Medicinal Flowers. XI.[1] Structures of New Dammarane-Type Triterpene Diglycosides with Hydroperoxide Group from Flower Buds of *Panax ginseng*

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Six new dammarane-type triterpene diglycosides with a hydroperoxide group, floralginsenosides A, B, C, D, E, and F, were isolated from ginseng flower, the flower buds of *Panax ginseng* C. A. MEYER, together with seven known dammarane-type triterpene oligoglycosides. The structures of new floralginsenosides were elucidated on the basis of chemical and physicochemical evidence.

Key words floralginsenoside; *Panax ginseng*; medicinal flower; dammarane-type triterpene diglycoside; hydroperoxide; ginseng flower

The roots of *Panax* (*P.*) *ginseng* C. A. MEYER (Araliaceae) is a most famous Chinese natural medicine, which is widely used for the treatment of gastrointestinal disorders as well as a tonic in traditional Chinese medicine and Japanese Kampo medicine. The biologically active constituents of ginseng roots have been pursued extensively and many dammarane-type triterpene oligoglycosides have been characterized as the principal ingredients.[2] On the other hand, the flower buds of *P. ginseng* have been used as a exhilarant. As the chemical constituents of ginseng flower, several dammarane-type triterpene glycosides were hitherto isolated.[3,4]

Recently, we have reported the isolation and structure elucidation of dammarane-type triterpene oligoglycosides termed notoginsenosides-O, -P, -Q, -S, and -T with hepatoprotective and immunological adjuvant activities from the flower buds of *P. notoginseng* (BURK.) F. H. CHEN.[5,6] As a continuing study on the bioactive constituents of medicinal flowers,[1,7] we have isolated new dammarane-type triterpene diglycosides named floralginsenosides A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), and F (**6**) from the flower buds of Chinese *P. ginseng* together with seven known dammarane-type triterpene oligoglycosides. In this paper, we describe the isolation and structure elucidation of six new floralginsenosides (**1**—**6**).[8]

Isolation of Floralginsenosides The methanolic extract from the flower buds of *P. ginseng* cultivated in Jilin province of China was partitioned into an ethyl acetate (EtOAc)–water mixture to furnish an EtOAc-soluble portion and an aqueous layer. The aqueous layer was further extracted with *n*-butanol to give an *n*-BuOH-soluble portion. The *n*-BuOH-soluble portion was subjected to normal-phase and reversed-phase silica gel column chromatography and finally HPLC to afford floralginsenosides A (**1**, 0.0053% from the dried flower buds), B (**2**, 0.057%), C (**3**, 0.014%), D (**4**, 0.0054%), E (**5**, 0.0014%), and F (**6**, 0.0046%) together with ginsenoside-F_1 (**7**,[4] 0.019%), ginsenoside-F_3 (**8**,[9] 0.20%), ginsenoside-F_5 (**9**,[9] 0.084%), ginsenoside Rg_1 (**10**,[10] 0.38%), ginsenoside Rg_2 (**11**,[11] 0.0016%), gypenoside XVII (**12**,[12] 0.010%), and pseudo-ginsenoside-RC_1 (**13**,[13] 0.030%).

Structures of Floralginsenosides Floralginsenoside A (**1**) was isolated as an amorphous powder with positive optical rotation ($[\alpha]_D^{21}$ +20.4° in MeOH). As shown by its positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent,[14] **1** was deduced to have a hydroperoxide residue. The IR spectrum of **1** showed strong absorption bands at 3469 and 1076 cm^{-1} suggestive of the glycosidic structure together with an absorption band at 1655 cm^{-1} due to a double bond. The molecular formula $C_{42}H_{72}O_{16}$ was determined from the quasimolecular ion peaks observed in the positive-ion and negative-ion fast atom bombardment (FAB)-MS and by high-resolution MS measurement. Namely, a quasimolecular ion peak was observed at *m/z* 855 $(M+Na)^+$ in the positive-ion FAB-MS of **1**, while its negative-ion FAB-MS showed the quasimolecular ion peak at *m/z* 831 $(M-H)^-$ in addition to fragment ion peaks at *m/z* 815 $(M-OH)^-$, *m/z* 799 $(M-OOH)^-$, and *m/z* 651 $(M-OH-C_6H_{11}O_5)^-$, which was derived by cleavage of the glycoside linkage of the terminal hexose. Acid hydrolysis of **1** with 1.0 M aqueous HCl liberated D-glucose, which was identified by HPLC analysis using an optical rotation detector.[6] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra of **1**, which were assigned by various NMR experiment,[15] showed signals assignable to an aglycon part [δ 0.82, 1.04, 1.15, 1.568, 1.573, 1.85, 2.03 (3H each, all s, H_3-30, 19, 18, 29, 21, 27, 28), 3.49 (1H, dd, J=4.6, 11.8 Hz, H-3), 4.10 (1H, m, H-12), 4.40 (1H, m, H-6), 4.68 (1H, dd, J=5.2, 7.5 Hz, H-24), 5.02, 5.20 (1H each, both br s, H_2-26)], together with two β-D-glucopyranosyl moieties [δ 4.99 (1H, d, J=7.7 Hz, H-1′), 5.12 (1H, d, J=8.0 Hz, H-1″)]. The proton and carbon signals due to the tetracarbocyclic moiety (C-1—C-20, C-28—C-30) including the 6- and 20-*O*-β-D-glucopyranosyl parts in the ^{1}H- and ^{13}C-NMR spectra of **1** were superimposable on those of ginsenoside Rg_1 (**10**),[10] whrereas the signals designated to the side chain moiety (C-20—C-27) of the aglycon part were similar to those of notoginsenoside-C.[16] As shown in Fig. 1, the ^{1}H–^{1}H correlation spectroscopy (^{1}H–^{1}H COSY) experiment on **1** indicated the presence of partial structures written in bold lines, and in the heteronuclear multiple-bond correlations (HMBC) experiment, long-range correlations were observed between the following protons and carbons: H-5 and C-6; H-9 and C-8, 10; H-13 and C-14; H-15 and C-14; H-18 and C-7, 8; 19-H and C-5, 10; H-21 and C-17, 20, 22; H-22 and C-20, 23; H-26 and C-24, 27; H-27 and C-24, 25, 26; H-1′ and C-6; H-1″ and C-20. Finally, treatment of **1** with pyridine yielded a known dammarane-type triterpene glycoside, vina-ginsenoside R_{25} (**14**), which was isolated from Vietnamese ginseng.[17] On the basis of this evidence, the struc-

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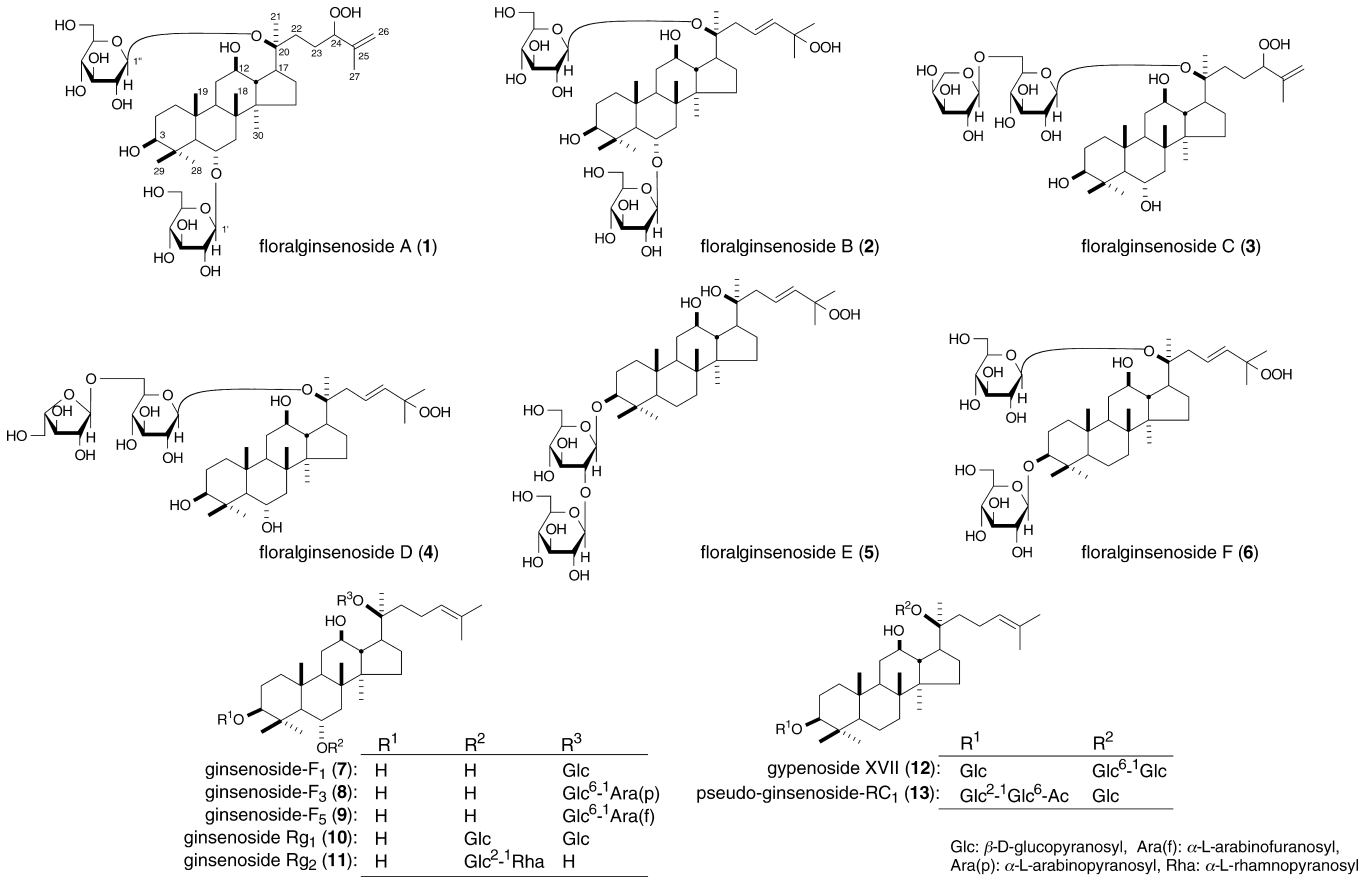

Chart 1. Structures of New Floralginsenosides (**1**—**6**) and Known Saponins (**7**—**13**) from the Flower Buds of *P. ginseng*

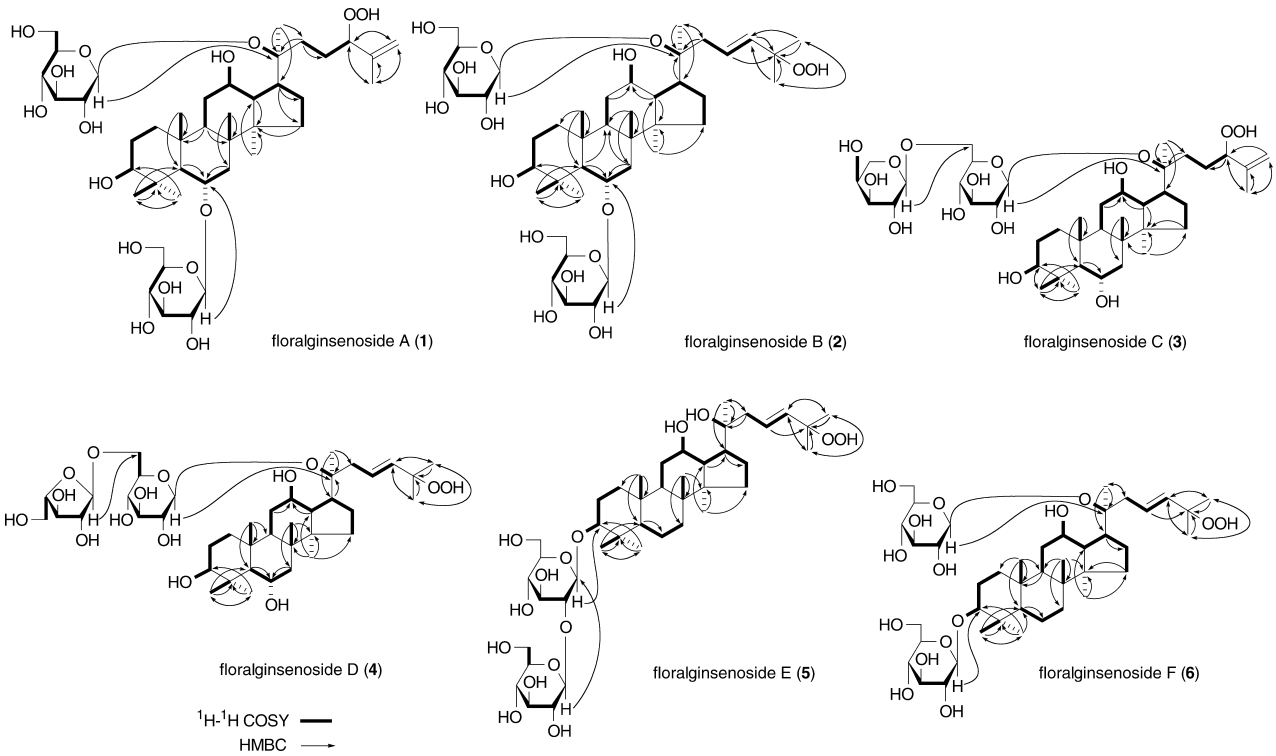

Fig. 1. Significant ^{1}H–^{1}H COSY and HMBC Correlations for New Floralginsenosides (**1**—**6**) from the Flower Buds of *P. ginseng*

Table 1. ^{13}C-NMR Data for Floralginsenosides A (**1**), B (**2**), C (**3**), D (**4**), E (**5**), and F (**6**)

	1	2	3	4	5	6
C-1	39.6	39.5	39.4	39.4	39.3	39.3
C-2	28.0	28.0	28.1	28.2	26.8	26.8
C-3	78.8	78.9	78.6	78.6	89.0	88.9
C-4	40.4	40.4	40.3	40.4	39.8	39.8
C-5	61.5	61.5	61.8	61.8	56.5	56.5
C-6	80.1	80.1	67.8	67.8	18.5	18.5
C-7	45.3	45.2	47.5	47.5	35.3	35.2
C-8	41.2	41.2	41.2	41.3	40.2	40.2
C-9	50.1	50.3	50.0	49.9	50.5	50.2
C-10	39.8	39.8	39.4	40.4	37.1	37.1
C-11	31.1	31.2	30.9	30.9	32.2	31.1
C-12	70.3	70.5	70.2	70.6	71.1	70.5
C-13	49.3	49.3	49.2	49.2	49.0	49.7
C-14	51.5	51.5	51.4	51.5	51.8	51.6
C-15	30.7	30.6	30.8	30.7	31.4	30.7
C-16	26.8	26.5	26.7	26.4	26.8	26.5
C-17	51.5	52.2	52.1	52.1	54.2	52.3
C-18	17.6	17.6	17.6	17.7	16.0	16.0
C-19	17.6	17.6	17.5	17.5	16.5	16.3
C-20	83.2	83.2	83.3	83.2	73.3	83.2
C-21	22.6	23.2	21.8	23.3	27.9	23.3
C-22	32.9	39.7	32.8	39.9	40.4	39.7
C-23	26.7	126.6	26.7	126.7	127.3	126.6
C-24	89.9	138.0	90.1	138.1	135.8	138.1
C-25	145.8	81.3	146.2	81.3	81.3	81.3
C-26	113.3	25.2	113.3	25.4	25.2	25.2
C-27	17.8	25.4	17.8	25.2	25.3	25.4
C-28	31.8	31.8	32.0	32.0	28.2	28.2
C-29	16.4	16.4	16.5	16.5	16.7	16.8
C-30	17.3	17.1	17.4	17.3	17.1	17.2
C-1′	106.0	105.9	98.0	98.2	105.1	106.9
C-2′	75.5	75.5	74.9	75.1	83.6	75.8
C-3′	79.6	78.1	79.4	78.9	78.1	78.8
C-4′	72.0	72.0	72.1	72.2	71.8	72.0
C-5′	78.1	79.6	76.4	76.4	78.1	78.3
C-6′	63.1	63.1	69.5	68.5	63.0	63.1
C-1″	98.1	98.3	105.1	110.2	106.1	98.3
C-2″	75.1	75.3	72.2	83.3	77.1	75.3
C-3″	79.2	78.0	74.2	78.8	78.4	78.9
C-4″	71.8	71.1	68.8	86.2	71.9	71.7
C-5″	78.0	78.7	66.0	62.9	78.2	78.2
C-6″	63.1	63.2			62.9	63.2

Measured in pyridine-d_5 at 125 MHz and 150 MHz.

ture of floralginsenoside A (**1**)[18] was characterized as shown.

Floralginsenoside B (**2**) was also obtained as an amorphous powder with positive optical rotation ($[\alpha]_D^{22}$ +25.6° in MeOH) and was shown to possess a hydroperoxide group by its positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[14] The IR spectrum of **2** showed absorption bands at 3433, 1655, and 1076 cm^{-1} assignable to hydroxyl, olefin, and ether functions. In the positive-ion and negative-ion FAB-MS of **2**, quasimolecular ion peaks were observed at *m/z* 855 $(M+Na)^+$ and *m/z* 831 $(M-H)^-$, respectively and the fragment ion peaks at *m/z* 815 $(M-OH)^-$, *m/z* 799 $(M-OOH)^-$, and *m/z* 651 $(M-OH-C_6H_{11}O_5)^-$ were observed in the negative-ion FAB-MS. The high-resolution MS analysis revealed the molecular formula of **2** to be $C_{42}H_{72}O_{16}$. The acid hydrolysis of **2** liberated D-glucose, which was identified by HPLC analysis.[6] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[15] of **2** showed signals due to an aglycon part [δ 0.79, 1.09, 1.24, 1.55, 1.56, 1.58, 1.59, 2.04 (3H each, all s, H_3-30, 19, 18, 21, 26, 27, 29, 28), 3.50 (1H, dd, *J*=4.6, 11.8 Hz, H-3), 3.98 (1H, m, H-12), 4.43 (1H, ddd, *J*=2.9, 10.3, 10.6 Hz, H-6), 6.05 (1H, d, *J*=15.7 Hz, H-24), 6.20 (1H, ddd, *J*=6.3, 8.3, 15.7 Hz, H-23)] and two β-D-glucopyranosyl moieties [δ 5.01 (1H, d, *J*=7.8 Hz, H-1′), 5.17 (1H, d, *J*=7.8 Hz, H-1″)]. The proton and carbon signals due to the tetracarbocyclic moiety including the 6- and 20-*O*-β-D-glucopyranosyl parts in the ^{1}H- and ^{13}C-NMR spectra of **2** were superimposable on those of **1** and ginsenoside Rg_1 (**10**),[10] while the signals due to the side chain part very resembled those of notoginsenoside-E.[19] The structure of **2** was characterized by means of ^{1}H–^{1}H COSY and HMBC experiments (Fig. 1). Finally, reduction of **2** with sodium borohydride ($NaBH_4$) furnished a known dammarane-type triterpene glycoside, vina-ginsenoside-R15 (**15**), which was isolated from Vietnamese ginseng.[20] Consequently, the structure of floralginsenoside B (**2**) was determined as shown.

Floralginsenoside C (**3**) and D (**4**), obtained as an amorphous powder with positive optical rotation (**3**: $[\alpha]_D^{23}$ +49.8°; **4**: $[\alpha]_D^{26}$ +8.8° in MeOH), showed the positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[14] The IR spectra of **3** and **4** showed absorption bands due to hydroxyl, olefin, and ether group (**3**: 3415, 1670, and 1078 cm^{-1}; **4**: 3439, 1655, and 1078 cm^{-1}). The common molecular formula, $C_{41}H_{70}O_{15}$, for **3** and **4** were determined individually from the quasimolecular ion peaks [*m/z* 825 $(M+Na)^+$ and *m/z* 801 $(M-H)^-$] in the positive and negative-ion FAB-MS and by high-resolution MS measurement. The acid hydrolysis of **3** and **4** liberated D-glucose and L-arabinose, which were identified by HPLC analysis.[6] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[15] of **3** and **4** showed signals assignable to an aglycon part [**3**: δ 0.96, 1.01, 1.07, 1.42, 1.53, 1.94, 1.95 (3H each, all s, H_3-30, 19, 18, 29, 21, 27, 28), 3.49 (1H, dd, *J*=4.3, 11.5 Hz, H-3), 4.13 (1H, m, H-12), 4.36 (1H, m, H-6), 4.74 (1H, br s, H-24), 5.04, 5.23 (1H each, both br s, H_2-26); [**4**: δ 0.91, 1.04, 1.17, 1.43, 1.59, 1.96 (3H each, all s, H_3-30, 19, 18, 29, 21, 28), 1.60 (6H, s, H_3-26, 27), 3.50 (1H, dd, *J*=4.8, 11.7 Hz, H-3), 4.00 (1H, m, H-12), 4.39 (1H, dd, *J*=3.4, 10.3 Hz, H-6), 6.11 (1H, d, *J*=15.8 Hz, H-24), 6.18 (1H, dd-like, *J*=*ca.* 10, 16 Hz, H-23)], a β-D-glucopyranosyl moiety [**3**: δ 5.05 (1H, d, *J*=7.5 Hz, H-1′); **4**: δ 5.15 (1H, d, *J*=7.6 Hz, H-1′)], and an α-L-arabinopyranosyl moiety [**3**: δ 4.87 (1H, d, *J*=6.3 Hz, H-1″)] or an α-L-arabinofuranosyl moiety [**4**: δ 5.62 (1H, br s, H-1″)]. The proton and carbon signals due to the tetracarbocyclic part including the 20-*O*-diglycosyl moiety in the ^{1}H- and ^{13}C-NMR spectra of **3** and **4** were very similar to those of ginsenoside-F_3 (**8**)[9] and ginsenoside-F_5 (**9**),[9] respectively, whereas the signals due to the side chain part of **3** and **4** were superimposable on those of **1** and **2**, respectively. Furthermore, the ^{1}H–^{1}H COSY and HMBC experiments on **3** and **4** showed correlations as shown in Fig. 1. This evidence led us to formulate the structures of floralginsenoside C (**3**)[18] and D (**4**) as shown.

Floralginsenoside E (**5**), obtained as an amorphous powder with positive optical rotation ($[\alpha]_D^{22}$ +17.6° in MeOH) and positive response to the hydroperoxide reagent,[14] showed absorption bands at 3451, 1655, and 1078 cm^{-1} due to hydroxyl, olefin, and ether functions in the IR spectrum. The positive-ion and negative-ion FAB-MS of **5** exhibited quasimolecular ion peaks at *m/z* 839 $(M+Na)^+$ and *m/z* 815

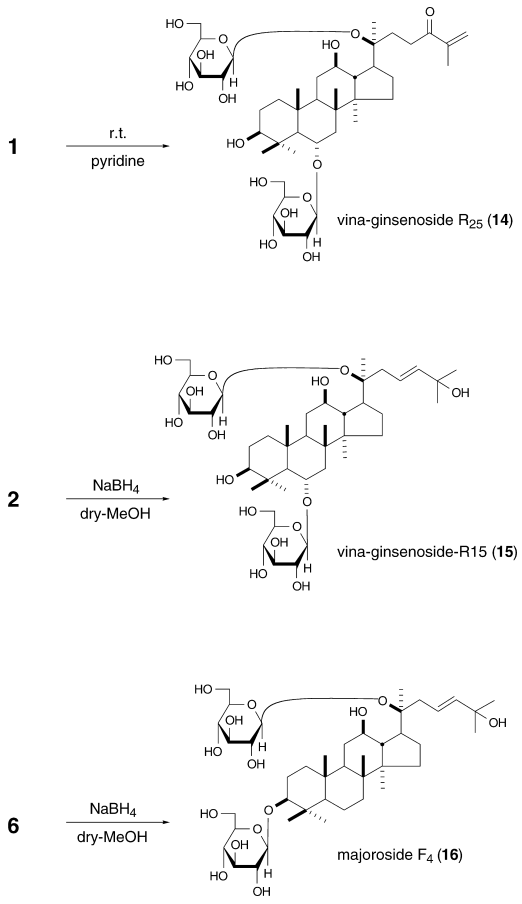

Fig. 2

$(M-H)^-$, respectively and the fragment ion peaks, *m/z* 799 $(M-OH)^-$ and *m/z* 635 $(M-OH-C_6H_{11}O_5)^-$, were observed in the negative-ion FAB-MS. The molecular formula $C_{42}H_{72}O_{15}$ of **5** was determined from the positive- and negative-ion FAB-MS and by high-resolution MS measurement. The acid hydrolysis of **5** yielded D-glucose.[6] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[15] of **5** showed signals due to an aglycon part [δ 0.87, 0.97, 1.06, 1.13, 1.31, 1.43, 1.56, 1.57 (3H each, all s, H_3-19, 30, 18, 29, 28, 21, 26, 27), 3.31 (1H, dd, *J*=4.5, 11.9 Hz, H-3), 3.92 (1H, m, H-12), 6.04 (1H, d, *J*=16.0 Hz, H-24), 6.25 (1H, ddd, *J*=5.7, 8.9, 16.0 Hz, H-23)] and two β-D-glucopyranosyl moieties [δ 4.92 (1H, d, *J*=7.7 Hz, H-1′), 5.35 (1H, d, *J*=7.7 Hz, H-1″)]. The proton and carbon signals due to the tetracarbocyclic part including the 3-*O*-diglycoside moiety in the ^{1}H- and ^{13}C-NMR spectra of **5** were superimposable on those of 20(*S*)-ginsenoside Rg_3,[21] while the signals due to the side chain part were similar to those of **2**. On the basis of this evidence and the ^{1}H–^{1}H COSY and HMBC experiments on **5** (Fig. 1), the structure of floralginsenoside E (**5**) was clarified as shown.

Floralginsenoside F (**6**) was isolated as an amorphous powder with positive optical rotation ($[\alpha]_D^{25}$ +14.8° in MeOH) and has a hydroperoxide function as shown by the positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[14] The IR spectrum of **6** showed absorption bands assignable to hydroxyl and olefin functions at 3566, 1655, and 1078 cm^{-1}. Here again, the molecular formula $C_{42}H_{72}O_{15}$ of **6** was determined from the positive-ion and negative-ion FAB-MS [*m/z* 839 $(M+Na)^+$ and *m/z* 815 $(M-H)^-$] and by high-resolution MS measurement. The acid hydrolysis of **6** furnished D-glucose.[6] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[15] of **6** showed signals due to an aglycon part [δ 0.87, 0.92, 1.01, 1.02, 1.32, 1.57, 1.58, 1.60 (3H each, all s, H_3-19, 30, 18, 29, 28, 26, 27, 21), 3.38 (1H, dd, *J*=4.3, 11.8 Hz, H-3), 3.95 (1H, m, H-12), 6.03 (1H, d, *J*=16.0 Hz, H-24), 6.18 (1H, ddd, *J*=6.0, 8.3, 16.0 Hz, H-23)] and two β-D-glucopyranosyl moieties [δ 4.92 (1H, d, *J*=7.7 Hz, H-1′), 5.19 (1H, d, *J*=7.8 Hz, H-1″)]. The proton and carbon signals due to the tetracarbocyclic part including the 3- and 20-*O*-β-D-glucopyranosyl moieties in the ^{1}H- and ^{13}C-NMR spectra of **6** were similar to those of ginsenoside-F_2,[22] while the signals due to the side chain part resembled those of **2**. Finally, reduction of **6** with $NaBH_4$ yielded a known dammarane-type triterpene glycoside, majoroside F_4 (**16**), which was isolated from *Panax japonics* C. A. MEYER var. *major* (BURK.).[23] This evidence and the examination of the ^{1}H–^{1}H COSY and HMBC data on **6** (Fig. 1) led us to elucidate the structure of floralginsenoside F (**6**) as shown.

Experimental

The following instruments were used to obtain physical data: specific rotations, Horiba SEPA-300 digital polarimeter (*l*=5 cm); IR spectra, Shimadzu FTIR-8100 spectrometer; FAB-MS and high-resolution MS, JEOL JMS-SX 102A mass spectrometer; ^{1}H-NMR spectra, JEOL EX-270 (270 MHz), JNM-LA500 (500 MHz), and JEOL ECA-600K (600 MHz) spectrometers; ^{13}C-NMR spectra, JEOL EX-270 (68 MHz) JNM-LA500 (125 MHz), and JEOL ECA-600K (150 MHz) spectrometers with tetramethylsilane as an internal standard; and HPLC detector, Shimadzu RID-6A refractive index and SPD-10A*vp* UV–VIS detectors. HPLC column, COSMOSIL-5C_{18}-MS-II (250×4.6 mm i.d.) and (250×20 mm i.d.) columns were used for analytical and preparative purposes, respectively.

The following experimental conditions were used for chromatography: ordinary-phase silica gel column chromatography, Silica gel BW-200 (Fuji Silysia Chemical, Ltd., 150—350 mesh); reverse-phase silica gel column chromatography, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100—200 mesh); TLC, precoated TLC plates with Silica gel 60F_{254} (Merck, 0.25 mm) (ordinary phase) and Silica gel RP-18 F_{254S} (Merck, 0.25 mm) (reverse phase); reversed-phase HPTLC, precoated TLC plates with Silica gel RP-18 WF_{254S} (Merck, 0.25 mm); and detection was achieved by spraying with 1% $Ce(SO_4)_2$–10% aqueous H_2SO_4 followed by heating.

Plant Material The flower buds of *P. ginseng* were cultivated in Jilin province of China at Nov., 2005 and identified by one of authors (M. Y.).

Extraction and Isolation The dried flower buds of *Panax ginseng* (1.0 kg) were finely cut and extracted four times with methanol under reflux for 3 h. Evaporation of the solvent under reduced pressure provided the methanolic extract (386 g, 38.6%). The methanolic extract (370 g) was partitioned in an EtOAc–H_2O (1 : 1, v/v) mixture, and the aqueous phase was further extracted with *n*-BuOH. Removal of the solvent from the EtOAc-soluble, *n*-BuOH-soluble, and H_2O-soluble fractions under reduced pressure yielded 43.3 g (4.3%), 216.7 g (21.7%), and 107.1 g (12.0%) of the residue, respectively.

Normal-phase silica gel column chromatography [BW-200 (Fuji Silysia Co., Ltd., 3.0 kg), $CHCl_3$–MeOH–H_2O (50 : 10 : 1—35 : 10 : 1—7 : 3 : 1 lower layer–6 : 4 : 1, v/v/v)–MeOH] of the *n*-BuOH-soluble fraction (134.0 g) gave nine fractions [Fr. 1 (0.3 g), 2 (1.1 g), 3 (13.5 g), 4 (13.6 g), 5 (55.0 g), 6 (15.9 g), 7 (12.1 g), 8 (5.9 g), 9 (4.3 g)]. Fraction 2 (1.1 g) was separated by reversed-phase silica gel column chromatography [Chromatorex ODS DM1020T (Fuji Silysia Co., Ltd., 40 g), MeOH–H_2O [(10 : 90—20 : 80—30 : 70—40 : 60—50 : 50—60 : 40—70 : 30—80 : 20, v/v)–MeOH] to furnish nine fractions [Fr. 2-1 (0.16 g), Fr. 2-2 (0.20 g), Fr. 2-3 (0.18 g), Fr. 2-4 (0.09 g), Fr. 2-5 (0.18 g), Fr. 2-6 (0.09 g), Fr. 2-7 (0.04 g), Fr. 2-8 (0.08 g), Fr. 2-9 (0.09 g)]. Fraction 2-4 (0.09 g) was separated by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (70 : 30, v/v)] to give ginsenosides- F_1 (**7**, 37 mg, 0.0054%), and -F_5 (**9**, 11 mg, 0.0017%). Fraction 2-7 (0.12 g) was purified by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.),

MeOH–H_2O (70 : 30, v/v)] to give **7** (98 mg, 0.014%). Fraction 3 (13.5 g) was separated by reversed-phase silica gel column chromatography [400 g, MeOH–H_2O (20 : 80—30 : 70—40 : 60—50 : 50—60 : 40—70 : 30, v/v)–MeOH] to furnish fourteen fractions [Fr. 3-1 (0.86 g), Fr. 3-2 (0.23 g), Fr. 3-3 (0.18 g), Fr. 3-4 (0.96 g), Fr. 3-5 (0.56 g), Fr. 3-6 (3.74 g), Fr. 3-7 (0.18 g), Fr. 3-8 (0.09 g), Fr. 3-9 (0.05 g), Fr. 3-10 (2.91 g), Fr. 3-11 (0.28 g), Fr. 3-12 (0.15 g), Fr. 3-13 (0.55 g), Fr. 3-14 (2.00 g)]. Fraction 3-4 (0.12 g) was separated by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (50 : 50, v/v)] to give floralginsenosides A (**1**, 46 mg, 0.053%), and B (**2**, 39 mg, 0.046%). Fraction 3-5 (0.26 g) was purified by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (50 : 50, v/v)] to give **2** (30 mg, 0.0094%), floralginsenosides C (**3**, 44 mg, 0.014%), and D (**4**, 17 mg, 0.0054%). Fraction 3-6 (0.22 g) was purified by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (55 : 45, v/v)] to give ginsenoside Rg_1 (**10**, 145 mg, 0.36%). Fraction 3-7 (0.18 g) was purified by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (60 : 40, v/v)] to give **10** (120 mg, 0.018%). Fraction 3-8 (0.09 g) was separated by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (60 : 40, v/v)] to give **10** (23 mg, 0.0033%). Fraction 3-10 (0.21 g) was purified by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (65 : 35, v/v)] to give **9** (41 mg, 0.082%), and ginsenoside-F_3 (**8**, 99 mg, 0.20%). Fraction 3-11 (0.28 g) was purified by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (65 : 35, v/v)] to give **8** (20 mg, 0.0029%), and ginsenoside Rg_2 (**11**, 11 mg, 0.0016%). Fraction 3-12 (0.15 g) was separated by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (70 : 30, v/v)] to give floralginsenosides E (**5**, 10 mg, 0.0014%), and F (**6**, 32 mg, 0.0046%). Fraction 3-13 (0.20 g) was purified by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (75 : 25, v/v)] to give gypenoside XVII (**12**, 25 mg, 0.010%), pseudo-ginsenoside-RC_1 (**13**, 72 mg, 0.030%).

Floralginsenoside A (**1**): A white amorphous powder; $[\alpha]_D^{21}$ +20.4° (c=0.59, MeOH); IR (KBr) ν_{max} 3469, 1655, 1462, 1076 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.82, 1.04, 1.15, 1.568, 1.573, 1.85, 2.03 (3H each, all s, H_3-30, 19, 18, 29, 21, 27, 28), 3.49 (1H, dd, J=4.6, 11.8 Hz, H-3), 4.10 (1H, m, H-12), 4.40 (1H, m, H-6), 4.68 (1H, dd, J=5.2, 7.5 Hz, H-24), 4.99 (1H, d, J=7.7 Hz, H-1′), 5.02, 5.20 (1H each, both br s, H_2-26), 5.12 (1H, d, J=8.0 Hz, H-1″); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 855 $(M+Na)^+$; negative-ion FAB-MS m/z 831 $(M-H)^-$, 815 $(M-OH)^-$, 799 $(M-OOH)^-$, and 651 $(M-OH-C_6H_{11}O_5)^-$; HR-FAB-MS: m/z 855.4718 [Calcd for $C_{42}H_{72}O_{16}Na$ $(M+Na)^+$, 855.4726].

Floralginsenoside B (**2**): A white amorphous powder; $[\alpha]_D^{22}$ +25.6° (c=0.13, MeOH); IR (KBr) ν_{max} 3433, 1655, 1363, 1076 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.79, 1.09, 1.24, 1.55, 1.56, 1.58, 1.59, 2.04 (3H each, all s, H_3-30, 19, 18, 21, 26, 27, 29, 28), 3.50 (1H, dd, J=4.6, 11.8 Hz, H-3), 3.98 (1H, m, H-12), 4.43 (1H, ddd, J=2.9, 10.3, 10.6 Hz, H-6), 5.01 (1H, d, J=7.8 Hz, H-1′), 5.17 (1H, d, J=7.8 Hz, H-1″), 6.05 (1H, d, J=15.7 Hz, H-24), 6.20 (1H, ddd, J=6.3, 8.3, 15.7 Hz, H-23); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 855 $(M+Na)^+$; negative-ion FAB-MS m/z 831 $(M-H)^-$, 815 $(M-OH)^-$, 799 $(M-OOH)^-$, and 651 $(M-OH-C_6H_{11}O_5)^-$; HR-FAB-MS: m/z 855.4718 [Calcd for $C_{42}H_{72}O_{16}Na$ $(M+Na)^+$, 855.4726].

Floralginsenoside C (**3**): A white amorphous powder; $[\alpha]_D^{23}$ +49.8° (c=0.17, MeOH); IR (KBr) ν_{max} 3415, 2932, 1670, 1078 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.96, 1.01, 1.07, 1.42, 1.53, 1.94, 1.95 (3H each, all s, H_3-30, 19, 18, 29, 21, 27, 28), 3.49 (1H, dd, J=4.3, 11.5 Hz, H-3), 4.13 (1H, m, H-12), 4.36 (1H, m, H-6), 4.74 (1H, br s, H-24), 4.87 (1H, d, J=6.3 Hz, H-1″), 5.04, 5.23 (1H each, both br s, H_2-26), 5.05 (1H, d, J=7.5 Hz, H-1′); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 825 $(M+Na)^+$; negative-ion FAB-MS m/z 801 $(M-H)^-$, 669 $(M-C_5H_9O_4)^-$, 489 $(M-C_{11}H_{20}O_{10})^-$; HR-FAB-MS: m/z 825.4618 [Calcd for $C_{41}H_{70}O_{15}Na$ $(M+Na)^+$, 825.4612].

Floralginsenoside D (**4**): A white amorphous powder; $[\alpha]_D^{26}$ +8.8° (c=0.80, MeOH); IR (KBr) ν_{max} 3439, 1655, 1458, 1078 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 600 MHz) δ: 0.91, 1.04, 1.17, 1.43, 1.59, 1.96 (3H each, all s, H_3-30, 19, 18, 29, 21, 28), 1.60 (6H, s, H_3-26, 27), 3.50 (1H, dd, J=4.8, 11.7 Hz, H-3), 4.00 (1H, m, H-12), 4.39 (1H, dd, J=3.4, 10.3 Hz, H-6), 5.15 (1H, d, J=7.6 Hz, H-1′), 5.62 (1H, br s, H-1″), 6.11 (1H, d, J=15.8 Hz, H-24), 6.18 (1H, dd-like, J=*ca.* 10, 16 Hz, H-23); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 825 $(M+Na)^+$; negative-ion FAB-MS m/z 801 $(M-H)^-$, 669 $(M-C_5H_9O_4)^-$, 489 $(M-C_{11}H_{20}O_{10})^-$; HR-FAB-MS: m/z 825.4606 [Calcd for $C_{41}H_{70}O_{15}Na$ $(M+Na)^-$, 825.4612].

Floralginsenoside E (**5**): A white amorphous powder; $[\alpha]_D^{22}$ +17.6° (c=0.27, MeOH); IR (KBr) ν_{max} 3451, 2930, 1655, 1078 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 600 MHz) δ: 0.87, 0.97, 1.06, 1.13, 1.31, 1.43, 1.56, 1.57 (3H each, all s, H_3-19, 30, 18, 29, 28, 21, 26, 27), 3.31 (1H, dd, J=4.5, 11.9 Hz, H-3), 3.92 (1H, m, H-12), 4.92 (1H, d, J=7.7 Hz, H-1′), 5.35 (1H, d, J=7.7 Hz, H-1″), 6.04 (1H, d, J=16.0 Hz, H-24), 6.25 (1H, ddd, J=5.7, 8.9, 16.0 Hz, H-23); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 839 $(M+Na)^+$; negative-ion FAB-MS m/z 815 $(M-H)^-$, 799 $(M-OH)^-$, 635 $(M-OH-C_6H_{11}O_5)^-$; HR-FAB-MS: m/z 839.4775 [Calcd for $C_{42}H_{72}O_{15}Na$ $(M+Na)^+$, 839.4769].

Floralginsenoside F (**6**): A white amorphous powder; $[\alpha]_D^{25}$ +14.8° (c=0.93, MeOH); IR (KBr) ν_{max} 3566, 2972, 1655, 1078 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.87, 0.92, 1.01, 1.02, 1.32, 1.57, 1.58, 1.60 (3H each, all s, H_3-19, 30, 18, 29, 28, 26, 27, 21), 3.38 (1H, dd, J=4.3, 11.8 Hz, H-3), 3.95 (1H, m, H-12), 4.92 (1H, d, J=7.7 Hz, H-1′), 5.19 (1H, d, J=7.8 Hz, H-1″), 6.03 (1H, d, J=16.0 Hz, H-24), 6.18 (1H, ddd, J=6.0, 8.3, 16.0 Hz, H-23); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 839 $(M+Na)^+$; negative-ion FAB-MS m/z 815 $(M-H)^-$, 799 $(M-OH)^-$, 635 $(M-OH-C_6H_{11}O_5)^-$; HR-FAB-MS: m/z 839.4772 [Calcd for $C_{42}H_{72}O_{15}Na$ $(M+Na)^+$, 839.4769].

Pyridine Treatment of 1 A solution of **1** (27 mg) in pyridine (0.6 ml) was allowed to stand at 40 °C for 12 h. After removal of the solvent under reduced pressure, the reaction mixture was separated by HPLC [COSMOSIL 5C_{18}-MS-II, (250×20 mm i.d.), MeOH–H_2O (50 : 50, v/v)] to give vina-ginsenoside R_{25} (**14**, 9 mg) and **1** (10 mg), which were identified with authentic samples by ^{1}H- and ^{13}C-NMR and FAB-MS spectra comparisons.

$NaBH_4$ Reduction of 2 A solution of **2** (12 mg) in dry-MeOH (3.0 ml) was treated with $NaBH_4$ (24 mg) and the mixture was stirred at room temperature for overnight. The reaction mixture was quenched in acetone, and then removal of the solvent under reduced pressure yielded a reduction mixture. The reduction mixture was purified by normal-phase silica gel column chromatography [0.7 g, $CHCl_3$–MeOH–H_2O (7 : 3 : 1 lower-layer–65 : 35 : 10, v/v/v)] to give vina-ginsenoside-R15 (**15**, 11 mg), which was identified with authentic sample by ^{1}H- and ^{13}C-NMR and FAB-MS spectra comparisons.

$NaBH_4$ Reduction of 6 A solution of **6** (10 mg) in dry-MeOH (3.0 ml) was treated with $NaBH_4$ (26 mg) and the mixture was stirred at room temperature for overnight. The reaction mixture was quenched in acetone, and then removal of the solvent under reduced pressure yielded a reduction product. The reduction product was purified by normal-phase silica gel column chromatography [0.7 g, $CHCl_3$–MeOH–H_2O (7 : 3 : 1 lower-layer–65 : 35 : 10, v/v/v)] to give majoroside F_4 (**16**, 8 mg), which was identified with authentic sample by ^{1}H- and ^{13}C-NMR and FAB-MS spectra comparisons.

Acid Hydrolysis of Floralginsenosides A (1), B (2), C (3), D (4), E (5), and F (6) A solution of **1**—**6** (1 mg each) in 1.0 M HCl (1.0 ml) was heated under reflux for 3 h. After cooling, the reaction mixture was poured into ice-water and neutralized with Amberlite IRA-400 (OH^- form), and the resin was removed by filtration. Then, the filtrate was extracted with EtOAc. The aqueous layer was subjected to HPLC analysis under the following conditions: HPLC column, Kaseisorb LC NH_2-60-5, 4.6 mm i.d.×250 mm (Tokyo Kasei Co., Ltd., Tokyo, Japan); detection, optical rotation [Shodex OR-2 (Showa Denko Co., Ltd., Tokyo, Japan)]; mobile phase, MeCN–H_2O (75 : 25, v/v); flow rate 0.80 ml/min; column temperature, room temperature. Identification of D-glucose and L-arabinose present in the aqueous layer was carried out by comparison of its retention time and optical rotation with that of an authentic sample. t_R: 7.8 min (L-arabinose, positive optical rotation) and 8.6 min (D-glucose, positive optical rotation).

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