Monoterpenoids from the Fruit of *Gardenia jasminoides*

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Eight new monoterpenoids, jasminoside J (**1**), jasminoside K (**2**), 6′-*O*-*trans*-sinapoyljasminoside B (**3**), 6′-*O*-*trans*-sinapoyljasminoside L (**4**), jasminosides M–P (**5**–**8**), together with three known analogues, jasminoside C (**9**), jasminol E (**10**), and sacranoside B (**11**), were isolated from the fruit of *Gardenia jasminoides* ELLIS (Rubiaceae). Their structures were elucidated by spectral and chemical methods.

Introduction. – The fruit of *Gardenia jasminoides* ELLIS (Rubiaceae) has been used in folk medicine for its cholagogue, diuretic, and anti-inflammatory effects [1]. It has been also used as a yellow dye, and crocin and crocetin were isolated as yellow pigments [2]. Previous studies on *G. jasminoides* afforded a series of iridoid glucosides, monoterpenoids, triterpenoids, flavonoids, quinic acid derivatives, and crocin [3–6]. In this article, we report the isolation and structural elucidation of eight new and three known monoterpenoids **1**–**11**[1]) from the fruit of *G. jasminoides*.

Results and Discussion. – Compound **1** was obtained as a white amorphous powder, which showed a positive reaction to the *Molisch* reagent. The molecular formula, $C_{16}H_{24}O_7$, was deduced from the positive-ion-mode HR-ESI-Q-TOF-MS (*m*/*z* 351.1437 ($[M+Na]^+$)). The ^{1}H- and ^{13}C-NMR spectra (*Table 1*) of **1** indicated the presence of a β-glucosyl moiety [7]. Acid hydrolysis of **1** furnished D-glucose, which was identified by GC analysis [8–10]. Except for the signals due to the glucose, the ^{13}C-NMR and DEPT spectra of **1** exhibited ten C-signals arising from an ester C=O group (δ(C) 170.0), two olefinic quaternary C-atoms (δ(C) 134.9 and 133.8), two olefinic CH groups (δ(C) 130.2 and δ(H) 5.94 (*dt*, J = 9.5, 4.2 Hz); δ(C) 129.1 and δ(H) 5.86 (*dt*, J = 9.5, 1.6 Hz)), a CH_2 group (δ(C) 40.7 and δ(H) 2.10–2.14), a saturated quaternary C-atom (δ(C) 34.5), and three Me groups (δ(C) 26.3 and δ(H) 1.15 (*s*); δ(C) 26.2 and δ(H) 1.14 (*s*); δ(C) 20.0 and δ(H) 1.86 (*s*)). Analysis of ^{13}C-NMR, HSQC, and HMBC spectra allowed to deduce the constitution of the aglycone moiety (*Fig. 1*). The HMBC of the anomeric H-atom (δ(H) 5.59 (*d*, J = 8.1 Hz)) to the carboxylic C-atom (δ(C) 170.0)

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

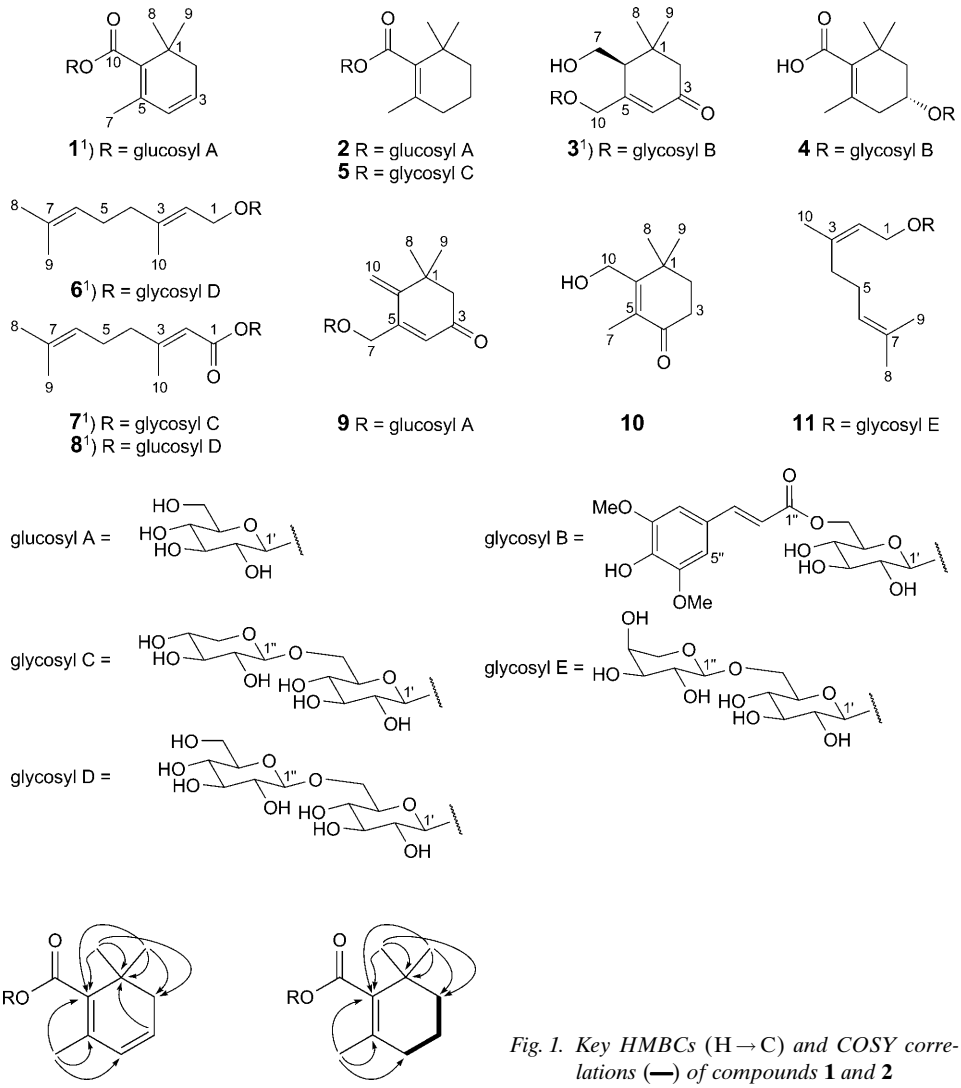

Fig. 1. Key HMBCs (H → C) *and COSY correlations* (—) *of compounds* **1** *and* **2**

indicated that the glucose moiety was linked to C(10). Thus, **1** was elucidated as β-D-glucopyranosyl 2,6,6-trimethylcyclohexa-1,3-diene-1-carboxylate and named jasminoside J.

Compound **2**, a white amorphous powder, had the molecular formula $C_{16}H_{26}O_7$, based on the HR-ESI-Q-TOF-MS. The ^{1}H- and ^{13}C-NMR data (*Table 1*) of **2** were similar to those of **1**, except for the absence of two sp^2 centers and the presence of two CH_2 groups instead (δ(C) 32.4 and δ(H) 1.99–2.04; δ(C) 19.8 and δ(H) 1.65–1.71). Analysis of the ^{1}H,^{1}H-COSY, HSQC, and HMBC data indicated that the C(3)=C(4) bond in **1** was replaced by two CH_2 groups in **2**. Therefore, **2** was elucidated to be β-D-glucopyranosyl 2,6,6-trimethylcyclohex-1-ene-1-carboxylate and named jasminoside K.

Table 1. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz, resp., CD_3OD) *of Compounds* **1**–**4**. δ in ppm, J in Hz.

	1		**2**		**3**		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
C(1)	34.5 (*s*)		34.2 (*s*)		36.3 (*s*)		36.4 (*s*)	
CH_2(2)	40.7 (*t*)	2.10–2.14 (*m*)	39.8 (*t*)	1.44–1.48 (*m*)	50.0 (*t*)	2.71 (*d*, *J* = 17.0), 1.99 (*d*, *J* = 17.0)	46.6 (*t*)	1.92 (*dd*, *J* = 12.3, 2.3), 1.47 (*t*, *J* = 12.2)
CH(3), CH_2(3), or C(3)	130.2 (*d*)	5.94 (*dt*, *J* = 9.5, 4.2)	19.8 (*t*)	1.65–1.71 (*m*)	202.7 (*s*)		73.9 (*d*)	4.07 (*dddd*, *J* = 11.9, 9.5, 5.8, 3.5)
CH(4) or CH_2(4)	129.1 (*d*)	5.86 (*dt*, *J* = 9.5, 1.6)	32.4 (*t*)	1.99–2.04 (*m*)	125.5 (*d*)	6.25 (*s*)	38.6 (*t*)	2.44 (*dd*, *J* = 17.2, 5.7), 2.07 (*dd*, *J* = 17.2, 9.3)
C(5)	134.9 (*s*)		136.7 (*s*)		163.9 (*s*)		131.6 (*s*)	
C(6) or CH(6)	133.8 (*s*)		135.6 (*s*)		50.6 (*d*)	2.09 (*t*, *J* = 3.8)	136.8 (*s*)	
Me(7) or CH_2(7)	20.0 (*q*)	1.86 (*s*)	21.6 (*q*)	1.72 (*s*)	62.1 (*t*)	3.82 (*d*, *J* = 3.8)	21.3 (*q*)	1.70 (*s*)
Me(8)	26.3 (*q*)	1.15 (*s*)	28.9 (*q*)	1.12 (*s*)	29.3 (*q*)	1.00 (*s*)	29.7 (*q*)	1.02 (*s*)
Me(9)	26.2 (*q*)	1.14 (*s*)	28.9 (*q*)	1.12 (*s*)	27.4 (*q*)	1.10 (*s*)	29.2 (*q*)	1.19 (*s*)
C(10) or CH_2(10)	170.0 (*s*)		170.9 (*s*)		72.0 (*t*)	4.58 (*dd*, *J* = 16.0, 1.2), 4.36 (br. *d*, *J* = 16.0)	174.1 (*s*)	
CH(1′)	95.8 (*d*)	5.59 (*d*, *J* = 8.1)	95.8 (*d*)	5.55 (*d*, *J* = 8.1)	104.6 (*d*)	4.39 (*d*, *J* = 7.7)	103.4 (*d*)	4.44 (*d*, *J* = 7.8)
CH(2′)	74.0 (*d*)	3.33–3.37 (*m*)	74.0 (*d*)	3.33–3.37 (*m*)	75.1 (*d*)	3.29 (*t*, *J* = 8.7)	75.1 (*d*)	3.20 (*t*, *J* = 8.7)
CH(3′)	78.4 (*d*)	3.42–3.47 (*m*)	78.4 (*d*)	3.42–3.47 (*m*)	77.9 (*d*)	3.38–3.44 (*m*)	78.0 (*d*)	3.37–3.44 (*m*)
CH(4′)	71.2 (*d*)	3.38–3.41 (o)[a])	71.2 (*d*)	3.38–3.41 (o)[a])	71.7 (*d*)	3.34–3.40 (*m*)	72.0 (*d*)	3.32–3.37 (*m*)
C(5′)	78.9 (*d*)	3.38–3.41 (o)[a])	78.9 (*d*)	3.38–3.41 (o)[a])	75.6 (*d*)	3.54 (*ddd*, *J* = 9.1, 6.2, 1.8)	75.4 (*d*)	3.57 (*ddd*, *J* = 9.3, 7.1, 1.9)
CH_2(6′)	62.5 (*t*)	3.85 (*dd*, *J* = 12.0, 1.8), 3.71 (*dd*, *J* = 12.0, 4.5)	62.5 (*t*)	3.85 (*dd*, *J* = 12.0, 1.7), 3.71 (*dd*, *J* = 12.0, 4.4)	64.6 (*t*)	4.52 (*dd*, *J* = 12.0, 2.0), 4.31 (*dd*, *J* = 12.0, 6.1)	64.9 (*t*)	4.51 (*dd*, *J* = 11.8, 2.0), 4.35 (*dd*, *J* = 11.8, 7.0)
C(1″)					169.1 (*s*)		168.9 (*s*)	
CH(2″)					115.7 (*d*)	6.41 (*d*, *J* = 15.8)	115.8 (*d*)	6.39 (*d*, *J* = 15.9)
CH(3″)					147.4 (*d*)	7.61 (*d*, *J* = 15.8)	147.2 (*d*)	7.62 (*d*, *J* = 15.9)
C(4″)					125.5 (*s*)		126.6 (*s*)	
CH(5″,9″)					107.1 (*d*)	6.93 (*s*)	107.1 (*d*)	6.88 (*s*)
C(6″,8″)					149.6 (*s*)		149.5 (*s*)	
C(7″)					140.0 (*s*)		140.0 (*s*)	
2 MeO					56.9 (*q*)	3.88 (*s*)	56.9 (*q*)	3.87 (*s*)

[a]) o = Overlapped.

Compound **3**, a yellow amorphous powder, had the molecular formula $C_{27}H_{36}O_{12}$ as established by HR-ESI-Q-TOF-MS. The presence of a 1,3,4,5-tetrasubstituted phenyl group was deduced from the H-atom signals at δ(H) 6.93 (*s*, 2 H, H–C(5″,9″)) and the C-atom signals at δ(C) 107.1 (C(5″,9″)), 125.5 (C(4″)), 140.0 (C(7″)), and 149.6 (C(6″,8″)). Two MeO groups (δ(H) 3.88) are located at C(6″) and C(8″) due to the HMBCs MeO/C(6″) and C(8″) (*Fig. 2*). Two *d* due to *trans*-olefinic H-atoms at δ(H) 7.61 (*d*, $J = 15.8$ Hz, H–C(3″)) and 6.41 (*d*, $J = 15.8$ Hz, H–C(2″)) in the ^{1}H-NMR spectrum of **3** (*Table 1*), together with the HMBCs H–C(3″)/C(1″), C(4″), C(5″), and C(9″) and H–C(2″)/C(1″) and C(4″), revealed the presence of a *trans*-sinapoyl group (sinapoic acid = 3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid). The remaining ^{1}H- and ^{13}C-NMR signals were similar to those of jasminoside B (=(4*S*)-3-[(*β*-D-glucopyranosyloxy)methyl]-4-(hydroxymethyl)-5,5-dimethylcyclohex-2-en-1-one) [6]. The downfield shift of CH_2(6′) (δ(H) 4.52 and 4.31) and the correlations between CH_2(6′) and C(1″) (δ(C) 169.1) in the HMBC plot suggested the sinapoyl group to be attached at C(6′) of the glucose moiety of jasminoside B. The CD spectrum of **3** showed a negative *Cotton* effect at 231 nm ($\Delta\varepsilon$ −1.67), suggesting the (6*S*) absolute configuration [6][11]. Therefore, **3** was elucidated as (4*S*)-{{[6-*O*-[(2*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-*β*-D-glucopyranosyl}oxy}methyl}-4-(hydroxymethyl)-5,5-dimethylcyclohex-2-en-1-one and named 6′-*O*-*trans*-sinapoyljasminoside B.

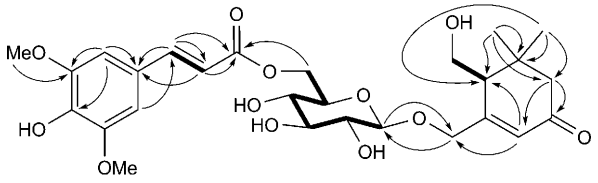

Fig. 2. *Key HMBCs* (H → C) *and COSY correlations* (—) *of compound* **3**

Compound **4** was obtained as yellow needles with the molecular formula $C_{27}H_{36}O_{12}$, as determined by HR-ESI-Q-TOF-MS analysis. The ^{1}H- and ^{13}C-NMR data (*Table 1*) of **4** exhibited the signals due to a *trans*-sinapoyl group and a *β*-D-glucopyranose. The remaining 10 C-signals arising from the aglycone moiety were deduced to be the same as those of jasminoside F (=*β*-D-glucopyranosyl (4*R*)-4-hydroxy-2,6,6-trimethylcyclohex-1-ene-1-carboxylate) [12]. The assignments of ^{1}H- and ^{13}C-NMR data were based on ^{1}H,^{1}H-COSY, HSQC, and HMBC data (*Fig. 3*). Similarly, the linkage of the sinapoyl moiety to the glucose was established to be at C(6′) (δ(C) 64.9) by the observed HMBCs at H–C(6′) (δ(H) 4.51 and 4.35)/C(1″) (δ(C) 168.9). From the key HMBC cross-peaks between H–C(1′) (δ(H) 4.44 (*d*, $J = 7.8$ Hz)) and C(3) (δ(C) 73.9), the glucose unit was deduced to be attached to C(3). The CD spectrum of **4** showed a negative *Cotton* effect at 232.4 nm ($\Delta\varepsilon$ −2.4), suggesting the (3*R*) absolute configuration [12]. The absolute configuration was further confirmed by X-ray diffraction analysis (*Fig. 4*). Therefore, the structure of **4** was elucidated as (4*R*)-4-{{6-*O*-[(2*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-*β*-D-glucopyranosyl}oxy}-2,6,6-trimethylcyclohex-1-ene-1-carboxylic acid and named 6′-*O*-*trans*-sinapoyljasminoside L.

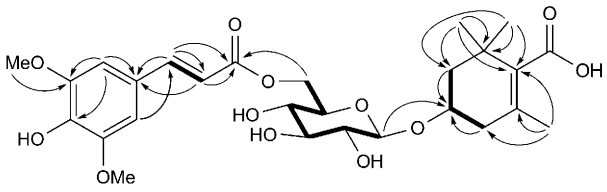

Fig. 3. *Key HMBCs* (H → C) *and COSY correlations* (—) *of compound* **4**

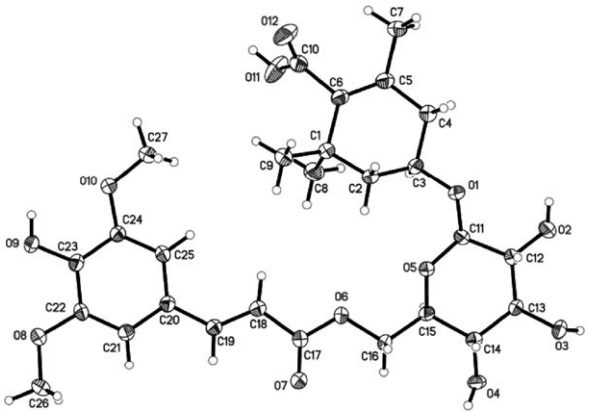

Fig. 4. *Perspective drawing of the X-ray structure of compound* **4**[1])

Compound **5** was obtained as a white amorphous powder, with the molecular formula $C_{21}H_{34}O_{11}$ determined from the HR-ESI-Q-TOF-MS. The ^{1}H- and ^{13}C-NMR data (*Table 2*) of **5** were similar to those of **2**, except for the differences due to the presence of additional *β*-D-xylosyl signals. The acid hydrolysis and GC analysis confirmed the above deduction. The glycosidic linkage was established from the HMBCs at H−C(1″)/C(6′) and H−C(6′)/C(1″). Consequently, **5** was elucidated to be a monoterpenoid diglycoside, named jasminoside M.

Compound **6**, obtained as a yellow amorphous powder, had the molecular formula $C_{22}H_{38}O_{11}$ as determined by HR-ESI-Q-TOF-MS. The ^{1}H- and ^{13}C-NMR data (*Table 2*) of **6** displayed signals attributed to two glucose residues, which were identified from the two anomeric H-atoms (δ(H) 4.37 (*d*, $J = 7.8$ Hz) and 4.29 (*d*, $J = 7.8$ Hz)) and C-atoms signals (δ(C) 104.9 and 103.0). The remaining 1D-NMR spectra showed the presence of three Me, three CH_2, two CH groups, and two quaternary C-atoms. Analysis of COSY and HSQC data led to the deduction of the fragments C(6)−C(5)−C(4) and C(2)−C(1). The constitution of the aglycone moiety was deduced on the basis of the HMBC cross-peaks Me(8,9)/C(6) and C(7), and Me(10)/C(3), C(2), and C(4). The HMBCs H−C(1″)/C(6′) and H−C(6′)/C(1″) suggested that the two sugar units were 1″ → 6′ linked. The key HMBCs found for the anomeric H-atom at δ(H) 4.29 (*d*, $J =$ 7.8 Hz) and C(1) (δ(C) 66.6) indicated that the sugar chain was attached at C(1) of the aglycon. The (2*E*)-configuration was determined by the downfield shift of C(4) (δ(C) 40.7). Thus, **6** was elucidated as (2*E*)-3,7-dimethylocta-2,6-dien-1-yl 6-*O*-*β*-D-glucopyranosyl-*β*-D-glucopyranoside and named jasminoside N.

Table 2. *^{1}H- and ^{13}C-NMR Data of Compounds* **5**–**8**. 400 MHz for ^{1}H and 100 MHz for ^{13}C, in CD_3OD; δ in ppm, J in Hz.

	5		**6**		**7**		**8**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
C(1) or CH_2(1)	34.2 (*s*)		66.6 (*t*)	4.35 (br. *d*, *J* = 11.6), 4.21 (*dd*, *J* = 11.6, 7.3)	166.5 (*s*)		166.5 (*s*)	
CH_2(2) or H–C(2)	39.8 (*t*)	1.44–1.48 (*m*)	121.5 (*d*)	5.37 (*t*, *J* = 6.4)	115.9 (*d*)	5.75 (*d*, *J* = 0.9)	115.8 (*d*)	5.74 (*d*, *J* = 0.9)
CH_2(3) or C(3)	19.8 (*t*)	1.65–1.71 (*m*)	141.9 (*s*)		164.4 (*s*)		164.5 (*s*)	
CH_2(4)	32.3 (*t*)	1.99–2.04 (*m*)	40.7 (*t*)	2.02–2.08 (*m*)	42.0 (*t*)	2.18–2.23 (o)[a])	42.0 (*t*)	2.17–2.24 (o)[a])
C(5) or CH_2(5)	136.6 (*s*)		27.5 (*t*)	2.09–2.16 (*m*)	27.0 (*t*)	2.18–2.23 (o)[a])	27.1 (*t*)	2.17–2.24 (o)[a])
C(6) or H–C(6)	135.6 (*s*)		125.1 (*d*)	5.11 (*t*, *J* = 6.4)	124.1 (*d*)	5.08–5.13 (*m*)	124.1 (*d*)	5.08–5.14 (*m*)
Me(7) or C(7)	21.6 (*q*)	1.71 (*s*)	132.9 (*s*)		133.5 (*s*)		133.5 (*s*)	
Me(8)	28.9 (*q*)	1.12 (*s*)	25.9 (*q*)	1.68 (*s*)	25.8 (*q*)	1.68 (*s*)	25.8 (*q*)	1.68 (*s*)
Me(9)	28.9 (*q*)	1.12 (*s*)	17.8 (*q*)	1.61 (*s*)	17.7 (*q*)	1.62 (*s*)	17.8 (*q*)	1.62 (*s*)
C(10) or Me(10)	170.9 (*s*)		16.6 (*q*)	1.69 (*s*)	19.3 (*q*)	2.19 (*d*, *J* = 1.1)	19.3 (*q*)	2.17 (*d*, *J* = 1.1)
CH(1′)	95.7 (*d*)	5.53 (*d*, *J* = 7.4)	103.0 (*d*)	4.29 (*d*, *J* = 7.8)	95.2 (*d*)	5.47 (*d*, *J* = 8.0)	95.2 (*d*)	5.48 (*d*, *J* = 8.0)
CH(2′)	73.9 (*d*)	3.33–3.38 (*m*)	75.0 (*d*)	3.18–3.23 (o)[a])	73.9 (*d*)	3.32–3.38 (*m*)	73.9 (*d*)	3.33–3.39 (o)[a])
CH(3′)	78.2 (*d*)	3.40–3.45 (o)[a])	78.0 (*d*)	3.33–3.37 (o)[a])	77.9 (*d*)	3.38–3.44 (o)[a])	77.9 (*d*)	3.33–3.39 (o)[a])
CH(4′)	71.1 (*d*)	3.40–3.45 (o)[a])	71.5 (*d*)	3.33–3.37 (o)[a])	71.1 (*d*)	3.38–3.44 (o)[a])	71.0 (*d*)	3.42–3.45 (o)[a])
CH(5′)	78.0 (*d*)	3.57 (*ddd*, *J* = 9.5, 5.2, 1.9)	77.1 (*d*)	3.40–3.43 (*m*)	77.7 (*d*)	3.55 (*ddd*, *J* = 9.3, 5.6, 2.2)	77.7 (*d*)	3.56 (*ddd*, *J* = 8.1, 5.7, 2.5)
CH_2(6′)	69.5 (*t*)	4.07 (*dd*, *J* = 11.7, 1.9), 3.77 (*dd*, *J* = 11.7, 5.2)	69.8 (*t*)	4.14 (*dd*, *J* = 11.5, 2.0), 3.81 (*dd*, *J* = 11.4, 5.2)	69.5 (*t*)	4.09 (*dd*, *J* = 11.3, 1.8), 3.73 (*dd*, *J* = 11.2, 5.4)	69.5 (*t*)	4.16 (*dd*, *J* = 11.3, 1.8), 3.77 (*dd*, *J* = 11.3, 5.2)
CH(1″)	105.2 (*d*)	4.33 (*d*, *J* = 8.1)	104.9 (*d*)	4.37 (*d*, *J* = 7.8)	105.1 (*d*)	4.28 (*d*, *J* = 7.4)	104.5 (*d*)	4.33 (*d*, *J* = 7.7)
CH(2″)	74.8 (*d*)	3.20 (*t*, *J* = 8.3)	75.1 (*d*)	3.18–3.23 (o)[a])	74.9 (*d*)	3.20 (*t*, *J* = 7.6)	75.1 (*d*)	3.21 (*t*, *J* = 7.6)
CH(3″)	77.5 (*d*)	3.28–3.33 (*m*)	78.0 (*d*)	3.36–3.40 (o)[a])	77.8 (*d*)	3.28–3.34 (*m*)	77.9 (*d*)	3.42–3.45 (o)[a])
CH(4″)	71.1 (*d*)	3.45–3.52 (*m*)	71.6 (*d*)	3.25–3.33 (o)[a])	71.2 (*d*)	3.44–3.51 (*m*)	71.5 (*d*)	3.29–3.34 (*m*)
CH_2(5″) or CH(5″)	66.8 (*t*)	3.85 (*dd*, *J* = 11.4, 5.2), 3.18 (br. *d*, *J* = 11.4)	78.0 (*d*)	3.25–3.33 (o)[a])	66.9 (*t*)	3.84 (*dd*, *J* = 11.4, 5.3), 3.18 (br. *d*, *J* = 11.4)	77.9 (*d*)	3.23–3.28 (*m*)
CH_2(6″)			62.8 (*t*)	3.87 (*dd*, *J* = 11.9, 1.8), 3.69 (*dd*, *J* = 11.9, 5.2)			62.7 (*t*)	3.85 (*dd*, *J* = 12.0. 2.2), 3.66 (*dd*, *J* = 12.0, 5.4)

[a]) o = Overlapped.

Compound **7** was obtained as a yellow amorphous powder. The molecular formula of **7**, $C_{21}H_{34}O_{11}$, was deduced from the HR-ESI-Q-TOF-MS. The ^{1}H- and ^{13}C-NMR data of **7** lacked the signals due to an CH_2O group (C(1)) in **6** and showed instead signals characteristic of an ester C=O group (δ(C) 166.5). The aglycone moiety was determined as 3,7-dimethylocta-2,6-dienoic acid by the same method as in the case of **6**. Compared with **5**, **7** possessed the same sugar chain as **5**. Additionally, the HMBC between H–C(1′) and C(1) confirmed the linkage of the sugar chain to C(1). Thus, **7** was elucidated as 6-*O*-β-D-xylopyranosyl-β-D-glucopyranosyl (2*E*)-3,7-dimethylocta-2,6-dienoate.

Compound **8** was obtained as a yellow amorphous powder with a molecular formula $C_{22}H_{36}O_{12}$. The ^{1}H- and ^{13}C-NMR data of **8** were similar to those of the aglycone moiety in **7**, together with those of the sugar chain in **6**. Thus, the structure of **8** was elucidated as 6-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl (2*E*)-3,7-dimethylocta-2,6-dienoate.

The structures of the other known compounds were identified as jasminoside C (**9**) [6], jasminol E (**10**) [6], and sacranoside B (**11**) [13] by comparing their spectroscopic data with those reported.

Plants of the genus *Gardenia* are known to be rich of terpenoids, including monocyclic monoterpenoids and their glycosides, as well as of iridoids and their glycosides, crocetin and their glucosides, and triterpenoids. Previous investigations resulted in the isolation of a number of monocyclic monosaccharide glucosides. In this article, the reported compounds **6**–**8** and **11** were chain-monoterpenoid disaccharide glucosides, which were unknown in the *Gardenia* genus before. The pyronane-type monocyclic monoterpenoids with a sinapoyl substituent are rare among terpenoids [11].

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Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Haiyang Chemical Group Corporation*), *Sephadex LH-20* (*Amersham Biosciences AB*), *Toyopearl HW-40* (*Toyo Soda MFG*), and *ODS* (60–80 μm; *Merck*). TLC: SiO_2 GF_{254} (*Qingdao Haiyang Chemical Group Corporation*). HPLC: *Dionex* system equipped with a *Dionex-PDA-100* diode-array detector (DAD) and a *Dionex-ASP-100* auto-sampler (*Dionex*, *USA*); *RP-18* column (5 μm, 4.6 × 250 mm; *Purospher STAR*) for analysis; *RP-18* column (5 μm, 20 × 250 mm; *Purospher STAR*) for prep. separations. Optical rotations: *Jasco-P-1020* digital polarimeter. CD Spectra: *Jasco-810* spectrometer; in nm ($\Delta\varepsilon$). IR Spectra: *Jasco-FT/IR-480-plus* spectrometer; $\tilde{\nu}$ in cm^{-1}. UV Spectra: *Jasco-V-550* UV/VIS spectrometer; λ_{max} (log ε) in nm. NMR Spectra: *Bruker-Avance-400* spectrometer; at 400 MHz for ^{1}H and 100 MHz for ^{13}C; in CD_3OD; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI- and HR-ESI-Q-TOF-MS: *Finnigan-LCQ-Advantage-MAX* mass spectrometer and *Micromass-Q-TOF* mass spectrometer; in *m*/*z* (rel. %).

Plant Material. The fruits of *G. jasminoides* were purchased from *Guangzhou Qingping Medical Material Market*, P. R. China, in April 2007, and identified by Prof. *Danyan Zhang*, Guangzhou Chinese Medicine University. A voucher specimen has been deposited with the Institute of Traditional Chinese Medicine & Natural Products, Jinan University, Guangzhou, P. R. China.

Extraction and Isolation. Dried fruits of *G. jasmonoides* (8.0 kg) were cut into small pieces and refluxed 3 × for 2 h with 60% (*v*/*v*) EtOH. After evaporation of the EtOH, the aq. residue was subjected to CC (*D101*; EtOH/H_2O) *Fractions 1–5*. *Fr. 3* (105.0 g) was separated by CC (SiO_2; gradient $CHCl_3$/MeOH): *Frs. 3.1–3.16*. *Fr. 3.7* (eluted with $CHCl_3$/MeOH 9:1) was submitted to repeated CC (*ODS*, *Sephadex LH-20*, and *Toyopearl HW-40*; MeOH/H_2O), followed by prep. HPLC (MeOH/H_2O 4:6): **1** (3.2 mg), **2** (3.7 mg), **3** (40.7 mg), **4** (55.2 mg), and **9** (3.0 mg). Compounds **5** (28.6 mg), **7** (6.0 mg), **8** (19.8 mg), **6** (8.7 mg), and **11** (17.6 mg) were obtained from the successive purification by CC (*ODS*, *Toyopearl HW-40*), and prep. HPLC (MeOH/H_2O 4:6) from *Fr. 3.9*, resp. Compound **10** (14.1 mg) was obtained from *Fr. 3.2* by prep. HPLC (MeOH/H_2O 7:3).

Jasminoside J (=*β*-D-*Glucopyranosyl 2,6,6-Trimethylcyclohexa-1,3-diene-1-carboxylate*; **1**): White amorphous powder. $[\alpha]_D^{23.8} = -35.2$ ($c = 1.25$, MeOH). UV (MeOH): 201 (3.88), 278 (4.07). IR (KBr): 3414, 1713, 1644, 1515, 2925, 1068. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-Q-TOF-MS (pos.): 351.1437 ($[M+Na]^+$, $C_{16}H_{24}NaO_7^+$; calc. 351.1420).

Jasminoside K (=*β*-D-*Glucopyranosyl 2,6,6-Trimethylcyclohex-1-ene-1-carboxylate*; **2**): White amorphous powder. $[\alpha]_D^{23.8} = -42.5$ ($c = 1.2$, MeOH). UV (MeOH): 204 (3.68). IR (KBr): 3398, 2928, 2867, 1725, 1645, 1455, 1226, 1063, 1024. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-Q-TOF-MS (pos.): 353.1564 ($[M+Na]^+$, $C_{16}H_{26}NaO_7^+$; calc. 353.1576).

6′-O-trans-*Sinapoyljasminoside B* (=*(4*S*)-3-{{[6*-O-*[(2*E*)-3-(4-Hydroxy-3,5-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-β*-D-*glucopyranosyl}oxy}methyl}-4-(hydroxymethyl)-5,5-dimethylcyclohex-2-en-1-one*; **3**): Yellow amorphous powder. $[\alpha]_D^{23.2} = -21.2$ ($c = 0.5$, MeOH). UV (MeOH): 204 (4.34), 240 (4.44), 329 (4.29). CD ($c = 0.025$, MeOH): 231 (−1.67). IR (KBr): 3424, 2926, 2361, 1644, 1515, 1114. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-Q-TOF-MS (pos.): 575.2074 ($[M+Na]^+$, $C_{27}H_{36}NaO_{12}^+$; calc. 575.2104).

6′-O-trans-*Sinapoyljasminoside L* (=*(4*R*)-4-[{6*-O-*[(2*E*)-3-(4-Hydroxy-3,5-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-β*-D-*glucopyranosyl}oxy}-2,6,6-trimethylcyclohex-1-ene-1-carboxylic Acid*; **4**): Yellow needles. $[\alpha]_D^{23.2} = -25.6$ ($c = 0.5$, MeOH). UV (MeOH): 204 (3.04), 240 (3.27), 329 (3.27). CD ($c = 0.05$, MeOH): 232.4 (−2.4). IR (KBr): 3424, 2926, 2362, 1692, 1515, 1116. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-Q-TOF-MS (pos.): 575.2128 ($[M+Na]^+$, $C_{27}H_{36}NaO_{12}^+$; calc. 575.2104).

Jasminoside M (=*6*-O-*β*-D-*Xylopyranosyl-β*-D-*glucopyranosyl 2,6,6-Trimethylcyclohex-1-ene-1-carboxylate*; **5**): White amorphous powder. $[\alpha]_D^{23.8} = -53.6$ ($c = 1.4$, MeOH). UV (MeOH): 208 (3.96). IR (KBr): 3389, 2929, 2856, 1717, 1645, 1056. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-Q-TOF-MS (pos.): 485.1997 ($[M+Na]^+$, $C_{21}H_{34}NaO_{11}^+$; calc. 485.1999).

Jasminoside N (=*(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl 6*-O-*β*-D-*Glucopyranosyl-β*-D-*glucoparanoside*; **6**): Yellow amorphous powder. $[\alpha]_D^{23.8} = -38.3$ ($c = 1.2$, MeOH). UV (MeOH): 206 (3.75). IR (KBr): 3397, 2928, 1609, 1567, 1420, 1384, 1073. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-Q-TOF-MS (pos.): 501.2307 ($[M+Na]^+$, $C_{22}H_{38}NaO_{11}^+$; calc. 501.2311).

Jasminoside O (=*6*-O-*β*-D-*Xylopyranosyl-β*-D-*glucopyranosyl (2*E*)-3,7-Dimethylocta-2,6-dienoate*; **7**): Yellow amorphous powder. $[\alpha]_D^{23.8} = -37.5$ ($c = 1.6$, MeOH). UV (MeOH): 221 (3.98). IR (KBr): 3407, 2926, 1715, 1644, 1418, 1384, 1073. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-Q-TOF-MS (pos.): 485.1994 ($[M+Na]^+$, $C_{21}H_{34}NaO_{11}^+$; calc. 485.1999).

Jasminoside P (=*6*-O-*β*-D-*Glucopyranosyl-β*-D-*glucopyranosyl (2*E*)-3,7-Dimethylocta-2,6-dienoate*; **8**): Yellow amorphous powder. $[\alpha]_D^{23.8} = -33.3$ ($c = 1.2$, MeOH). UV (MeOH): 223 (4.10). IR (KBr): 3388, 2926, 1721, 1643, 1383, 1071. ^{1}H- and ^{13}C- NMR: *Table 2*. HR-ESI-Q-TOF-MS (pos.): 515.2112 ($[M+Na]^+$, $C_{22}H_{36}NaO_{12}^+$; calc. 515.2104).

Crystallographic Data of **4**. Yellow crystals, $C_{27}H_{36}O_{12}$, M_r 552, crystal size 0.20 × 0.30 × 0.40 mm, space group $P2_1$, T 150(2) K, $a = 14.1176(2)$ Å, $b = 7.9354(1)$ Å, $c = 14.6295(2)$ Å, $\alpha = 90.00°$, $\beta = 100.864(1)°$, $\gamma = 90.00°$, $V = 1609.55(1)$ Å^3, $Z = 2$, $F_{000} = 684$, $D_{calc} = 1.322$ mg/m^3. Data were collected with a *Bruker-APEX-CCD* diffractometer with graphite-monochromated CuK_α radiation (λ 1.54178 Å). The crystal structure was solved by direct methods, expanded by difference *Fourier* syntheses, and refined by full-matrix least-squares on F^2 with the SHELXTL V.6.10 software package. A total of 4079 reflections was collected, with 3467 independent ones (R(int) = 0.0376), data/restraints/parameters 3467/1/411, goodness-of-fit on $F^2 = 1.025$, final indices $R_1 = 0.0384$, $wR_2 = 0.0904$, largest difference peak and hole, 0.259 and −0.251 eÅ^{-3}. CCDC-742820 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

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