Studies of the Constituents of *Gardenia* Species. I. Monoterpenoids from Gardeniae Fructus

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Nine new monoterpenoids, gardenamide (1), 6α-butoxygeniposide (2), 6β-butoxygeniposide (3), 6″-*O*-*p*-*cis*-coumaroylgenipin gentiobioside (4), and jasminosides A (6), B (7), C (8), D (9), E (10), were isolated from Gardeniae Fructus. Their structures were established on the basis of spectral analysis.

Key words Gardeniae Fructus; Rubiaceae; iridoidal amide; iridoid; safranal-type monoterpene

The fruit of *Gardenia jasminoides* ELLIS forma *grandiflora* (LOUR.) MAKINO (Rubiaceae) ("Shan-zhi-i" in Chinese) has been used in Japan as an herbal drug for its antiphlogistic, diuretic, and cholagogue effects. It has been also used as a yellow dye and used to treat contusions. Furthermore, it is an important crude drug in Kanpo (traditional Chinese medicine) prescriptions, Shishishi-to, Shishikankyo-to, Inchinko-to, *etc.*, and it has sedative, anti-inflammatory, choleretic, anti-pyretic, and diuretic effects. The chemical constituents from the fruits of this plant and their effects have been examined by many investigators, and iridoid, a *p*-hydroxycinnamic acid derivative, and carotenoid, have been identified. Geniposide is the main constituent of this plant, and genipin is its aglycone. These constituents have been reported to exhibit various activities, including a choleretic effect. For example, they inhibit the writhing behavior in mice induced by acetic acid, and genipin has a weak anti-acetylcholine and anti-histamine actions on the isolated ilea of mouse and guinea pig, respectively. The *p*-hydroxycinnamic acid derivatives isolated from this plant, inhibit 5-lipoxygenase activity.[1-9] We have now examined the chemical constituents of Gardeniae Fructus in detail and this paper describes the structure elucidation of nine new monoterpenoids (**1**—**4**, **6**—**10**) isolated, along with a known safranol-type monoterpene (**5**), from this plant. The isolation procedure is described in detail in the Experimental section.

Compound **1**, named gardenamide A, was obtained as an amorphous powder, $[\alpha]_D$ +404.4° (MeOH). Its molecular formula $C_{11}H_{13}NO_4$ (obs. *m/z*: 223.0845) was determined from the high resolution electron impact mass spectrum (HR-EI-MS). The ^{1}H- and ^{13}C-NMR spectral data in $CDCl_3$ revealed that **1** has two tri-substituted double bonds [one of the olefinic proton signals at δ 7.20 (1H, d, J=5.6 Hz) collapsed to a singlet by addition of D_2O], two methylenes [a set of methylene proton signals at δ 4.37 (1H, dt, J=13.0, 6.7 Hz) and 4.31 (1H, dd, J=13.0, 5.1 Hz) collapsed to a broad doublet by addition of D_2O], two methines, and carbomethoxyl and carbonyl moieties. The ^{1}H-NMR spectrum in $CDCl_3$ also showed amino [δ 7.49 (1H, br s, 1H, disappearing on D_2O exchange)] and hydroxyl [δ 3.88 (1H, dd, J=6.7, 5.1 Hz, 1H, disappearing on D_2O exchange)] signals. Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of **1** were undertaken with the aid of ^{1}H–^{1}H shift correlation spectroscopy (COSY) and ^{1}H-detected multiple-bond correlation (HMBC, Fig. 1) experiments. From these data,

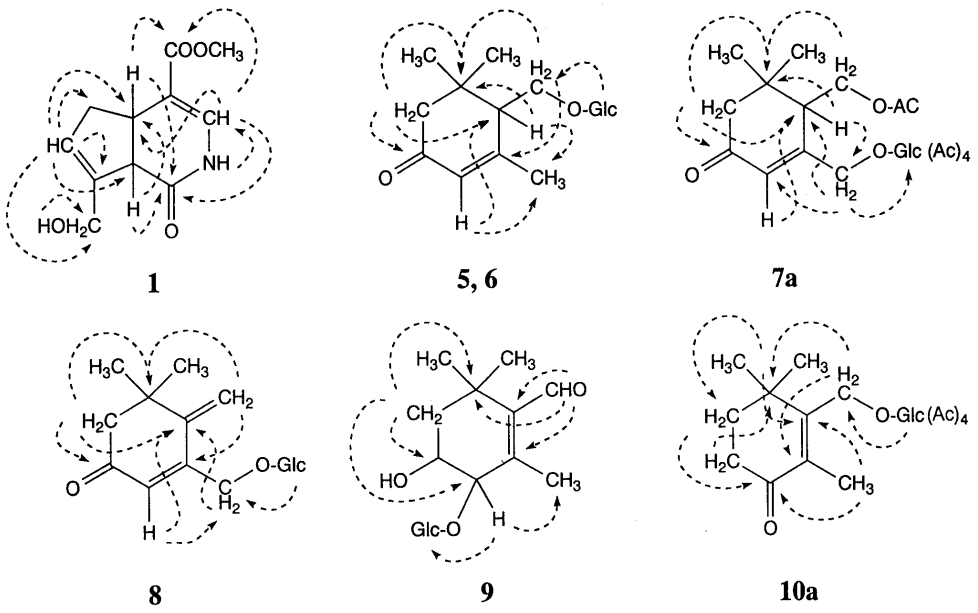

Fig. 1. The Main HMBC Correlations

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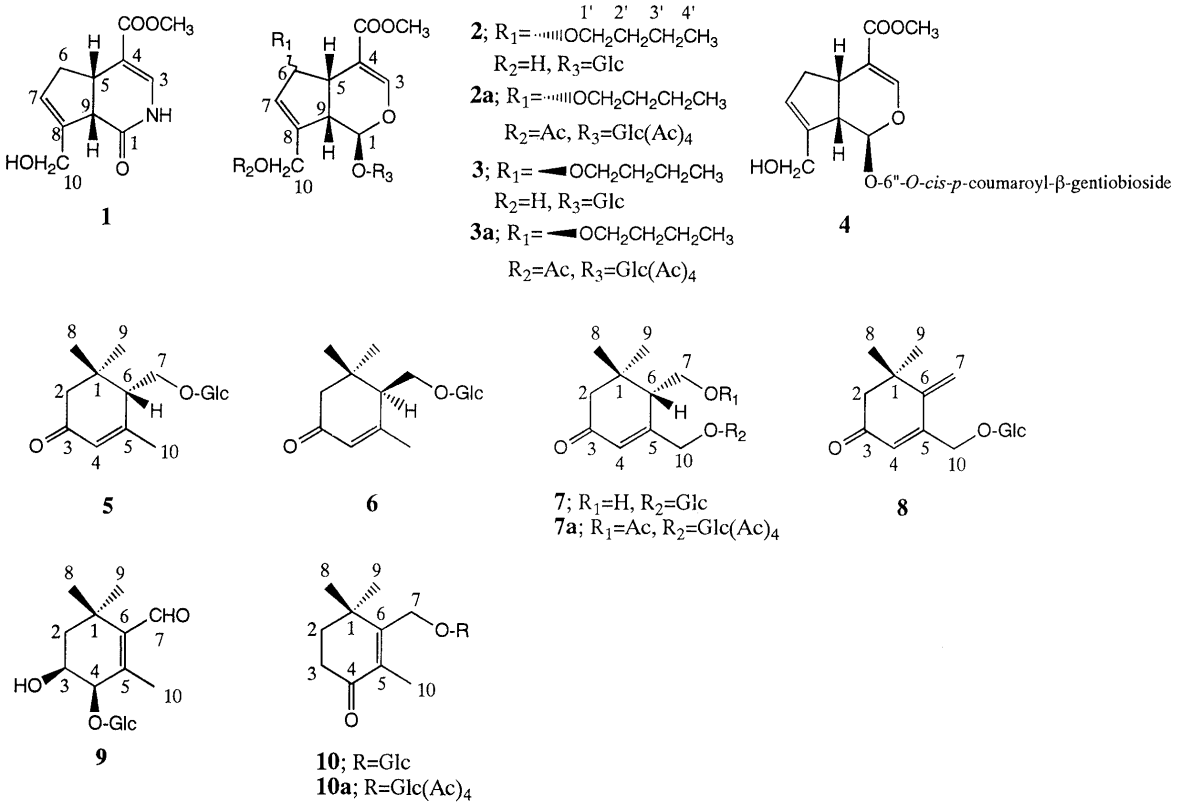

Chart 1

1 was suggested to be an iridoid derivative, having a δ-lactam structure. The stereochemistry of **1** was clarified from the coupling constant (see Experimental) and the difference in the nuclear Overhauser effect (NOE) experiment. An NOE was observed between 5-H and 9-H, suggesting that the δ-lactam ring is fused *cis* at the C-5 and C-9 position (see Chart 1). Thus, the relative structure of **1** is established to be as shown.

Compounds **2** and **3** were obtained as an amorphous powder, $[\alpha]_D$ +15.0° and −78.6° (MeOH), respectively. In the ^{1}H- and ^{13}C-NMR spectra of **2** and **3**, signal patterns were very similar to those of 6α-[5] and 6β-hydroxygeniposides,[3] respectively, except for the presence of signals due to an *n*-butoxyl group. The location of the *n*-butoxyl group on C-6 in **2** and **3** was deduced from comparison of the ^{1}H-NMR spectra of **2** and **3** with those of their acetates, **2a** and **3a**, respectively. The HMBC data of **2a** and **3a** also corroborated the above deduction. Thus, acetylation shifts were not observed at C-6 positions but were observed at C-10 and Glc-2, 3, 4 and 6 positions in **2a** and **3a**. The configuration of the *n*-butoxyl group at C-6 in **2** and **3** was determined as α and β from the coupling constants of 6-H in **2a** and **3a**, respectively [6-H of **2a**: double doublet (δ 4.43, J=6.1, 2.4 Hz), 6-H of **3a**: broad singlet (δ 4.24)]. From the above data, the structures of **2** and **3** were concluded to be 6α- and 6β-*n*-butoxygeniposide, respectively.

Compound **4** was obtained as an amorphous powder, $[\alpha]_D$ +7.05°. Its ^{1}H-NMR spectrum closely resembled that of 6″-*O*-*trans*-*p*-coumaroylgenipin gentiobioside isolated from this plant,[9] except that the olefin proton signal at δ 5.81 and 6.87 (each 1H, d) were shifted upfield and their coupling constant (J=12.9 Hz) was smaller than that of 6″-*O*-*trans*-*p*-coumaroylgenipin gentiobioside. This indicated that the olefin in the *p*-coumaroyl moiety of **4** has a *cis*-configuration. The ^{13}C-NMR spectrum confirmed that **4** is the *cis*-isomer of 6″-*O*-*trans*-*p*-coumaroylgenipin gentiobioside. On the basis of the above data, the structure of **4** was determined to be 6″-*O*-*cis*-*p*-coumaroylgenipin gentiobioside.

Compound **5** was identified as (4*S*)-4-(hydroxymethyl)-3,5,5-trimethylcyclohex-2-enone-β-D-glucopyranoside, which has been isolated from the stigmasta of *Crocus sativus* L., by comparison of various diagnostic data with reported values.[10] This is the first time that the glycoside itself has been isolated, and so we named this compound epijasminoside A.

Compound **6**, named jasminoside A, was obtained as an amorphous powder, $[\alpha]_D$ −33.0° (MeOH). The ^{1}H- and ^{13}C-NMR spectra of **6** revealed the presence of an α, β-unsaturated ketone [δ_H 5.89 (1H, br s). δ_C 203.2 (s), 165.5 (s), 127.6 (d)], a methylene group adjacent to the α, β-unsaturated ketone [δ_H 1.97, 2.80 (each 1H, d, J=17.0 Hz). δ_C 49.5 (t)], an oxygenated methylene [δ_H 3.77 (1H, dd, J=10.6, 4.0 Hz), 4.25 (1H, dd, J=10.6, 3.8 Hz). δ_C 69.3 (t)], and a methine [δ_H 2.21 (1H, br t, J=3.8 Hz). δ_C 52.8 (d)] adjacent to the oxygenated methylene moiety. Further, NMR analysis showed the presence of two methyl groups attached to a quaternary carbon [δ_H 1.04, 1.15 (each 3H, s). δ_C 27.3, 29.4 (each q), 36.3 (s)], a vinyl methyl group [δ_H 2.09 (3H, d, J=1.3 Hz). δ_C 24.2 (q)], and β-glucose in **6**. These NMR spectral data of **6** were very similar to those of **5** (see Experimental). The HMBC data of **6** also corroborated the above deduction (Fig. 1). The relative configurations of C-6 in **5** and **6** were determined by ^{1}H–^{1}H COSY and the NOE

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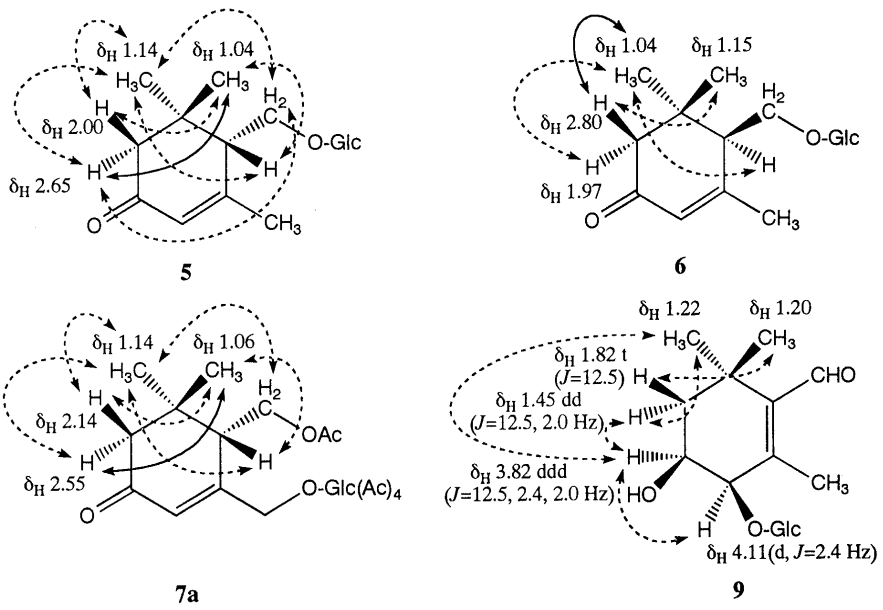

Fig. 2. NOE Correlations and W-Couplings
(⋯⋯▸ NOE, ⟷ W-Coupling)

spectroscopy (NOESY) experiments. As shown in Fig. 2, the ^{1}H–^{1}H COSY and NOESY spectra of **5** and **6** indicated both C-7 oxymethylene groups to be quasi-axial with respect to the half-chair form of the cyclohexenone, so that the aglycone parts of **5** and **6** were deduced to be enantiomeric structures. The absolute configurations of **5** and **6** were determined from the circular dichroism (CD) spectra (Fig. 3).[11] The CD spectrum of **6** showed positive Cotton effects at 237.5 nm ($\Delta\varepsilon$ +1.85) and 211.0 nm ($\Delta\varepsilon$ +1.55), suggesting the C-7 oxymethylene group and one of the methylene protons (δ 2.80) at C-2 to have β-quasi-axial orientations.[11] On the other hand, the CD spectrum of **5** showed negative Cotton effects at 240.5 nm ($\Delta\varepsilon$ −2.06) and 207.5 nm ($\Delta\varepsilon$ −1.99), suggesting the C-7 oxymethylene group and one of the methylene protons (δ 2.65) at C-2 to have α-quasi-axial orientations. On the basis of these results, the configuration of the chiral center at C-6 was assigned as *S* in **5** and *R* in **6**, and the full structure of **5** and **6** were established as shown. The location of glucose in **5** and **6** was determined from the HMBC data.

Compound **7**, named jasminoside B, was purified as its pentaacetate (**7a**), $[\alpha]_D$ −60.0° (MeOH). Its ^{1}H- and ^{13}C-NMR spectral patterns were similar to those of **6**. The ^{1}H- and ^{13}C-NMR spectra of **7a**, however, lacked signals of the allylic methyl moiety at C-10 in **6** and instead showed signals characteristic of an oxygenated methylene moiety [δ_H 4.29 (1H, dd, J=15.5, 2.3 Hz), 4.53 (1H, dd, J=15.5, 1.3 Hz), δ_C 70.4]. The assignment of this oxygenated methylene moiety at C-10 and the location of a glucosyl group on the C-10 were determined from the HMBC spectrum; that is, the anomeric carbon of glucose (δ 100.8) showed an HMBC correlation with the oxygenated methylene protons, which are also correlated to C-4 [δ 125.9 (d)] and C-5 [δ 157.3 (s)]. From the above data, including the other HMBC correlations of **7a** (Fig. 1), **7** was shown to have a planar structure. The relative configuration of C-6 was determined from the ^{1}H–^{1}H

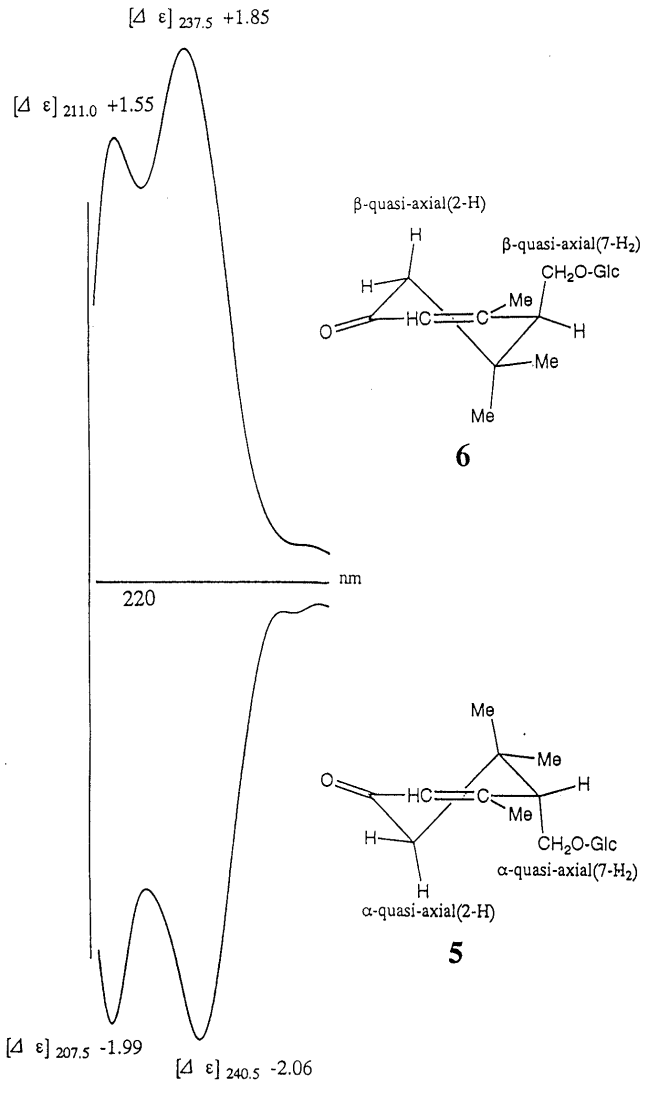

Fig. 3. The CD Spectra of **5** and **6** (MeOH)

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Table 1. ^{1}H-NMR Chemical Shifts (270 MHz)

H	5[a]	6[a]	7a[b]	8[a]	9[a]	10a[b]
2	α; 2.65 d (17.0) β; 2.00 d (17.0)	α; 1.97 d (17.0) β; 2.80 d (17.0)	α; 2.55 d (17.5) β; 2.14 d (17.5)	2.39 s	α; 1.45 dd (12.5, 2.0) β; 1.82 t (12.5)	1.82 br t (6.9)
3	—	—	—	—	3.82 ddd (12.5, 2.4, 2.0)	2.50 br t (6.9)
4	5.89 br s	5.89 br s	6.07 br s	6.35 br s	4.11 d (2.4)	—
6	2.26 br t (4.3)	2.21 br t (3.8)	2.29 br t (4.3)	—	—	—
7	3.83 dd (10.4, 4.3) 4.18 dd (10.4, 4.3)	3.77 dd(10.6, 4.0) 4.25 dd (10.6, 3.8)	4.15 dd (11.9, 4.5) 4.45 dd (11.9, 4.3)	5.45 d (1.7) 5.53 br s	10.14 s	4.22 d (11.0) 4.53 d (11.0)
8	1.04 s	1.15 s	1.06 s	1.214 s[c]	1.20 s	1.15 s[c]
9	1.14 s	1.04 s	1.14 s	1.208 s[c]	1.22 s	1.16 s[c]
10	2.10 d (1.3)	2.09 d (1.3)	4.29 dd (15.5, 2.3) 4.53 dd (15.5, 1.3)	4.51 dd (15.8, 1.7) 4.81 dd (15.8, 1.7)	2.27 s	1.80 s
Glc-1	4.22 d (7.8)	4.24 d (7.8)	4.59 d (7.8)	4.37 d (7.6)	4.50 d (7.6)	4.54 d (8.1)
Glc-2	3.12 dd (8.9, 7.8)	3.09 t (7.8)	5.05 dd (9.7, 7.8)	3.22—3.40	3.22—3.40	5.01 dd (9.5,8.1)
Glc-3	3.20—3.38	3.20—3.38	5.22 t (9.7)	3.22—3.40	3.22—3.40	5.21 t (9.5)
Glc-4	3.20—3.38	3.20—3.38	5.09 t (9.7)	3.22—3.40	3.22—3.40	5.09 t (9.5)
Glc-5	3.20—3.38	3.20—3.38	3.71 ddd (9.7, 4.4, 2.5)	3.22—3.40	3.22—3.40	3.70 ddd (9.5, 4.8, 2.9)
Glc-6	3.65 dd (12.0, 5.2) 3.87 dd (12.0, 1.6)	3.64 dd (12.0, 5.6) 3.87 dd (12.0, 1.8)	4.14 dd (12.7, 2.5) 4.20 dd (12.7, 4.4)	3.66 dd (11.8, 5.8) 3.89 dd (11.8, 1.3)	3.68 dd (12.0, 5.4) 3.87 dd (12.0, 2.3)	4.22 m
Ac	—	—	2.09, 2.08, 2.03, 2.013, 2.01	—	—	2.09, 2.03, 2.01, 2.00

Values in (δ) ppm. The coupling constants (J) in parentheses are in Hz. *a*) Measured in CD_3OD. *b*) Measured in $CDCl_3$. *c*) May be reversed in each vertical column.

COSY and NOESY spectra. As shown in Fig. 2, the ^{1}H–^{1}H COSY spectrum indicated the relationship between one of the methylene protons (δ 2.55) at C-2 and one of the methyl protons (δ 1.06) at C-1 to be quasi-*trans*-axial with respect to the half-chair form of the cyclohexenone. NOEs were observed between 6-H at δ 2.29 and both of the methyls at C-1, showing that 6-H is quasi-equatorial. Furthermore, an NOE was observed between the oxymethylene proton at C-7 (δ 4.15, 4.45) and the quasi-equatorial methyl protons at C-1 (δ 1.14), suggesting that the oxymethylene group at C-7 is quasi-axial. The absolute configuration of **7a** was determined from the CD spectrum.[11] The CD spectrum of **7a** showed negative Cotton effects at 235.0 nm (sh) ($\Delta\varepsilon -1.75$) and 209.5 nm ($\Delta\varepsilon -3.29$), suggesting that the oxymethylene group at C-7 and one of the two methylene protons at C-2 (δ 2.55) are α-quasi-axial. Therefore, the configuration of **7** at C-6 was determined as *S*. From this evidence, the full structure of **7** was established to be as shown in Chart 1.

Compound **8**, named jasminoside C, was obtained as an amorphous powder, $[\alpha]_D$ −68.0° (MeOH). The NMR spectra of **8** lacked the signals due to a methine (C-6) and a hydroxymethylene (C-7) in **7** and instead showed signals characteristic of an exocyclic methylene group [δ_H 5.45 (1H, d, J=1.7Hz), 5.53 (1H, br s), δ_C 114.6 (t), 150.1 (s)]. In the ^{1}H–^{1}H COSY, cross-peaks were observed between 4-H and 10-H_2 and one of the exocyclic methylene protons (δ 5.45). Furthermore, a UV maximum at 269.0 nm in the spectrum of **8** supports the presence of a dienone moiety. From the above data, including the HMBC correlations (Fig. 1), **8** was established to be as depicted in Chart 1.

Compound **9**, named jasminoside D, was obtained as an amorphous powder, $[\alpha]_D$ −59.3° (MeOH). The ^{1}H-NMR spectrum of **9** showed signals of an aldehyde proton [δ 10.14 (1H, s)], an anomeric proton [δ 4.50 (1H, d, J=7.6 Hz)], two oxygenated methine protons [δ 4.11 (1H, d, J=2.4 Hz), 3.80 (1H, m)], a methylene proton [δ 1.82 (1H, t, J=12.5 Hz), 1.45 (1H, dd, J=12.5, 2.0Hz)], a vinyl methyl proton [δ 2.27 (3H, s)] and two tertiary methyl protons [δ 1.22, 1.20 (each 3H, s)]. The ^{13}C-

Table 2. ^{13}C-NMR Chemical Shifts (67.8 MHz)

C	5[a]	6[a]	7a[b]	8[a]	9[a]	10a[b]
1	36.5	36.3	35.2	39.8	36.7	35.3
2	49.5	49.5	48.6	52.9	44.0	37.3
3	202.9	203.2	198.5	201.9	67.0	34.3
4	127.5	127.6	125.9	125.1	84.2	199.3
5	165.8	165.5	157.3	154.9	151.2	134.9
6	52.8	52.8	45.9	150.1	142.6	155.5
7	69.2	69.3	61.8	114.6	194.9	65.4
8	29.3	27.3	28.8	28.6	29.2	26.6[c]
9	27.1	29.4	27.2	28.6	27.3	26.5[c]
10	24.4	24.2	70.4	68.5	17.4	11.4
Glc-1	104.6	104.4	100.8	103.9	106.5	99.6
Glc-2	75.2	75.1	71.1	75.1	75.1	71.2
Glc-3	78.1	78.1	72.7	78.1	78.1	72.8
Glc-4	71.7	71.7	68.2	71.7	71.4	68.5
Glc-5	78.4	78.5	72.1	78.2	78.4	71.9
Glc-6	62.9	62.9	62.6	62.9	62.5	62.0
Ac	—	—	170.6, 170.5, 170.2, 169.3, 169.2,20.8, 20.7,20.6, 20.55, 20.5	—	—	170.6, 170.3, 169.4, 169.1, 20.7, 20.6, 20.59, 20.5

a) Measured in CD_3OD. *b*) Measured in $CDCl_3$. *c*) May be reversed.

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NMR and UV spectra suggested the presence of an α, β-unsaturated aldehyde [241.0 nm, δ 194.9, 151.2, 142.6 (each s)] and a glucosyl moiety. Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of **9** were undertaken with the aid of ^{1}H–^{1}H COSY and HMBC (Fig. 1) spectra. The relative configurations of C-3 and C-4 were determined from the NOESY spectrum and the coupling constant-analyses. As shown in Fig. 2, the NOESY spectrum indicated 3-H and 4-H to be respectively quasi-axial and quasi-equatorial with respect to the half-chair form of the cyclohexene. The absolute configuration of **9** was determined as follows. The CD spectrum showed a negative Cotton effect at 241.0 nm ($\Delta\varepsilon$ −9.15), suggesting that the glucosyl group at C-4 and the methyl at C-1 (δ 1.20) are oriented β-quasi-axial and α-quasi-axial, respectively.[11] Therefore, the configurations of **9** at C-3 and C-4 were determined as *S* and *R*, respectively. From this evidence, the full structure of **9** was established to be as shown in Chart 1.

Compound **10**, named jasminoside E, was purified as its pentaacetate (**10a**), $[\alpha]_D$ −33.3° (MeOH). The ^{13}C-NMR spectrum of **10a** lacked the signals of **9** due to an aldehyde and two oxygenated methine moieties and instead showed signals characteristic of a carbonyl [δ 199.3 (s)] and an ethylene [δ 65.4, 34.3 (each t)] moiety. The maximum at 241.0 nm in the UV spectrum of **10a** supports the presence of an α, β-unsaturated ketone moiety. From the above data, including the HMBC correlations (Fig. 1), **10** was established to be as depicted in Chart 1.

Experimental

Optical rotation were determined with a JASCO DIP-360 digital polarimeter. UV spectra were recorded with a Beckman DU-64 spectrometer. The CD spectra were obtained with a JASCO J-700 spectropolarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded with JOEL JNM-EX 270 (270 and 67.8 MHz, respectively) and JEOL JNM-GSX 400 (400 and 100 MHz, respectively) spectrometers. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; dd, double doublet, q, quartet; ddd, double double doublet; m, multiplet; br, broad). MS were recorded on a JEOL JMS-DX 303 mass spectrometer [FAB-MS were obtained with glycerol or *m*-nitrobenzyl alcohol–triethanol amine (1 : 1) as the matrix]. Column chromatography was carried out on Kieselgel 60 (Merck; 70—230 mesh), Sephadex LH-20 (Pharmacia Fine Chemicals) and a Cosmosil 75C_{18}-OPN (Nacalai Tesque). Preparative HPLC was carried out on a Tosoh HPLC system (pump, CCPD; detector, UV-8010) using a Cosmosil 5C18-AR (Nacalai Tesque, 10 mm i.d. × 25 cm) column. TLC carried out with precoated Kieselgel 60 plates (Merck) and detection was achieved by spraying with 5% H_2SO_4 followed by heating.

Isolation Procedure Dried fruit of *G. jasminoides* Ellis forma *grandiflora* (Lour.) Makino (1.0 kg) collected in Guangxi prefecture (広西), China were extracted with MeOH under reflux for 5.0 h. The MeOH extract was concentrated under reduced pressure and the residue was suspended in water (400 ml). This suspension was successively extracted with $CHCl_3$, Et_2O, EtOAc, *n*-BuOH and H_2O. The $CHCl_3$-soluble fraction was concentrated under reduced pressure to produce a residue (29.8 g). This residue was chromatographed on a silica-gel column using hexane–AcOEt (4 : 1—1 : 1) and the eluate was separated into twelve fractions (frs. 1—12). Fraction 10 was rechromatographed on a C18 open column using MeOH–H_2O (2 : 1) and the eluate was separated into thirty-eight fractions (frs. 10-1—10-38). Fraction 10 was subjected to prep. HPLC [MeOH–H_2O (1 : 1), flow rate: 1.0 ml/min, 271 nm] to give **1** (2.5 mg). The *n*-BuOH-soluble fraction was concentrated under reduced pressure to produce a residue (51.0 g). This residue was chromatographed on a silica-gel column using $CHCl_3$–MeOH–H_2O (30 : 10 : 1) and the eluate was separated into thirteen fractions (frs. 1—13). Fraction 5 was rechromatographed on a Sephadex LH-20 column using 50% MeOH and the eluate was separated into three fractions (frs. 5-1—5-3). Fraction 5-1 was rechromatographed on a C18 open column using 50% MeOH and the eluate was separated into seven fractions (frs. 5-1-1—5-1-7). Fraction 5-1-2 was subjected to prep. HPLC [MeOH–H_2O (1 : 2), flow rate: 1.5 ml/min, 235 nm] to give **2** (4.0 mg) and **3** (4.0 mg), **8** (1.2 mg), **9** (0.7 mg) and **10**. Compound **10** was converted to its acetate to allow purification and identification. Thus, the ^{1}H-NMR spectrum of crude compound **10** showed no acetyl group signal. Crude compound **10** was acetylated with Ac_2O in pyridine. After the usual work-up, the crude product was purified by prep. HPLC [MeOH–H_2O (3 : 1), flow rate: 1.0 ml/min, 258 nm] to give **10a** (1.0 mg). Fraction 6 was subjected to prep. HPLC [MeOH–H_2O (1 : 2), flow rate: 1.5 ml/min, 232 nm] to give **4** (1.5 mg) and 6″-*O*-*trans*-*p*-coumaroylgenipin gentiobioside (2.3 mg), **5** (3.5 mg), **6** (0.6 mg) and **7**. Crude compound **7** was acetylated with Ac_2O in pyridine. After the usual work-up, the crude product was purified by prep. HPLC [MeOH–H_2O (3 : 1), flow rate: 1.0 ml/min, 230 nm] to give **7a** (1.0 mg). For compound **4** and 6″-*O*-*trans*-*p*-coumaroylgenipin gentiobioside, purification and instrumental analysis were carried out while avoiding daylight.[12]

Gardenamide (1) An amorphous powder, $[\alpha]_D$ +404.0° (*c* = 0.25, MeOH). UV λ_{max} (MeOH) nm (log ε): 242.0 (4.07). EI-MS *m/z*: 223 M^+. HR-MS *m/z*: 223.0845 M^+ (Calcd for $C_{11}H_{13}NO_4$; 223.0845). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.49 (1H, br s, 2-NH), 7.20 (1H, d, *J* = 5.6 Hz, 3-H), 5.86 (1H, br t, *J* = 1.3 Hz, 7-H), 4.37 (1H, dt, *J* = 13.0, 6.7 Hz, 10-H_B), 4.31 (1H, dd, *J* = 13.0, 5.1 Hz, 10-H_A), 3.88 (1H, dd, *J* = 6.7, 5.1 Hz, 10-OH), 3.77 (3H, s, $COOCH_3$), 3.65 (1H, br dd, *J* = 10.9, 2.0 Hz, 9-H), 3.57 (1H, ddd, *J* = 10.9, 8.7, 8.4 Hz, 5-H), 2.94 (1H, ddt, *J* = 16.7, 8.4, 1.3 Hz, 6-H_B), 2.25 (1H, dddd, *J* = 16.7, 8.7, 4.2, 2.0 Hz, 6-H_A). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ: 171.7 (C-1), 132.1 (C-3), 111.5 (C-4), 37.2 (C-5), 40.2 (C-6), 129.5 (C-7), 140.7 (C-8), 49.6 (C-9), 61.0 (C-10), 166.7 ($\underline{C}OOCH_3$), 51.7 ($COO\underline{C}H_3$).

6α-*n*-Butoxygeniposide (2) An amorphous powder, $[\alpha]_D$ +15.0° (*c* = 0.4, MeOH). UV λ_{max} (MeOH) nm (log ε): 235.0 (3.92). FAB-MS *m/z*: 483 $[M+Na]^+$. ^{1}H-NMR (270 MHz, CD_3OD) δ: 7.60 (1H, d, *J* = 1.2 Hz, 3-H), 6.13 (1H, br d, *J* = 2.0 Hz, 7-H), 5.01 (1H, d, *J* = 8.9 Hz, 1-H), 4.71 (1H, d, *J* = 7.8 Hz, Glc-H_1), 4.47 (1H, d, *J* = 15.8 Hz, 10-H_B), *ca.* 4.47 (6-H, overlapped 10-H_B), 4.20 (1H, d, *J* = 15.8 Hz, 10-H_A), 3.80 (1H, dd, *J* = 12.1, 2.4 Hz, Glc-H_{6B}), 3.73 (3H, s, $COOCH_3$), 3.68 (1H, dd, *J* = 12.1, 5.0 Hz, Glc-H_{6A}), *ca.* 3.35 (1′-H_2, overlapped Glc-$H_{2,3,4,5}$), 3.08 (1H, br t, *J* = 8.9 Hz, 5-H), 2.53 (1H, br t, *J* = 8.9 Hz, 9-H), 1.40 (2H, m, 2′-H_2), 1.28 (2H, m, 3′-H_2), 0.86 (3H, t, *J* = 7.3 Hz, 4′-H_3). ^{13}C-NMR (67.8 MHz, CD_3OD) δ: 101.9 (C-1), 154.9 (C-3), 108.6 (C-4), 42.2 (C-5), 83.4 (C-6), 128.3 (C-7), 152.2 (C-8), 46.0 (C-9), 61.8 (C-10), 169.6, 51.8 ($COOCH_3$), 70.3 (C-1′), 33.3 (C-2′), 20.4 (C-3′), 14.2 (C-4′), 100.9 (Glc-1), 75.0 (Glc-2), 77.9 (Glc-3), 71.4 (Glc-4), 78.3 (Glc-5), 62.5 (Glc-6).

Acetylation of 2 Compound **2** (4.5 mg) was acetylated with Ac_2O-pyridine in the usual manner to give **2a** (3.8 mg). An amorphous powder, $[\alpha]_D$ +22.2° (*c* = 0.3, MeOH). UV λ_{max} (MeOH) nm (log ε): 234.0 (3.95). FAB-MS *m/z*: 693 $[M+Na]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.54 (1H, d, *J* = 1.2 Hz, 3-H), 6.10 (1H, br s, 7-H), 5.23 (1H, t, *J* = 9.5 Hz, Glc-H_3), 5.12 (1H, dd, *J* = 9.8, 9.5 Hz, Glc-H_4), 5.03 (1H, dd, *J* = 9.5, 8.1 Hz, Glc-H_2), 4.88 (1H, d, *J* = 8.1 Hz, Glc-H_1), 4.84 (1H, d, *J* = 8.5 Hz, 1-H), 4.79 (2H, br s, 10-H_2), 4.43 (1H, dd, *J* = 6.1, 2.4 Hz, 6-H), 4.22 (1H, dd, *J* = 12.2, 4.6 Hz, Glc-H_{6B}), 4.12 (1H, dd, *J* = 12.2, 2.6 Hz, Glc-H_{6A}), 3.74 (3H, s, $COOCH_3$), 3.69 (1H, ddd, *J* = 9.8, 4.6, 2.6 Hz, Glc-H_5), 3.41 (1H, m, 1′-H_B), 3.29 (1H, m, 1′-H_A), 3.08 (1H, dd, *J* = 7.8, 6.1 Hz, 5-H), 2.53 (1H, dd, *J* = 8.5, 7.8 Hz, 9-H), 2.10, 2.08, 2.05, 2.03, 2.01 (each 3H, s, $COCH_3$), 1.41 (2H, m, 2′-H_2), 1.25 (2H, m, 3′-H_2), 0.85 (3H, t, *J* = 7.3 Hz, 4′-H_3).

6β-*n*-Butoxygeniposide (3) An amorphous powder, $[\alpha]_D$ −78.6° (*c* = 0.4, MeOH). UV λ_{max} (MeOH) nm (log ε): 236.0 (3.82). FAB-MS *m/z*: 483 $[M+Na]^+$. ^{1}H-NMR (270 MHz, CD_3OD) δ: 7.39 (1H, d, *J* = 0.8 Hz, 3-H), 5.81 (1H, br d, *J* = 1.6 Hz, 7-H), 5.63 (1H, d, *J* = 3.0 Hz, 1-H), 4.59 (1H, d, *J* = 7.9 Hz, Glc-H_1), 4.28 (1H, d, *J* = 15.6 Hz, 10-H_B), *ca.* 4.23 (6-H, overlapped 10-H_B), 4.18 (1H, d, *J* = 15.6 Hz, 10-H_A), 3.89 (1H, dd, *J* = 12.0, 2.0 Hz, Glc-H_{6B}), 3.71 (3H, s, $COOCH_3$), 3.68 (3H, m, 1′-H_2, Glc-H_{6A}), *ca.* 3.35 (Glc-$H_{2,3,4,5}$), 3.20 (2H, m, 5-H, 9-H), 1.56 (2H, m, 2′- H_2), 1.40 (2H, m, 3′- H_2), 0.94 (3H, t, *J* = 7.3 Hz, 4′-H_3). ^{13}C-NMR (67.8 MHz, CD_3OD) δ: 95.2 (C-1), 153.4 (C-3), 110.6 (C-4), 39.6 (C-5), 88.6 (C-6), 127.9 (C-7), 149.2 (C-8), 47.4 (C-9), 60.4 (C-10), 169.1, 51.7 ($COOCH_3$), 70.1 (C-1′), 33.2 (C-2′), 20.3 (C-3′), 14.3 (C-4′), 100.0 (Glc-1), 74.7 (Glc-2), 78.0 (Glc-3), 71.6 (Glc-4), 78.4 (Glc-5), 62.8 (Glc-6).

Acetylation of 3 Compound **3** (4.0 mg) was acetylated with Ac_2O-

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pyridine in the usual manner to give **3a** (3.3 mg). An amorphous powder, $[\alpha]_D$ −66.6° (c=0.3, MeOH). UV λ_{max} (MeOH) nm (log ε): 234.0 (3.78). FAB-MS m/z: 693 $[M+Na]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.32 (1H, br s, 3-H), 5.89 (1H, br s, 7-H), 5.50 (1H, d, J=2.2 Hz, 1-H), 5.22 (1H, t, J=9.8 Hz, Glc-H_3), 5.11 (1H, t, J=9.8 Hz, Glc-H_4), 4.99 (1H, dd, J=9.8, 8.3 Hz, Glc-H_2), 4.81 (1H, d, J=8.3 Hz, Glc-H_1), 4.74 (1H, d, J=14.1 Hz, 10-H_B), 4.66 (1H, d, J=14.1 Hz, 10-H_A), 4.30 (1H, dd, J=12.4, 4.6 Hz, Glc-H_{6B}), 4.24 (1H, br s, 6-H), 4.16 (1H, dd, J=12.4, 2.4 Hz, Glc-H_{6A}), 3.75 (2H, m, 1′-H_B, Glc-H_5), 3.72 (3H, s, $COOCH_3$), 3.51 (1H, m, 1′-H_A), 3.44 (1H, br d, J=7.1 Hz, 9-H), 3.16 (1H, br d, J=7.1 Hz, 5-H), 2.10, 2.08, 2.03, 2.01, 1.91 (each 3H, s, $COCH_3$), 1.55 (2H, m, 2′-H_2), 1.37 (2H, m, 3′-H_2), 0.93 (3H, t, J=7.3 Hz, 4′-H_3).

6″-*O*-*p*-*cis*-Coumaroylgenipin Gentiobioside (4) An amorphous powder, $[\alpha]_D$ +7.05° (c=0.15, MeOH). UV λ_{max} (MeOH) nm (log ε): 308.0 (4.09), 230.0 (4.14). FAB-MS m/z: 719 $[M+Na]^+$. ^{1}H-NMR (270 MHz, CD_3OD) δ: 7.65 (2H, d, J=8.6 Hz, 5′,9′-H), 7.47 (1H, d, J=1.0 Hz, 3-H), 6.87 (1H, d, J=12.9 Hz, 3′-H), 6.76 (2H, J=8.6 Hz, 6′,8′-H), 5.82 (1H, br s, 7-H), 5.81 (1H, d, J=12.9 Hz, 2′-H), 5.14 (1H, d, J=7.8 Hz, 1-H), 4.70 (1H, d, J=7.8 Hz, Glc-H_1), 4.47 (1H, dd, J=12.0, 2.0 Hz, Glc-$H_{6B'}$), 4.36 (1H, d, J=7.8 Hz, Glc-$H_{1'}$), 4.30 (1H, br d, J=16.0 Hz, 10-H_B), 4.20 (1H, dd, J=12.0, 5.8 Hz, Glc-$H_{6A'}$), 4.19 (1H, br d, J=16.0 Hz, 10-H_A), 4.07 (1H, dd, J=11.9, 1.8 Hz, Glc-H_{6B}), 3.70 (1H, dd, J=11.9, 7.9 Hz, Glc-H_{6A}), 3.70 (3H, s, $COOCH_3$), 3.52 (2H, m, Glc-$H_{5,5'}$), 3.14—3.38 (7H, m, 5-H, Glc-H_2, 2′, 3, 3′, 4, 4′), 2.77 (1H, m, 6-H_B), 2.67 (1H, br t, J=7.8 Hz, 9-H), 2.14 (1H, m, 6-H_A). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ: 98.9 (C-1), 153.5 (C-3), 112.4 (C-4), 36.8 (C-5), 39.8 (C-6), 129.1 (C-7), 144.8 (C-8), 47.0 (C-9), 61.6 (C-10), 169.4, 51.8 ($COOCH_3$), 100.7 (Glc-1), 75.3 (Glc-2), 77.9 (Glc-3), 71.8 (Glc-4), 77.9 (Glc-5), 70.3 (Glc-6), 105.1 (Glc-1′), 74.9 (Glc-2′), 77.6 (Glc-3′), 71.6 (Glc-4′), 75.1 (Glc-5′), 64.6 (Glc-6′), 168.2 (C-1′), 116.4 (C-2′), 145.3 (C-3′), 127.6 (C-4′), 133.8 (C-5′, 9′), 116.0 (C-6′, 8′), 160.2 (C-7′).

Epijasminoside A (5) An amorphous powder, $[\alpha]_D$ −91.4° (c=0.35, MeOH). UV λ_{max} (MeOH) nm (log ε): 236.0 (3.95). FAB-MS m/z: 331 $[M+H]^+$, 353 $[M+Na]^+$. CD $\Delta\varepsilon$ (nm) ($c=1.11\times10^{-4}$ M, MeOH): −2.06 (240.5), −1.99 (211.0). ^{1}H- and ^{13}C-NMR: Table 1 and 2.

Jasminoside A (6) An amorphous powder, $[\alpha]_D$ −33.0° (c=0.06, MeOH). UV λ_{max} (MeOH) nm (log ε): 236.0 (3.75). FAB-MS m/z: 331 $[M+H]^+$, 353 $[M+Na]^+$. CD $\Delta\varepsilon$ (nm) ($c=1.04\times10^{-4}$ M, MeOH): +1.85 (237.5), +1.55 (211.0). ^{1}H- and ^{13}C-NMR: Table 1 and 2.

Jasminoside B Pentaacetate (7a) An amorphous powder, $[\alpha]_D$ −60.0° (c=0.1, MeOH). UV λ_{max} (MeOH) nm (log ε): 230.0 (3.93). FAB-MS m/z: 557 $[M+H]^+$, 579 $[M+Na]^+$. CD $\Delta\varepsilon$ (nm) ($c=1.12\times10^{-4}$ M, MeOH): *ca.* −1.75 (235 sh), −3.29 (209.5). ^{1}H- and ^{13}C-NMR: Table 1 and 2.

Jasminoside C (8) An amorphous powder, $[\alpha]_D$ −68.0° (c=0.12, MeOH). UV λ_{max} (MeOH) nm (log ε): 269.0 (3.86). FAB-MS m/z: 329 $[M+H]^+$, 351 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Table 1 and 2.

Jasminoside D (9) An amorphous powder, $[\alpha]_D$ −59.3° (c=0.07, MeOH). UV λ_{max} (MeOH) nm (log ε): 241.0 (3.90). FAB-MS m/z: 347 $[M+H]^+$, 369 $[M+Na]^+$. CD $\Delta\varepsilon$ (nm) ($c=1.11\times10^{-4}$ M, MeOH): −9.15 (241.0). ^{1}H- and ^{13}C-NMR: Table 1 and 2.

Jasminoside E Tetraacetate (10a) An amorphous powder, $[\alpha]_D$ −33.3° (c=0.06, MeOH). UV λ_{max} (MeOH) nm (log ε): 241.0 (4.00). FAB-MS m/z: 499 $[M+H]^+$, 521 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Table 1 and 2.

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