Nonalkaloid Constituents from *Stemona japonica*

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Five new nonalkaloid constituents, a neolignan, japonin A (**1**), a macrocyclic lactone, japonin B (**2**), a (phenylethyl)benzoquinone, japonin C (**3**), a phenanthraquinone, japonin D (**4**), as well as a dihydrostilbene, stilbostemin M (**5**), were isolated from the roots of *Stemona japonica*, together with eight known compounds. Their structures were established by spectroscopic analyses.

Introduction. – *Stemona japonica* (BL.) MIQ (Stemonaceae), a climbing vine, is widely distributed in China, the Korean Peninsula, and Japan [1]. Its roots, known as 'Bai-bu', have long been prescribed in traditional Chinese medicine as insecticide and antitussive agent [1–3]. So far, remedies from *Stemona* roots are still used for treatments of respiratory disorders, including pulmonary tuberculosis and bronchitis, and, externally, for killing insect pests [4][5]. Previous investigations have led to the isolation of protostemonine-type, croomine-type, and maistemonine-type alkaloids as well as dihydrostilbenes and dihydrophenanthrenes [6].

The present paper describes the isolation of a neolignan dibenzoate, japonin A (**1**), a macrocyclic lactone, japonin B (**2**), a (phenylethyl)benzoquinone, japonin C (**3**), a phenanthraquinone, japonin D (**4**), and a dihydrostilbene, stilbostemin M (**5**) (see *Fig. 1*), as well as known compounds, stilbostemin C (**6**), 4-hydroxybenzaldehyde, stigmasterol, 4-methoxybenzoic acid, sesamin [7], lyciumamide [8], β-tocopherol [9] and γ-tocopherol [9], which were isolated from the title plant for the first time. Japonin C (**3**) is the first example of a (phenylethyl)benzoquinone from natural resources. Stilbostemin C (**6**) has been previously isolated from *S. collinsae* [7], while its complete ^{13}C-NMR data are herein reported for the first time.

Results and Discussion. – Japonin A (**1**) was isolated as optically inactive colorless oil. The HR-EI-MS showed a molecular ion M^+ at m/z 566.1939, in agreement with the molecular formula $C_{34}H_{30}O_8$, requiring twenty double-bond equivalents. Further spectral data (^{1}H- and ^{13}C-NMR (*Table 1*), ^{1}H,^{1}H-COSY, ROESY (*Fig. 2*), HSQC, and HMBC (*Fig. 2*)) established the structure of **1** as (2*RS*,3*SR*)-5-[(1*E*)-3-(benzoyloxy)-prop-1-enyl]-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-7-methoxybenzofuran-3-methanol benzoate.

The ^{1}H-NMR spectrum and ^{1}H,^{1}H-COSY plot of **1** showed the presence of an (*E*)-HOCH$_2$CH=CH moiety (δ 6.71 (*d*, J = 15.6 Hz), 6.25 (*dt*, J = 15.6, 6.3 Hz), 4.95 (*d*, J = 6.3 Hz)), two aromatic broad *s* (δ

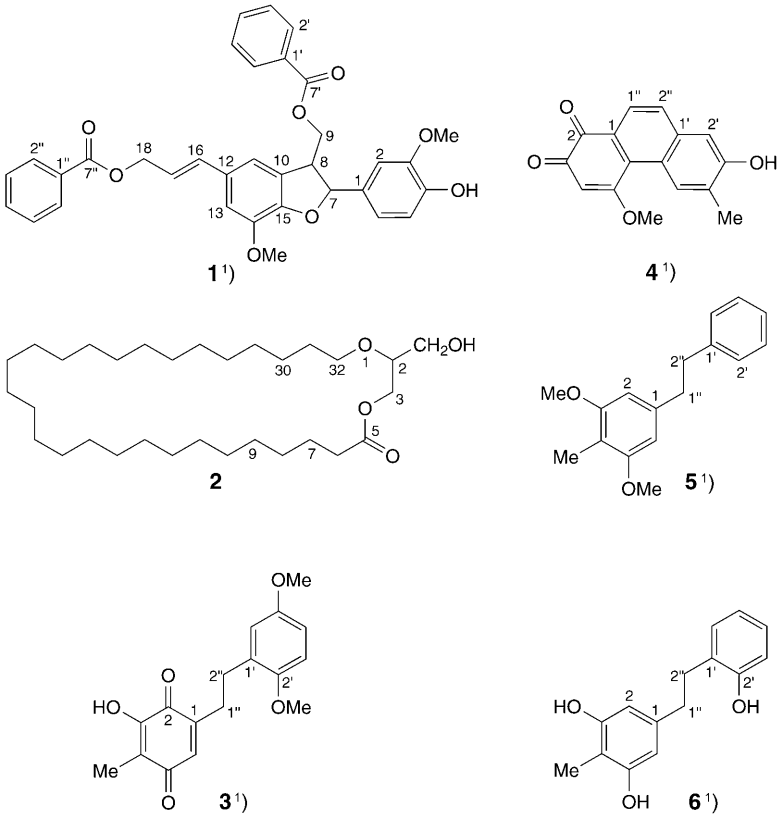

Fig. 1. *Compounds* **1**–**6** *isolated from* Stemona japonica[1])

6.95, 6.90), a MeO *s* (δ 3.95), and a (O)CHCHCH$_2$(O) moiety (δ 5.56 (*d*, *J* = 7.3 Hz), 3.90–3.94 (*m*), 4.69 (*dd*, *J* = 11.2, 5.3 Hz), 4.52 (*dd*, *J* = 11.2, 5.3 Hz)), similar to those of the A and B rings of a neolignan, (−)-simulanol [10]. Remaining signals, including those of three aromatic protons (δ 6.86 (br. *s*), 6.84 (*d*, *J* = 8.3 Hz), 6.88 (*dd*, *J* = 8.3, 1.9 Hz)), a MeO *s* (δ 3.87), and an OH *s* (δ 5.59), suggested the presence of a 4-hydroxy-3-methoxyphenyl substitution for ring C. The existence of two benzoate moieties was suggested by signals of two monosubstituted benzene moieties (δ 7.91 (br. *d*, *J* = 7.3 Hz, 2 H), 7.39 (*dd*, *J* = 7.8, 7.3 Hz, 2 H), 7.51–7.55 (*m*, 2 H), 8.06 (br. *d*, *J* = 7.8 Hz, 2 H), 7.42 (*dd*, *J* = 7.8, 7.4 Hz, 2 H)) and of 12 C-atoms at δ 128.3–133.2, as well as of two carbonyl resonances at δ 166.2 and 166.4. The HMBC correlations CH$_2$(9) (δ 4.52 and 4.69)/C(7′) (δ 166.2) and CH$_2$(18) (δ 4.95)/C(7″) (δ 166.4) confirmed that two benzoate moieties were attached to C(9) and C(18), respectively[1]). According to the above data, the structure of **1** was elucidated as shown in *Fig. 1*. The planar structure of **1** was further confirmed by the combined analyses of ROESY, HSQC, and HMBC data (*Fig. 2*). The optical inactivity of **1** suggested that it was racemic. The relative configuration at C(7) and C(8) was determined as (7*R*,8*S*) and (7*S*,8*R*) (racemate) since the coupling constant of 7.3 Hz for H–C(7) was less than 8.0 Hz and similar to *J* = 7.2 Hz for H–C(7) in (−)-simulanol [10].

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[1]) Arbitrary numbering; for systematic names, see *Exper. Part.*

Table 1. *^{1}H-NMR and ^{13}C-NMR Data for Compounds* **1** *and* **2**. δ in ppm, J in Hz.

	1[1])			**2**	
	δ(H)[a])[b])	δ(C)[a])[c])		δ(H)[d])[e])	δ(C)[d])[f])
C(1)		132.3	H–C(2)	4.51–4.54 (*m*)	71.1
H–C(2)	6.86 (br. *s*)	108.7	CH_2(3)	4.78 (*dd*, *J* = 11.0, 5.5)	66.9
C(3)		146.7	C(5)		173.9
C(4)		145.8	CH_2(6)	2.48 (*t*, *J* = 7.6)	34.5
H–C(5)	6.84 (*d*, *J* = 8.3)	114.3	CH_2(7)	1.62–1.68 (*m*)	25.4
H–C(6)	6.88 (*dd*, *J* = 8.3, 1.9)	119.6	CH_2(8) to CH_2(29)	1.37–1.43 (*m*)	30.0
H–C(7)	5.56 (*d*, *J* = 7.3)	89.2	CH_2(30)	1.60–1.64 (*m*)	26.7
H–C(8)	3.90–3.94 (*m*)	50.4	CH_2(31)	1.75–1.81 (*m*)	33.9
CH_2(9)	4.69 (*dd*, *J* = 11.2, 5.3),	66.0	CH_2(32)	3.98 (*t*, *J* = 6.5)	62.3
	4.52 (*dd*, *J* = 11.2, 5.3)		CH_2OH	4.20 (*d*, *J* = 5.4)	64.4
C(10)		127.6			
H–C(11)	6.95 (br. *s*)	115.3			
C(12)		130.6			
H–C(13)	6.90 (br. *s*)	110.7			
C(14)		144.5			
C(15)		148.3			
H–C(16)	6.71 (*d*, *J* = 15.6)	134.3			
H–C(17)	6.25 (*dt*, *J* = 15.6, 6.3)	121.2			
CH_2(18)	4.95 (*d*, *J* = 6.3)	65.6			
C(1′)		130.6			
H–C(2′)	7.91 (br. *d*, *J* = 7.3)	129.6			
H–C(3′)	7.39 (*dd*, *J* = 7.8, 7.3)	128.4			
H–C(4′)	7.51–7.55 (*m*)	133.2			
H–C(5′)	7.39 (*dd*, *J* = 7.8, 7.3)	128.4			
H–C(6′)	7.91 (br. *d*, *J* = 7.3)	129.6			
C(7′)		166.2			
C(1″)		130.2			
H–C(2″)	8.06 (br. *d*, *J* = 7.8)	129.6			
H–C(3″)	7.42 (*dd*, *J* = 7.8, 7.4)	128.3			
H–C(4″)	7.51–7.55 (*m*)	133.0			
H–C(5″)	7.42 (*dd*, *J* = 7.8, 7.4)	128.3			
H–C(6″)	8.06 (br. *d*, *J* = 7.8)	129.6			
C(7″)		166.4			
MeO–C(3)	3.87 (*s*)	55.8			
OH–C(4)	5.59 (*s*)				
MeO–C(14)	3.95 (*s*)	56.0			

[a]) In $CDCl_3$. [b]) At 600 MHz. [c]) At 150 MHz. [d]) In (D_5)pyridine. [e]) At 400 MHz. [f]) At 100 MHz.

Japonin B (**2**) was isolated as an optically inactive colorless gum. Its molecular ion M^+ at *m/z* 496.4501 in the HR-EI-MS was consistent with the molecular formula $C_{31}H_{60}O_4^+$. IR Absorptions at 3415, 2848, 1473, 719, and 1735 cm^{-1} showed the existence of OH groups, long-chain CH_2 groups and a lactone C=O, respectively. The complete ^{1}H- and ^{13}C-NMR (*Table 1*) and 2D spectral analyses (^{1}H,^{1}H-COSY, HSQC, and HMBC (*Fig. 2*)) led to the conclusion that **2** had the structure of (2*RS*)-2-(hydroxymethyl)-1,4-dioxacyclodotriacontan-5-one.

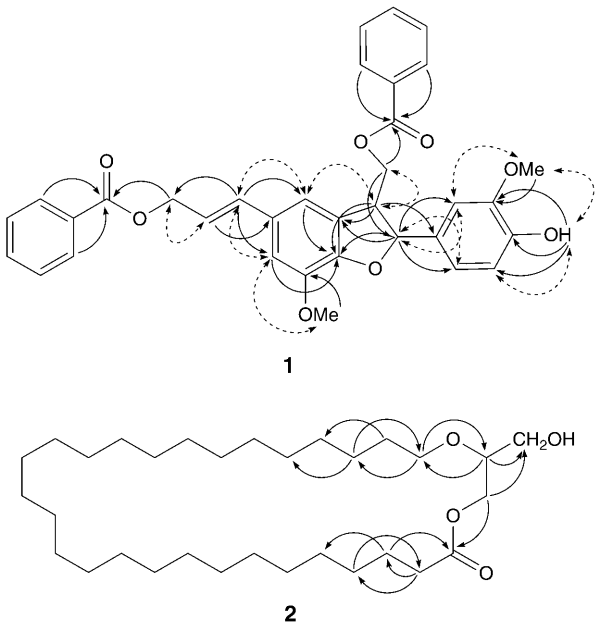

Fig. 2. *Key HMBC* (→) *and ROESY* (←– – –→) *correlations for* **1** *and* **2**

The ^{13}C-NMR spectrum of **2** indicated 31 signals, which were assigned by HSQC and DEPT experiments as signals of a lactone C=O, a CH, and 29 CH_2 groups. At δ 30.0, 22 of the long-chain CH_2 signals were overlapped. The absence of a Me signal and the presence of the long-chain CH_2 signals in the ^{1}H- and ^{13}C-NMR spectra suggested the existence of a macrocycle. Analyses of the ^{13}C-NMR and DEPT spectra allowed to allocate two unsaturated degrees to a lactone C=O resonating at δ 173.9 and to a macrocycle. The ^{1}H-NMR spectrum and ^{1}H,^{1}H-COSY plot showed a characteristic glycerol moiety attributable to a *d* at δ 4.20 (J = 5.4 Hz, 2 H), a *dd* at δ 4.78 (J = 11.1, 5.5 Hz, 2 H), and a *m* at δ 4.51–4.54 (1 H), a $(CH_2)_nCH_2CH_2CH_2O$ moiety due to a *m* within δ 1.37–1.43 (2 H), a *m* at δ 1.60–1.64 (2 H), a *m* at δ 1.75–1.81 (2 H), and a *t* at δ 3.98 (J = 6.5 Hz, 2 H), and a $OCOCH_2CH_2(CH_2)_n$ moiety for a *t* at δ 2.48 (J = 7.6 Hz, 2 H), a *m* at δ 1.62–1.68 (2 H), and a *m* within δ 1.37–1.43 (2 H). The HMBC (*Fig. 2*) correlations H–C(2) (δ 4.51–4.54)/C(32) (δ 62.3) and CH_2(3) (δ 4.78)/C(5) (δ 173.9) confirmed the key connection of the above partial structures, and the macrocycle lactone was deduced as shown in *Fig. 1*. Moreover, in view of the optical inactivity, the presence of racemic **2** was assumed.

Japonin C (**3**) was obtained as an orange amorphous powder. Its molecular formula $C_{17}H_{18}O_5$ was revealed by the HR-EI-MS (M^+ at m/z 302.1159) and ^{13}C-NMR DEPT spectrum. The IR spectrum showed OH and C=O bands at 3388 and 1649 cm^{-1}. The UV spectrum indicated the presence of a benzoquinone moiety by the absorption at 207, 269, and 407 nm [11]. The ^{1}H-NMR spectrum (*Table 2*) displayed typical proton signals of bibenzyls (two CH_2 at δ 2.61–2.76) [7], suggesting that **3** was a (phenylethyl)-benzoquinone. According to further data illation (^{13}C-NMR, ROESY (*Fig. 3*), HSQC, and HMBC(*Fig. 3*)), **3** was characterized as 5-[2-(2,5-dimethoxyphenyl)ethyl]-3-hydroxy-2-methyl-1,4-benzoquinone.

Table 2. *^{1}H-NMR and ^{13}C-NMR Data for Compounds* **3**–**5**. δ in ppm, J in Hz.

	3		**4**		**5**	
	δ(H)[a][b]	δ(C)[a][c]	δ(H)[d][b]	δ(C)[d][c]	δ(H)[a][e]	δ(C)[a][f]
C(1)		144.2		130.5		140.2
C(2) or H–C(2)		187.9		182.9	6.26 (*s*)	103.8
C(3)		151.6		190.8		158.1
C(4) or H–C(4)		116.9	6.17 (*s*)	112.5		111.8
C(5)		183.4		160.5		158.1
H–C(6) or C(6)	6.31 (*s*)	134.2		128.5	6.26 (*s*)	103.8
C(1′) or H–C(1′)		129.7		140.5		141.8
C(2′), H–C(2′)		151.3	7.09 (*s*)	110.3	7.20–7.22 (*m*)	128.5
H–C(3′) or C(3′)	6.66 (*d*, J=8.6)	111.6		159.0	7.27–7.31 (*m*)	128.3
H–C(4′) or C(4′)	6.63 (*dd*, J=8.6, 2.8)	116.4		134.0	7.17–7.21 (*m*)	125.9
C(5′) or H–C(5′)		151.6	9.29 (*s*)	130.9	7.27–7.31 (*m*)	128.3
H–C(6′) or C(6′)	6.61 (*d*, J=2.8)	111.1		126.3	7.20–7.22 (*m*)	128.5
CH_2(1″) or H–C(1″)	2.61–2.65 (*m*)	29.2	7.95 (*d*, J=8.5)	122.7	2.88–2.90 (*m*)	38.1
CH_2(2″) or H–C(2″)	2.72–2.76 (*m*)	28.7	7.87 (*d*, J=8.5)	133.4	2.90–2.92 (*m*)	38.5
OH–C(3)	6.85 (*s*)					
Me–C(4)	1.86 (*s*)	8.2			2.06 (*s*)	7.9
Me–C(4′)			2.39 (*s*)	18.0		
MeO–C(3)					3.78 (*s*)	55.6
MeO–C(5)			3.87 (*s*)	57.4	3.78 (*s*)	55.6
MeO–C(2′)	3.63 (*s*)	55.7				
MeO–C(5′)	3.68 (*s*)	55.6				

[a]) In $CDCl_3$. [b]) At 600 MHz. [c]) At 150 MHz. [d]) In CD_3OD. [e]) At 400 MHz. [f]) At 100 MHz.

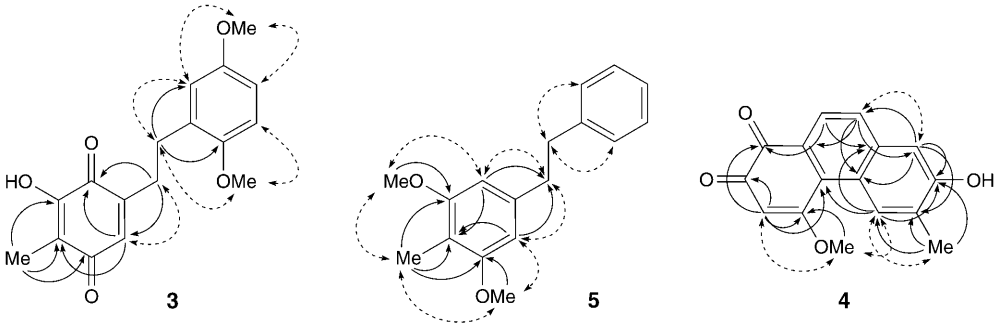

Fig. 3. *Key HMBC* (→) *and ROESY* (←– – –→) *correlations for* **3**–**5**

The ^{1}H-NMR spectrum showed signals for a 1,2,5-trisubstituted benzene ring (δ 6.66 (*d*, J=8.6 Hz), 6.63 (*dd*, J=8.6, 2.8 Hz), 6.61 (*d*, J=2.8 Hz)), a *s* (δ 6.31 (*s*)), two CH_2 (δ 2.61–2.65 (*m*), 2.72–2.76 (*m*)), two MeO (δ 3.63 (*s*), 3.68 (*s*)), a Me (δ 1.86 (*s*)) and an OH group (δ 6.85 (*s*)). The ROESY correlations MeO–C(2′) (δ 3.63)/CH_2(2″) (δ 2.72–2.76) and H–C(3′) (δ 6.66) and MeO–C(5′) (δ 3.68)/H–C(4′) (δ 6.63) and H–C(6′) (δ 6.61) confirmed the location of two MeO at C(2′) and C(5′), respectively. The HMBC correlations H–C(6) (δ 6.31)/C(2) (δ 187.9) and C(4) (δ 116.9), and Me–C(4) (δ 1.86)/C(3) (δ 151.6), C(4) (δ 116.9) and C(5) (δ 183.4) further confirmed the positions of OH and Me at C(3) and

C(4), respectively (*Fig. 3*)[1]). Additionally, a (phenylethyl)benzoquinone unit was established by ROESY signals (*Fig. 3*) between H–C(6) and H–C(1″), ^{1}H,^{1}H coupling between H–C(1″) and H–C(2″), and HMBC correlations CH_2(1″)/C(2) and C(6) and CH_2(2″)/C(2′) and C(6′).

Japonin D (**4**) was obtained as a yellow power. Its molecular formula was established as $C_{16}H_{12}O_4$ by HR-EI-MS (M^+ at *m/z* 268.0738). The UV spectrum showed absorption maxima at 240, 305, 325 (sh), and 406 nm, and the IR spectrum displayed strong bands at 1670, 1630, 1598, and 1495 cm^{-1}, suggesting a phenanthraquinone moiety [12]. Based on detailed spectral evidences (^{1}H- and ^{13}C-NMR (*Table 2*), ROESY (*Fig. 3*), HSQC, and HMBC (*Fig. 3*)), the structure of **4** was established as 7-hydroxy-4-methoxy-6-methylphenanthrene-1,2-dione.

The ^{1}H-NMR spectrum of **4** exhibited two *d* (δ 7.95 (J = 8.5 Hz), 7.87 (J = 8.5 Hz)), assignable to H–C(9) (= H–C(1″)) and H–C(10) (= H–C(2″)) of phenanthraquinones, three isolated *s* (δ 6.17, 7.09, 9.29), a MeO *s* (δ 3.87), and a Me *s* (δ 2.39), which were very similar to those of isotanshinone II [12]. The low-field aromatic *s* at δ 9.29, very close to H–C(5′) of isotanshinone II, suggested that a proton was located at C(5′)[1]). Moreover, the ROESY correlations between H–C(4) (δ 6.17) and MeO–C(5) (δ 3.87), between MeO–C(5) and H–C(5′) (δ 9.29) and between H–C(5′) and Me–C(4′) (δ 2.39), as well as between H–C(2′) (δ 7.09) and H–C(2″) (δ 7.87) revealed that the MeO and Me were attached to C(5) and C(4′), respectively. The remaining position C(3′) should be substituted by an OH group. The structure of **4** was further confirmed by the ^{1}H,^{13}C-HMBC correlations H–C(4)/C(2), C(3), C(5), and C(6), MeO–C(5)/C(5), H–C(1″)/C(2), and C(1′), H–C(2″)/C(1), C(2′), and C(6′), H–C(2′)/C(3′), C(4′), C(6′), and C(2″), Me–C(4′)/C(3′), C(4′), and C(5′), and H–C(5′)/C(6) and C(1′) (*Fig. 3*).

Stilbostemin M (**5**) was obtained as a colorless crystal. Its molecular formula $C_{17}H_{20}O_2$ was determined by HR-EI-MS (M^+ at *m/z* 256.1456). UV Absorptions at 210 and 272 nm revealed the presence of benzyl moieties. The ^{1}H-NMR spectrum showed two representative CH_2 at δ 2.88–2.92 [7], suggesting that **5** was a bibenzyl. According to further spectral data, **5** was determined as 1,3-dimethoxy-2-methyl-5-(2-phenylethyl)benzene.

The ^{1}H-NMR spectrum of **5** (*Table 2*) disclosed signals for a monosubstituted benzene ring (δ 7.20–7.22 (*m*, 2 H), 7.27–7.31 (*m*, 2 H), 7.17–7.21 (*m*, 1 H)), two equivalent *s* (δ 6.26), two equivalent MeO *s* (δ 3.78), and a Me *s* (δ 2.06), as well as two CH_2 *m* (δ 2.88–2.90, 2.90–2.92), indicating a trisubstituted bibenzyl. The ^{13}C-NMR spectrum exhibited four signals in the aromatic region (δ 140.2, 103.8, 158.1, 111.8), suggesting the presence of a symmetrically substituted aromatic moiety, *i.e.*, a 3,5-dimethoxy-4-methylbenzyl or 2,6-dimethoxy-4-methylbenzyl group. The deduction was also confirmed by the presence of two fragment ions at *m/z* 91 (C_7H_7) and 165 ($C_{10}H_{13}O_2$) in the EI-MS. The 3,5-dimethoxy-4-methylbenzyl pattern was established by the HMBC correlations H–C(2,6) (δ 6.26)/C(1″) and C(4) (δ 38.1, 111.8) and Me–C(4) (δ 2.06)/C(3,5) and C(4) (δ 158.1, 111.8), and the ROESY correlations MeO–C(3,5) (δ 3.78)/H–C(2,6) and Me–C(4) and Me–C(4)/MeO–C(3,5) (*Fig. 3*).

This work was financially supported by the *National Natural Science Foundation of China* (grant No. 30123005) and the *Science and Technology Committee of Shanghai* (No. 036505003).

Experimental Part

General. Column chromatography (CC): commercial silica gel (*Qing Dao Hai Yang Chemical Group Co.*; 200–300 and 300–400 mesh). TLC: precoated silica gel plates (*Yan Tai Zi Fu Chemical Group Co.*; *GF254*). M.p.: *Fisher–Jones* melting-point apparatus; uncorrected. Optical rotation: *Perkin-Elmer-341*

polarimeter. UV Spectra: *Hewlett-Packard 8452A* diode-array spectrophotometer, λ_{max} in nm (log ε). IR Spectra: *Nicolet-Magna FT-IR-750* spectrometer, $\tilde{\nu}_{max}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker DRX-400* and *Varian-Unity Inova-600* (spectrometers; chemical shifts δ in ppm, with residual $CHCl_3$ (δ(H) 7.26, δ(C) 77.0) or CH_3OH (δ(H) 3.30, δ(C) 49.0) or C_5H_5N (δ(H) 7.21, δ(C) 123.5) as internal standard, coupling constant *J* in Hz; assignments supported by $^1H,^1H$-COSY, HSQC, ROESY, and HMBC experiments. EI-MS and HR-EI-MS: *Finnigan MAT-95* spectrophotometer; in *m/z*.

Plant Material. The fresh roots of *Stemona japonica* were collected in Anji County, Zhejiang Province, China, in September, 2002, and identified by Prof. *Jin-gui Shen* of the Shanghai Institute of Materia Medica, Chinese Academy of Sciences. A voucher specimen (20020013B) is deposited in the Herbarium of the institute.

Extraction and Isolation. The air-dried and powdered roots of *S. japonica* (8.5 kg) were percolated with 95% EtOH (3 × 10 l) at r.t. The EtOH extract was filtered and concentrated. Then the concentrated extract was suspended in MeOH/H_2O 20:80 (*v*/*v*; 1 l) and partitioned successively with petroleum ether (60–90°), $CHCl_3$, AcOEt, and BuOH (each 3 × 1 l). The petroleum ether fraction (30 g) was dissolved in $CHCl_3$ and filtered. Then 500 mg of the filtered residue (1.5 g) was subjected to CC (silica gel (50 g), $CHCl_3$/MeOH 10:1) to afford japonin B (**2**, 210 mg). The filtrate was concentrated and subjected to CC (silica gel (500 g), petroleum ether/acetone 10:1 → 1:2) to afford *Frs. 1–5*. Stilbostemin M (**5**, 10 mg) was obtained by repeated CC (silica gel, hexane/AcOEt/formic acid 100:10:1 → 100:30:1) and prep. TLC (petroleum ether/AcOEt 8:1) from *Fr. 1* (7 g). *Fr. 3* (3 g) was subjected to repeated CC (silica gel, hexane/acetone/formic acid 100:20:1 → 100:33:1) and prep. TLC (hexane/AcOEt/formic acid 100:33:1) to yield japonin A (**1**; 2 mg), japonin C (**3**; 0.7 mg), and japonin D (**4**; 0.8 mg).

Japonin A (=*(2*RS*,3*SR*)-5-[(1*E*)-3-(Benzoyloxy)prop-1-enyl]-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-7-methoxybenzofuran-3-methanol Benzoate*; **1**): Colorless oil. UV (MeOH): 198, 231, 308 (sh). IR (KBr): 3428, 2935, 1716, 1602, 1517, 1452, 1273, 1118, 711. ^1H- and ^{13}C-NMR: *Table 1*. EI-MS: 566 (5, M^+), 444 (9), 322 (7), 291 (6), 122 (71), 105 (100), 77 (57). HR-EI-MS: 566.1939 ($C_{34}H_{30}O_8^+$; calc. 566.1941).

Japonin B (=*(2*RS*)-2-(Hydroxymethyl)-1,4-dioxacyclodotriacontan-5-one*; **2**): Colorless gum. M.p. 128–129°. IR (KBr): 3415, 2917, 2848, 1735, 1473, 1463, 1176, 1058, 719. ^1H- and ^{13}C-NMR: *Table 1*. EI-MS: 496 (34, M^+), 468 (14), 465 (11), 423 (35), 422 (44), 405 (26), 404 (30), 394 (19), 377 (14), 376 (17), 154 (15), 134 (48), 112 (28), 98 (100), 83 (68), 71 (35), 69 (76). HR-EI-MS: 496.4501 ($C_{31}H_{60}O_4^+$; calc. 496.4492).

Japonin C (=*5-[2-(2,5-Dimethoxyphenyl)ethyl]-3-hydroxy-2-methylcyclohexa-2,5-diene-1,4-dione*; **3**): Orange amorphous powder. UV (MeOH): 207, 269, 407. IR (KBr): 3388, 3026, 2924, 1649, 1634, 1499, 1394, 1360, 1307, 1167, 1126, 1050, 765. ^1H- and ^{13}C-NMR: *Table 2*. EI-MS: 302 (39, M^+), 274 (8), 151 (100), 121 (36), 91 (9). HR-EI-MS: 302.1159 ($C_{17}H_{18}O_5^+$; calc. 302.1154).

Japonin D (=*7-Hydroxy-4-methoxy-6-methylphenanthrene-1,2-dione*; **4**): Yellow power. UV (MeOH): 198, 240, 305, 325 (sh), 406. IR (KBr): 3500, 2919, 2362, 1670, 1630, 1598, 1495, 1473, 1267, 1238, 1074, 858. ^1H- and ^{13}C-NMR: *Table 2*. EI-MS: 268 (100, M^+), 215 (14), 165 (11), 144 (35), 123 (44), 91 (26). HR-EI-MS: 268.0738 ($C_{16}H_{12}O_4^+$; calc. 268.0736).

Stilbostemin M (=*1,3-Dimethoxy-2-methyl-5-(2-phenylethyl)benzene*; **5**): Colorless crystals. M.p. 77–79°. UV (MeOH): 210 (4.01), 272 (3.24). IR (KBr): 3064, 3008, 2964, 2834, 1608, 1589, 1496, 1463, 1417, 1309, 1238, 1180, 1137, 975, 838, 771, 721. ^1H- and ^{13}C-NMR: *Table 2*. EI-MS: 256 (28, M^+), 165 (100), 91 (11), 77 (4). HR-EI-MS: 256.1456 ($C_{17}H_{20}O_2^+$; calc. 256.1463).

Stilbostemin C (=*5-[2-(2-Hydroxyphenyl)ethyl]-2-methylbenzene-1,2-diol*; **6**): Colorless crystals. M.p. 85–86°. ^{13}C-NMR ($CDCl_3$, 100 MHz): 140.9 (C(1)); 106.9 (C(2), C(6)); 156.4 (C(3), C(5)); 119.8 (C(4)); 130.2 (C(1′)); 156.5 (C(2′)); 107.0 (C(3′)); 127.3 (C(4′)); 119.8 (C(5′)); 130.2 (C(6′)); 36.2 (C(1″); 32.6 (C(2″)); 8.0 (Me(4)).

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Received September 28, 2006