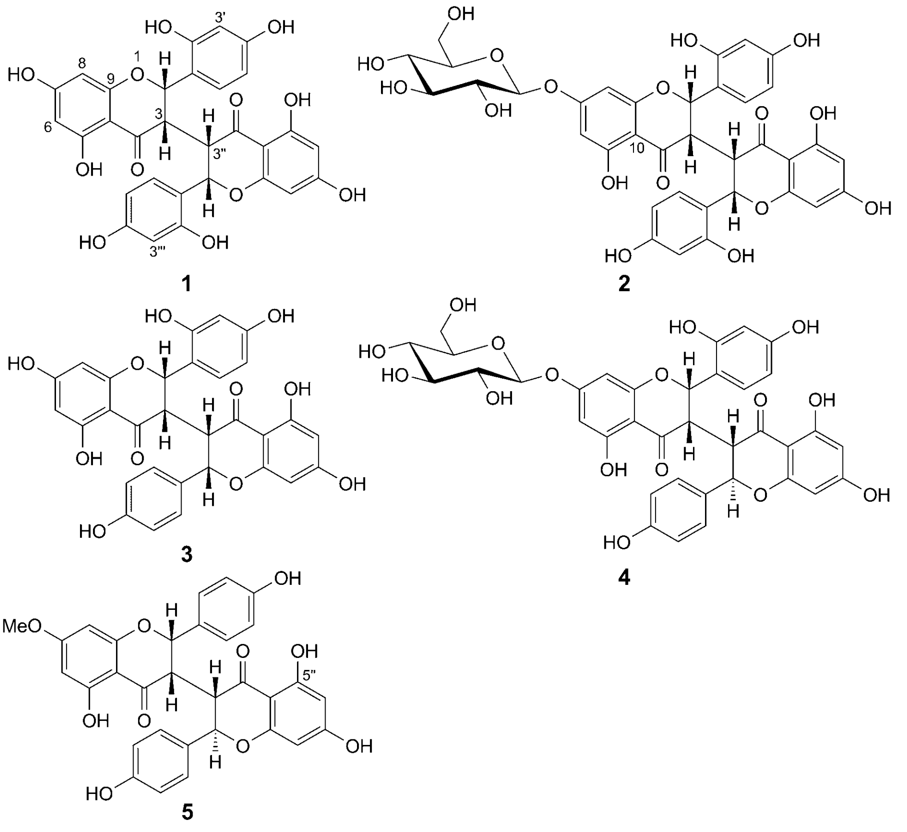

Fig. 1. *Structures of compounds* **1**–**5**

49.9 (C(3)), and δ(H) 2.99 (br. *s*, H–C(3))). The NMR spectra of **1** were analogous to those of steppogenin [7], except for the signals due to a CH group (δ(C) 49.9 (C(3))) instead of those due to a CH_2 group (δ(C) 42.3 (C(3))) in steppogenin. Thus, compound **1** was determined as 2,2″-bisteppogenin.

Compound **2** had a molecular formula $C_{36}H_{32}O_{17}$ as deduced from HR-ESI-MS (*m/z* 735.1580 ([*M* – H]$^-$)). The assignments of the ^{1}H- and ^{13}C-NMR data (*Table 1*) were accomplished by comparison with the data of compound **1**, and confirmed by COSY, HSQC, HMBC, and NOESY experiments.

In the ^{1}H-NMR spectrum, signals of two pairs of aromatic H-atoms in an *ABX* pattern (δ(H) 6.30 (*d*, $J = 2.0$, 2 H), 6.22 (*dd*, $J = 8.4$, 2.0, 2 H), and 6.65 (*d*, $J = 8.4$, 2 H)) revealed two 1,2,4-trisubstituted aromatic rings, and those of other two pairs of aromatic H-atoms in an *AX* pattern (δ(H) 6.17 (*d*, $J = 2.0$, 2 H), and 5.86 (*d*, $J = 2.0$, 1 H); 6.12 (*d*, $J = 2.0$, 2 H), and 5.81 (*d*, $J = 2.0$, 1 H)) established the presence of two 1,3,4,5-tetrasubstituted aromatic rings. The ^{13}C-NMR and DEPT data of **2** (*Table 1*) contained C-atom resonances due to two CO groups (δ(C) 199.6 (C(4)), and 198.6 (C(4″))), two O-bearing CH_2 groups (δ(C) 78.0 (C(2) and C(2″))), two CH groups

Table 1. *^{1}H- and ^{13}C-NMR Data of Compounds* **1**–**3**. In CD_3OD, δ in ppm, *J* in Hz. C-Atom numbering as indicated in *Fig. 1.*

	1		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
H–C(2)	6.24 (br. *s*)	78.8	6.20 (br. *s*)	78.0	6.15 (br. *s*)	82.3
H–C(3)	2.99 (br. *s*)	49.9	3.07 (br. *s*)	49.9	2.80 (br. *s*)	50.4
C(4)		198.9		199.6		198.9
C(5)		165.4		165.3		165.5
H–C(6)	6.20 (*d*, *J* = 2.0)	95.9	6.17 (*d*, *J* = 2.0)	97.9	6.20 (*d*, *J* = 2.0)	96.1
C(7)		167.9		166.5		168.2
H–C(8)	5.79 (*d*, *J* = 2.0)	95.9	5.86 (*d*, *J* = 2.0)	96.9	5.79 (*d*, *J* = 2.0)	96.0
C(9)		164.8		164.6		164.9
C(10)		103.5		103.3		103.4
C(1′)		116.2		116.0		116.3
C(2′)		158.0		157.9		159.4
H–C(3′)	6.27 (*d*, *J* = 2.0)	103.6	6.30 (*d*, *J* = 2.0)	103.3	6.30 (*d*, *J* = 2.0)	103.3
C(4′)		156.0		158.0		157.9
H–C(5′)	6.20 (*dd*, *J* = 8.4, 2.0)	108.4	6.22 (*dd*, *J* = 8.4, 2.0)	108.8	6.26 (*dd*, *J* = 8.4, 2.0)	108.4
H–C(6′)	6.61 (*d*, *J* = 8.4)	132.3	6.65 (*d*, *J* = 8.4)	130.5	6.66 (*d*, *J* = 8.4)	130.7
H–C(2″)	6.24 (br. *s*)	78.8	6.20 (br. *s*)	78.0	6.15 (br. *s*)	82.3
H–C(3″)	2.99 (br. *s*)	49.9	3.07 (br. *s*)	49.9	2.80 (br. *s*)	50.4
C(4″)		198.9		198.6		198.0
C(5″)		165.4		164.7		165.4
H–C(6″)	6.20 (*d*, *J* = 2.0)	95.9	6.12 (*d*, *J* = 2.0)	96.6	6.20 (*d*, *J* = 2.0)	97.1
C(7″)		167.9		167.9		168.2
H–C(8″)	5.79 (*d*, *J* = 2.0)	95.9	5.81 (*d*, *J* = 2.0)	95.9	5.79 (*d*, *J* = 2.0)	96.8
C(9″)		164.8		164.7		164.4
C(10″)		103.5		105.0		103.5
C(1‴)		116.2		115.8		129.1
H–C(2‴) or C(2‴)		158.0		159.9	6.87 (*d*, *J* = 8.4)	130.4
H–C(3′)	6.27 (*d*, *J* = 2.0)	103.6	6.30 (*d*, *J* = 2.0)	103.3	6.71 (*d*, *J* = 8.4)	116.5
C(4‴)		156.0		160.0		159.4
H–C(5‴)	6.20 (*dd*, *J* = 8.4, 2.0)	108.4	6.22 (*dd*, *J* = 8.4, 2.0)	108.8	6.71 (*d*, *J* = 8.4)	116.5
H–C(6‴)	6.61 (*d*, *J* = 8.4)	132.3	6.65 (*d*, *J* = 8.4)	130.5	6.87 (*d*, *J* = 8.4)	130.4
H–C(1⁗)			4.97 (*d*, *J* = 7.2)	101.1		
H–C(2⁗)			3.41–3.47 (*m*)	74.6		
H–C(3⁗)			3.41–3.47 (*m*)	77.7		
H–C(4⁗)			3.41–3.47 (*m*)	71.1		
H–C(5⁗)			3.41–3.47 (*m*)	78.1		
CH_2(6⁗)			3.68 (*dd*, *J* = 4.8, 12.0), 3.87 (*dd*, *J* = 1.6, 12.0)	62.3		

(δ(C) 49.9 (C(3) and C(3″))), and a glucose unit (δ(C) 101.1, 74.6, 77.7, 71.1, 78.1, and 62.3). The anomeric H-atom of the glucose moiety was determined to be β-oriented on the basis of the coupling constant (δ(H) 4.97 (*d*, *J* = 7.2)). The NMR data were very similar to those of **1**, except for the additional signals due to a β-glucosyl group. Thus, compound **2** was deduced as 2,2″-bisteppogenin 7-*O*-β-glucopyranoside.

Compound **3** was obtained as a brown oil (MeOH). The empirical molecular formula $C_{30}H_{22}O_{11}$ was established by HR-ESI-MS (*m*/*z* 557.1050 ($[M-H]^-$)). The assignments of the ^{1}H- and ^{13}C-NMR data (*Table 1*) were achieved by comparison with the data of **1**, and confirmed by COSY, HSQC, HMBC, and NOESY experiments.

In the ^{1}H-NMR spectrum, three aromatic H-atom signals with an *ABX* pattern (δ(H) 6.30 (*d*, $J = 2.0$, 1 H), 6.26 (*dd*, $J = 8.4, 2.0$, 1 H), and 6.66 (*d*, $J = 8.4$, 1 H)) indicated a 1,3,4-trisubstituted aromatic ring. Four aromatic H-atom signals with an A_2B_2 pattern (δ(H) 6.87 (*d*, $J = 8.4$, 2 H), and 6.71 (*d*, $J = 8.4$, 2 H)) discolosed the presence of a 1,2,3,5-tetrasubstituted aromatic ring. Moreover, two 1,3,4,5-tetrasubstituted aromatic rings were established based on the signals of two pairs of aromatic H-atoms in an *AX* pattern (δ(H) 6.20 (*d*, $J = 2.0$, 2 H), and 5.79 (*d*, $J = 2.0$, 2 H)). The ^{1}H-, ^{13}C-, and DEPT-NMR data of **3** (*Table 1*) contained signals assignable to two CO groups (δ(C) 198.9 (C(4)), and 198.0 (C(4″))), two O-bearing CH_2 groups (δ(C) 82.3 (C(2) and C(2″))), and two CH groups (δ(C) 50.4 (C(3) and C(3″))). The NMR spectra were very similar to those of **1**, except that a 1,3,4-trisubstituted and a 1,2,3,5-tetrasubstituted aromatic ring replaced two 1,2,3,5-tetrasubstituted aromatic rings in **1**. Thus, compound **3** was determined as 2‴-dehydroxy-2,2″-bisteppogenin.

Compound **4** had the molecular formula $C_{36}H_{32}O_{16}$ as deduced from HR-ESI-MS (*m*/*z* 719.1634 ($[M-H]^-$)). The NMR data (*Table 2*) were very similar to those of **3**, expect for the additional signals due to a *β*-glucosyl group. Thus, compound **4** was deduced as 2‴-dehydroxy-2,2″-bisteppogenin 7-*O*-*β*-glucopyranoside.

The relative configurations of compounds **1**–**4** were deduced by the coupling constants and NOESY spectra. In compound **4**, H–C(3″) and H–C(2″) gave rise to typical *doublet*s with coupling constants of 12.0 Hz; nevertheless, signals of both H–C(2) and H–C(3) were broad *singlet*s. These implied that the relative configurations of H–C(2), H–C(3), H–C(3″), and H–C(2″) in **4** were *β*, *β*, *β*, and *α*, respectively, which was further confirmed by the NOESY correlations H–C(2)/H–C(3) and H–C(3)/H–C(3″), and especially by the NOE H–C(2)/H–C(3″) (*Fig. 2*). Similarly, the relative configurations of H–C(2), H–C(3), H–C(2″), and H–C(3″) in compounds **1**–**3** were determined as *β*, based on the small coupling constants, and confirmed by the NOESY correlations H–C(2)/H–C(3), H–C(2)/H–C(3″), H–C(2″)/H–C(3″), and H–C(2″)/H–C(3) (*Fig. 2*).

The HR-ESI-MS of 7-methoxyneochamaejasmin B (**5**) exhibited a *pseudo*-molecular-ion peak at *m*/*z* 557.1434 ($[M+H]^+$), in accordance with the molecular formula $C_{31}H_{24}O_{10}$. The assignments of the ^{1}H- and ^{13}C-NMR data (*Table 2*) were achieved by comparison with the data of neochamaejasimin B [8], and confirmed by COSY, HSQC, HMBC, and NOESY experiments.

The ^{13}C-NMR spectrum exhibited 30 C-atom resonances with typical features of a flavonoid. Considering its molecular weight, **5** should be a biflavonoid. In the ^{1}H-NMR spectrum, signals of two pairs of aromatic H-atoms with an A_2B_2 coupling pattern (δ(H) 7.16 (*d*, $J = 8.4$, 2 H), and 6.77 (*d*, $J = 8.4$, 2 H); 7.03 (*d*, $J = 8.4$, 2 H), and 6.75 (*d*, $J = 8.4$, 2 H)), together with those of two pairs of aromatic H-atoms with an *AX* coupling pattern (δ(H) 5.96 (*d*, $J = 1.2$, 1 H) and 5.83 (*d*, $J = 1.2$, 1 H), as well as 5.77 (*d*, $J = 1.2$, 1 H) and 5.75 (*d*, $J = 1.2$, 1 H)) disclosed that both flavonoid units contained a 1′,4′-disubstituted *B* ring and a 5,7-disubtituted *A* ring. Detailed comparison of the NMR data of **5** (*Table 2*) with those known neochamaejasmin B

Table 2. *^{1}H- and ^{13}C-NMR Data of Compounds* **4** *and* **5**. In CD$_3$OD, δ in ppm, *J* in Hz. C-Atom numbering as indicated in *Fig. 1*.

	4		**5**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(2)	5.76 (br. *s*)	85.2	5.53 (*d*, *J* = 4.4)	81.5
H–C(3)	2.86 (br. *s*)	49.9	3.33 (*dd*, *J* = 3.2, 4.4)	49.6
C(4)		199.7		196.1
C(5)		166.7		165.2
H–C(6)	5.86 (*d*, *J* = 2.0)	96.8	5.96 (*d*, *J* = 1.2)	96.4
C(7)		168.1		168.2
H–C(8)	5.80 (*d*, *J* = 2.0)	96.0	5.83 (*d*, *J* = 1.2)	96.0
C(9)		164.9		163.3
C(10)		105.0		103.8
C(1′)		115.9		128.6
H–C(2′) or C(2′)		160.3	7.16 (*d*, *J* = 8.4)	128.7
H–C(3′)	6.30 (*d*, *J* = 2.0)	103.3	6.77 (*d*, *J* = 8.4)	114.8
C(4′)		158.0		158.6
H–C(5′)	6.25 (*dd*, *J* = 8.4, 2.0)	108.3	6.77 (*d*, *J* = 8.4)	114.8
H–C(6′)	6.89 (*d*, *J* = 8.4)	130.4	7.16 (*d*, *J* = 8.4)	128.7
H–C(2″)	5.75 (*d*, *J* = 12.0)	85.2	5.16 (*d*, *J* = 8.8)	82.9
H–C(3″)	3.00 (*d*, *J* = 12.0)	51.3	3.23 (*dd*, *J* = 3.2, 8.8)	50.8
C(4″)		197.8		198.6
C(5″)		165.3		165.5
H–C(6″)	6.16 (*d*, *J* = 2.0)	98.0	5.77 (*d*, *J* = 1.2)	97.3
C(7″)		168.1		168.4
H–C(8″)	6.11 (*d*, *J* = 2.0)	97.1	5.75 (*d*, *J* = 1.2)	97.1
C(9″)		164.3		165.1
C(10″)		103.3		105.1
C(1‴)		129.0		130.2
H–C(2‴)	6.89 (*d*, *J* = 8.4)	130.4	7.03 (*d*, *J* = 8.4)	130.2
H–C(3′)	6.72 (*d*, *J* = 8.4)	116.5	6.75 (*d*, *J* = 8.4)	116.4
C(4‴)		159.4		161.4
H–C(5‴)	6.72 (*d*, *J* = 8.4)	116.5	6.75 (*d*, *J* = 8.4)	116.4
H–C(6‴)	6.67 (*d*, *J* = 8.4)	130.4	7.03 (*d*, *J* = 8.4)	130.2
H–C(1⁗)	4.97 (*d*, *J* = 7.2)	101.1		
H–C(2⁗)	3.37–3.47 (*m*)	74.7		
H–C(3⁗)	3.37–3.47 (*m*)	77.8		
H–C(4⁗)	3.37–3.47 (*m*)	71.1		
H–C(5⁗)	3.37–3.47 (*m*)	78.2		
CH$_2$(6⁗)	3.68 (*dd*, *J* = 4.8, 12.0), 3.86 (*dd*, *J* = 1.2, 12.0)	62.3		
MeO			3.75 (*s*)	55.7

[8] indicated that the structure of **5** had one additional MeO group than neochamaejasimin B, and the signal of the MeO group (δ(H) 3.75) showed correlation with a C-atom signal at δ(C) 168.2 (C(7)) in the HMBC spectrum, suggesting that the MeO group was at C(7), which was further confirmed by COSY, HSQC, HMBC, and NOESY experiments (*Fig. 2*). Thus, compound **5** was determined as 7-methoxyneochamaejasmin B.

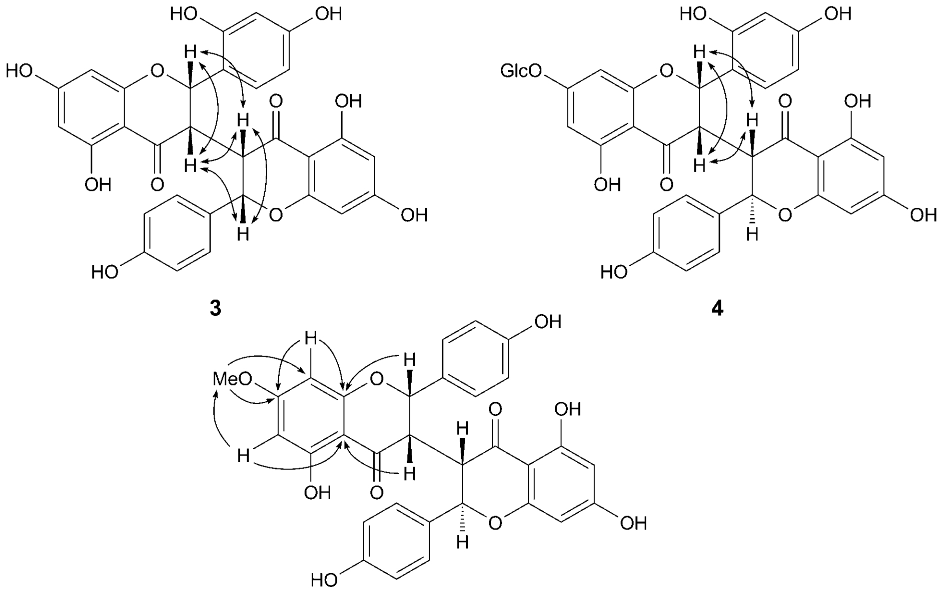

Fig. 2. *Key HMBC* (H → C) *and NOESY* (H ↔ H) *correlations of compounds* **3**, **4**, *and* **5**

This work was supported by *NCET Foundation*, NSFC(30725045), the *Special Program for New Drug Innovation of the Ministry of Science and Technology*, P. R. China (2009ZX09311-001, 2008ZX09308-005), *Shanghai Leading Academic Discipline Project* (B906), and in part by the *Scientific Foundation of Shanghai China* (09DZ1975700, 09DZ1971500).

Experimental Part

General. Column chromatography (CC): silica gel *H* (SiO_2, 10–40 μm; *Zhifu Huangwu Silica Gel D & R Plant*, Yantai, P. R. China), *Sephadex LH-20* (*Pharmacia*), and *ODS* (*Merck*). TLC: Plates precoated with silica gel HF_{254} (5–7 μm; *Zhifu Huangwu Silica Gel D & R Plant*, Yantai, P. R. China). Optical rotations: *Perkin-Elmer 343* polarimeter. UV Spectra: *Shimadzu UV-2550* UV/VIS spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Bruker Vector-22* spectrometer, KBr pellets, in cm^{-1}. NMR Spectra: *Bruker-DRX-400* spectrometer; at 400 (^1H) and 100 MHz (^{13}C, DEPT); (D_6)DMSO solns. with Me_4Si as internal standard, δ in ppm, J in Hz. HR-TOF-MS: ESI mode; *Q-Tof-Micro-Mass* spectrometer in m/z.

Plant Material. The plant material was collected in July 2006 in Kunming City, Yunnan Province, China, and identified as *Daphne aurantiaca* by Prof. *L.-S. Xie*, Kunming Institute of Botany. A voucher specimen has been deposited with the Herbarium of the School of Pharmacy, Second Military Medical University, Shanghai (No. 200607-11).

Extration and Isolation. The air-dried and powdered stem bark of *D. aurantiaca* (7.0 kg) was percolated with MeOH (25 l) at r.t. for 3 × 4 h. The solvent was evaporated under vacuum. Then, the extract was suspended in H_2O and partitioned with petroleum ether, AcOEt, and BuOH successively. The AcOEt extract (400 g) was subjected to CC (SiO_2 (1 kg); 9 × 100 cm column; $CHCl_3$/MeOH 100 : 1, 50 : 1, 25 : 1, 10 : 1, 8 : 1, and 5 : 1): *Frs. 1–6*. *Fr. 2* (35.0 g) was rechromatographed on CC (SiO_2 (1 kg); 9 × 100 cm column; $CHCl_3$/MeOH 100 : 1 and 50 : 1): *Frs. 2-1–2-9*. *Fr. 2-2* was subjected to CC (*ODS* (100 g), MeOH/H_2O 20 : 80–70 : 30): impure compound **5**, which was further purified by CC (*Sephadex LH-20*

(200 ml); MeOH): compound **5** (40 mg). By the same procedures, compounds **1** (25 mg) and **3** (80 mg) were obtained from *Fr. 2–4*. *Fr. 4* (50.0 g) was rechromatographed on CC (SiO_2 (1 kg); 9 × 100 cm column; $CHCl_3$/MeOH 25:1 and 10:1): *Frs. 4-1–4-7*. *Fr. 4-3* was subjected to CC (*ODS* (100 g); MeOH/H_2O 30:70–60:40): impure compound **2**, which was further purified by CC (*Sephadex LH-20* (200 ml); MeOH): compound **2** (30 mg). By the same procedures, compound **4** (4 mg) was obtained from *Fr. 4–5*.

2,2''-Bisteppogenin (= *(2*R*,2'*R*,3*R*,3'*R*)-2,2'-Bis(2,4-dihydroxyphenyl)-2,2',3,3'-tetrahydro-5,5',7,7'-tetrahydroxy-4*H*,4'*H*-3,3'-bichromene-4,4'-dione*; **1**). Brown viscous oil. $[\alpha]_D^{18} = -28$ ($c = 0.18$, MeOH). UV (MeOH): 226 (3.66), 294 (3.52), 335 (1.80). IR: 3232, 1634, 1458, 1266, 1162, 1087, 978, 833. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS (neg.): 573.1034 ($[M-H]^-$, $C_{30}H_{21}O_{12}^-$; calc. 573.1033).

*2,2''-Bisteppogenin 7-*O*-β-Glucopyranoside* (= *(2*R*,2'*R*,3*R*,3'*R*)-2,2'-Bis(2,4-dihydroxyphenyl)-3,3',4,4'-tetrahydro-5,5',7'-trihydroxy-4,4'-dioxo-2*H*,2'*H*-3,3'-bichromen-7-yl β-*D*-Glucopyranoside*; **2**). Brown viscous oil. $[\alpha]_D^{18} = -81$ ($c = 0.08$, MeOH). UV (MeOH): 228 (2.67), 290 (2.54), 334 (0.82). IR: 405, 1636, 1457, 1249,1169, 1078, 977, 834. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS (neg.): 735.1580 ($[M-H]^-$, $C_{36}H_{31}O_{17}^-$; calc. 735.1561).

2'''-Dehydroxy-2,2''-bisteppogenin (= *(2*R*,2'*R*,3*R*,3'*R*)-2-(2,4-Dihydroxyphenyl)-2,2',3,3'-tetrahydro-5,5',7,7'-tetrahydroxy-2'-(4-hydroxyphenyl)-4*H*,4'*H*-3,3'-bichromene-4,4'-dione*; **3**). Bown viscous oil. $[\alpha]_D^{18} = -78$ ($c = 0.08$, MeOH). UV (MeOH): 227 (2.90), 282 sh (2.68), 294 (2.72), 332 (1.06); IR: 3359, 1633, 1458, 1273, 1161, 1085, 978, 834. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS (neg.): 557.1050 ($[M-H]^-$, $C_{30}H_{21}O_{11}^-$; calc. 557.1084).

*2'''-Dehydroxy-2,2''-bisteppogenin 7-*O*-β-Glucopyranoside* (= *(2*R*,2'*S*,3*R*,3'*R*)-2-(2,4-Dihydroxyphenyl)-3,3',4,4'-tetrahydro-5,5',7'-trihydroxy-2'-(4-hydroxyphenyl)-4,4'-dioxo-2*H*,2'*H*-3,3'-bichromen-7-yl β-*D*-Glucopyranoside*; **4**). Brown viscous oil. $[\alpha]_D^{18} = -218$ ($c = 0.07$, MeOH). UV (MeOH): 227 (3.69), 294 (3.63), 336 (2.03). IR: 3382, 1636, 1456, 1286, 1168, 1082, 977, 833. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS (neg.): 719.1634 ($[M-H]^-$, $C_{36}H_{31}O_{16}^-$; calc. 719.1612).

7-Methoxyneochamaejasmin B (= *(2*R*,2'*S*,3*S*,3'*S*)-2,2',3,3'-Tetrahydro-5,5',7-trihydroxy-2,2'-bis(4-hydroxyphenyl)-7'-methoxy-4*H*,4'*H*-3,3'-bichromene-4,4'-dione*; **5**). Brown viscous oil. $[\alpha]_D^{18} = +185$ ($c = 0.33$, MeOH). UV (MeOH): 227 (3.48), 282 sh (3.10), 298 (3.13), 338 (1.91). IR: 3406, 2931, 1638, 1463, 1250, 1159, 1086. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS (pos.): 557.1434 ($[M+H]^+$, $C_{31}H_{25}O_{10}^+$; calc. 557.1448).

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Received October 18, 2010