Medicinal Flowers. XVII.[1] New Dammarane-Type Triterpene Glycosides from Flower Buds of American Ginseng, *Panax quinquefolium* L.

Seikou NAKAMURA, Sachiko SUGIMOTO, Hisashi MATSUDA, and Masayuki YOSHIKAWA*

Kyoto Pharmaceutical University; Misasagi, Yamashina-ku, Kyoto 607–8412, Japan.
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Five new dammarane-type triterpene glycosides, floralquinquenosides A, B, C, D, and E, were isolated from the flower buds of American ginseng, *Panax quinquefolium* L., together with 18 known dammarane-type triterpene glycosides and 3 flavonoid glycosides. The structures of new floralquinquenosides were elucidated on the basis of chemical and physicochemical evidence.

Key words floralquinquenoside; American ginseng; *Panax quinquefolium*; medicinal flower; dammarane-type triterpene glycoside; American ginseng flower

The Araliaceae plant, *Panax* (*P.*) *quinquefolium* L., which is called as American ginseng or North American ginseng, is widely cultivated in U.S.A., Canada, and China. The roots of this plant are used for the same medicinal purposes as Ginseng, the roots of *P. ginseng* C. A. MEYER. The biologically active constituents of the roots have been pursued extensively and many dammarane-type triterpene oligoglycosides have been characterized as the principal ingredients.[2—6] On the other hand, the flower buds of *P. quinquefolium* have been used as an exhilarant and tonic in the form of health tea. However, chemical and pharmacological studies on the bioactive constituents from the flower buds were yet left uncharacterized. Recently, we have reported the isolation and structure elucidation of dammarane-type triterpene oligoglycosides from the flower buds of *P. ginseng*[1,7,8] and *P. notoginseng*.[9] Among them, ginsenoside Rd, which is principal constituent from the flower buds of *P. ginseng*, was found to show gastroprotective effect and ginsenosides-Rb_3 (**6**) and Rc, which are principal constituents from the flower buds of *P. notoginseng*, were found to show hepatoprotective effects. As a continuing study on the bioactive constituents of medicinal flowers,[1,7—15] we have isolated new dammarane-type triterpene glycosides named floralquinquenosides A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**) from the flower buds of *P. quinquefolium* together with 18 known dammarane-type triterpene oligoglycosides and three flavonoid glycosides. In this paper, we describe the isolation and structure elucidation of new floralquinquenosides (**1**—**5**).

Isolation of Floralquinquenosides The methanolic extract from the flower buds of *P. quinquefolium* 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 (*n*-BuOH) to give an *n*-BuOH-soluble portion. The EtOAc-soluble fraction was subjected to normal-phase and reversed-phase silica gel column chromatography and finally HPLC to afford floralquinquenoside A (**1**, 0.0015% from the dried flower buds) together with 11 known compounds, ginsenoside Rb_3 (**6**,[9,16] 0.0057%), ginsenoside Rd (**7**,[17] 0.011%), ginsenoside I (**12**,[18] 0.0042%), ginsenoside Re (**14**,[19] 0.011%), ginsenoside Rg_2 (**16**,[19] 0.0047%), quinquenoside L_9 (**19**,[4] 0.0004%), pseudo-ginsenoside RT_5 (**20**,[20] 0.0040%), pseudo-ginsenoside F_{11} (**21**,[20] 0.088%), 24(*R*)-vina-ginsenoside R_1 (**23**,[20] 0.0018%), kaempferol 7-*O*-(2,3-di-*E*-*p*-coumaroyl-α-L-rhamnopyranoside) (**25**,[21] 0.0035%), kaempferol-3-*O*-α-L-rhamnopyranoside (**26**,[22] 0.0018%). The *n*-BuOH-soluble portion was subjected to normal-phase and reversed-phase silica gel column chromatography and finally HPLC to afford floralquinquenosides B (**2**, 0.0011%), C (**3**, 0.0036%), D (**4**, 0.0046%), and E (**5**, 0.0062%) together with 18 known compounds, ginsenoside Rb_3 (**6**,[9,16] 0.11%), ginsenoside Rd (**7**,[17] 0.23%), ginsenoside Rs_1 (**8**,[18] 0.034%), pseudo-ginsenoside-RC_1 (**9**,[23] 0.0096%), pseudo-ginsenoside-F_8 (**10**,[18] 0.030%), quinquenoside III (**11**,[2] 0.077%), ginsenoside I (**12**,[18] 0.083%), notoginsenoside-E (**13**,[23] 0.18%), ginsenoside Re (**14**,[19] 0.034%), ginsenoside Rg_1 (**15**,[24] 0.020%), ginsenoside Rg_2 (**16**,[19] 0.047%), ginsenoside-F_3 (**17**,[25] 0.0066%), ginsenoside Ia (**18**,[26] 0.017%), quinquenoside L_9 (**19**,[4] 0.0053%), pseudo-ginsenoside RT_5 (**20**,[20] 0.0066%), pseudo-ginsenoside F_{11} (**21**,[20] 6.1%), 24(*S*)-pseudo-ginsenoside F_{11} (**22**,[20] 0.015%), and kaempferol 3-*O*-β-D-sophoroside-7-*O*-α-L-rhamnopyranoside (**24**,[27] 0.0042%).

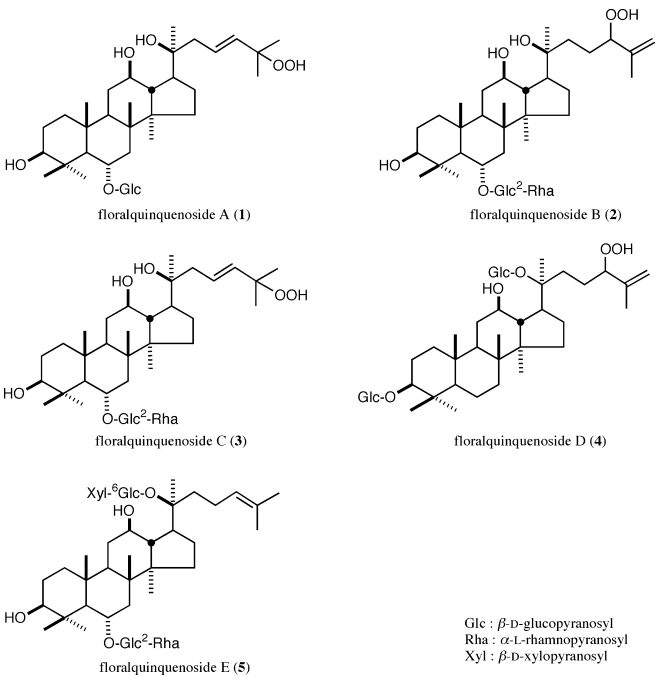

Chart 1. Structures of New Floralquinquenosides **1**—**5** from the Flower Buds of *P. quinquefolium*

* To whom correspondence should be addressed. e-mail: myoshika@mb.kyoto-phu.ac.jp

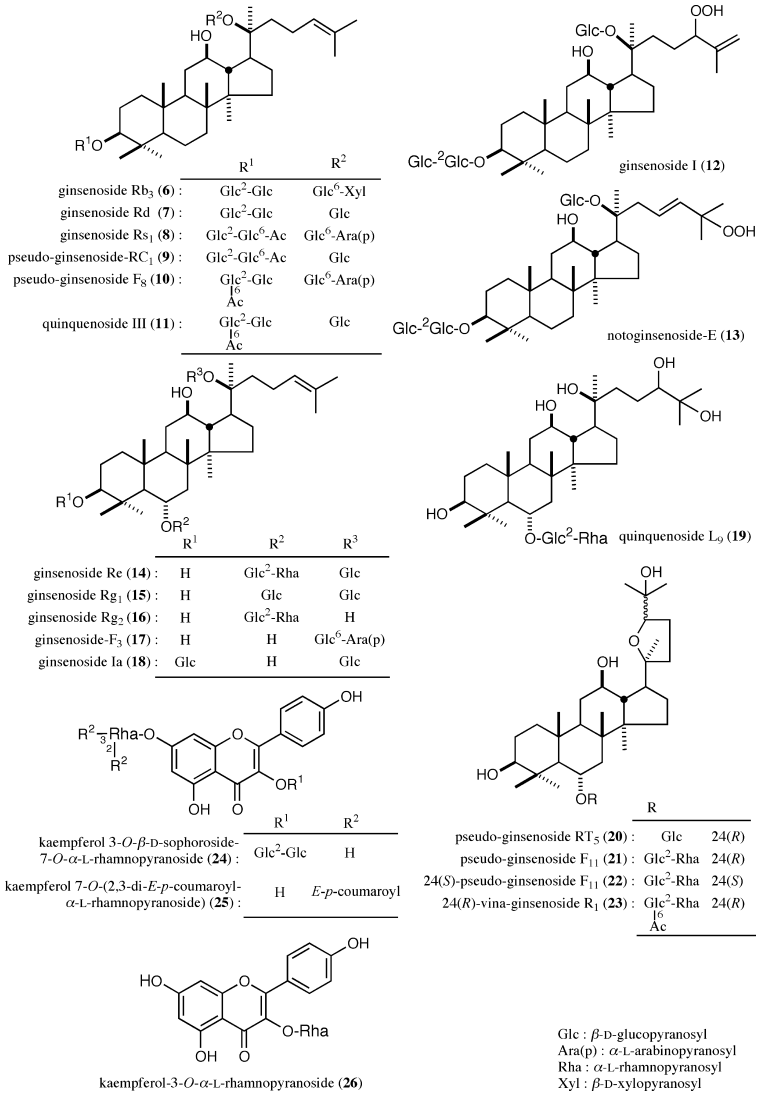

Chart 2. Structures of Known Compounds from the Flower-Buds of *P. quinquefolium*

Structures of Floralquinquenosides Floralquinquenoside A (**1**) was isolated as an amorphous powder with positive optical rotation ($[\alpha]_D^{23}$ +22.1° in MeOH). As shown by its positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent,[28] **1** was deduced to have a hydroperoxide residue. The IR spectrum of **1** showed strong absorption bands at 3415 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 $C_{36}H_{62}O_{11}$ was determined from the quasimolecular ion peaks observed in the positive-ion and negative-ion fast atom bombardment (FAB)-MS and by high-resolution (HR)-MS measurement. Namely, a quasimolecular ion peak was observed at *m*/*z* 693 $(M+Na)^+$ in the positive-ion FAB-MS of **1**, while its negative-ion FAB-MS showed the quasimolecular ion peak at *m*/*z* 669 $(M-H)^-$. Acid hydrolysis of **1** with 1.0 M aqueous HCl liberated D-glucose, which was identified by HPLC analysis using an optical rotation detector.[1,7,8] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra of **1**, which were assigned by various NMR experiment,[29] showed signals assignable to an aglycon part [δ 0.84, 1.10, 1.29, 1.41, 1.57, 1.58, 1.64, 2.10 (3H each, all s, H_3-30, 19, 18, 21, 26, 27, 29, 28), 3.55 (1H, dd, *J*=4.5, 11.5 Hz, H-3), 3.93 (1H, m, H-12), 4.48 (1H, ddd, *J*=2.8, 10.5, 13.5 Hz, H-6), 6.08 (1H, d, *J*=15.9 Hz, H-24), 6.28 (1H, ddd, *J*=5.7, 9.0, 15.9 Hz, H-23)], together with a β-D-glucopyranosyl moiety [δ 5.08 (1H, d, *J*=7.9 Hz, H-1′)]. The proton and carbon signals of **1** in the ^{1}H- and ^{13}C-NMR spectra resembled those of floralginsenoside B,[7] except for the signals due to the 20-*O*-β-D-glucopyranosyl part of floralginsenoside B. As shown in Fig. 1, the double quantum filter correlation spectroscopy (DQF 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-18 and C-7, 8, 14; H-19 and C-5, 9, 10; H-21 and C-17, 20, 22; H-22 and C-23, 24; H-26, 27 and C-24, 25; H-1′ and C-6. On the basis of this evidence, the structure of floralquinquenoside A (**1**) was characterized as shown.

Floralquinquenoside B (**2**) was also obtained as an amorphous powder with negative optical rotation ($[\alpha]_D^{20}$ −16.9° in MeOH) and was shown to possess a hydroperoxide group by its positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[28] The IR spectrum of **2**

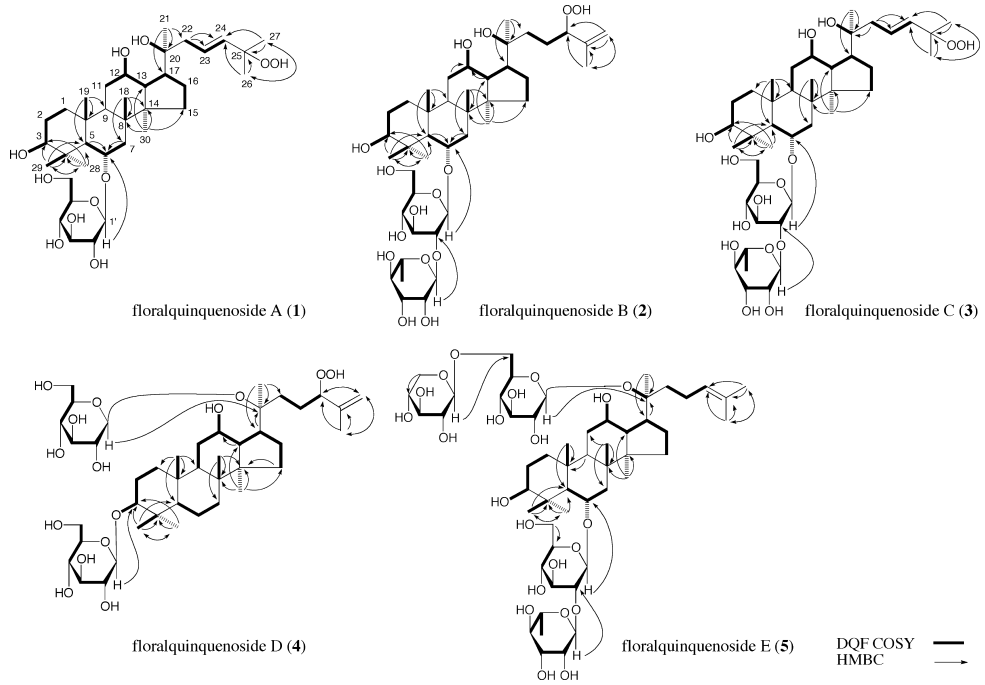

Fig. 1. Significant DQF COSY and HMBC Correlations for New Floralquinquenosides (**1**—**5**) from the Flower-Buds of *P. quinquefolium*

Table 1. ^{13}C-NMR Data for Floralquinquenosides A (**1**), B (**2**), C (**3**), D (**4**), E (**5**)[a]

	1	**2**	**3**	**4**	**5**		**1**	**2**	**3**	**4**	**5**
C-1	39.4	39.2	39.3	39.3	39.4	C-1′	106.0	101.6	101.8	106.9	101.8
C-2	27.7	27.0	27.7	26.6	27.7	C-2′	75.5	79.3	79.4	75.8	79.4
C-3	78.6	78.1	78.3	88.9	78.6	C-3′	78.2	78.4	78.5	78.8	78.3
C-4	40.1	39.8	39.6	39.7	40.0	C-4′	71.8	72.6	72.6	72.0	72.1
C-5	61.4	60.6	60.8	56.5	60.8	C-5′	79.7	78.4	78.4	78.3	78.4
C-6	80.0	74.0	74.4	18.5	74.8	C-6′	63.1	62.9	63.1	63.2	63.0
C-7	45.2	45.9	46.0	35.2	46.0	C-1″		101.8	101.9	98.3	101.8
C-8	41.1	40.9	41.2	40.1	41.1	C-2″		72.4	72.4	75.2	72.4
C-9	50.2	49.6	49.7	50.2	49.5	C-3″		72.2	72.3	79.0	72.2
C-10	39.7	39.4	40.0	37.0	39.6	C-4″		74.0	74.2	71.8	74.1
C-11	32.2	31.6	32.2	30.8	30.9	C-5″		69.3	69.4	78.2	69.4
C-12	71.0	70.8	71.0	70.3	70.1	C-6″		18.6	18.7	63.0	18.7
C-13	48.5	48.0	48.4	49.6	49.1	C-1‴					98.0
C-14	51.7	51.5	51.7	51.5	51.3	C-2‴					74.8
C-15	31.2	31.1	31.3	31.1	30.7	C-3‴					79.3
C-16	26.8	26.7	26.8	26.8	26.6	C-4‴					71.5
C-17	54.1	54.5	54.0	51.7	51.6	C-5‴					76.9
C-18	17.7	16.9	17.2	16.0	17.5	C-6‴					70.0
C-19	17.4	17.5	17.64	16.3	17.2	C-1⁗					105.8
C-20	73.2	72.1	73.2	83.4	83.4	C-2⁗					74.6
C-21	27.9	27.0	27.7	22.8	22.6	C-3⁗					78.3
C-22	40.4	40.0	40.0	32.9	36.0	C-4⁗					71.1
C-23	127.3	26.2	127.3	26.9	23.1	C-5⁗					67.0
C-24	137.6	90.0	137.5	90.0	126.0						
C-25	81.2	146.1	81.2	146.0	131.0						
C-26	25.1[b]	113.2	25.1[b]	113.3	25.8						
C-27	25.3[b]	17.8	25.3[b]	17.8	17.9						
C-28	31.7	32.2	32.2	28.2	32.2						
C-29	16.4	17.6	17.61	16.8	17.6						
C-30	16.8	16.7	16.9	17.8	17.4						

a) Measured in pyridine-d_5 at 125 MHz, 150 MHz. *b*) Reversible.

showed absorption bands at 3451, 1655, and 1075 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* 839 $(M+Na)^+$ and *m*/*z* 815 $(M-H)^-$, respectively. The HR-MS analysis revealed the molecular formula of **2** to be $C_{42}H_{72}O_{15}$. The acid hydrolysis of **2** liberated D-glucose and L-rhamnose, which was identified by HPLC analysis.[1,7,8] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[29] of **2** showed signals due to an aglycon part [δ 0.87, 0.90, 1.13, 1.30, 1.39, 1.86, 2.16 (3H

each, all s, H_3-30, 19, 18, 21, 29, 26, 28), 3.42 (1H, dd, J=4.8, 11.0 Hz, H-3), 3.85 (1H, m, H-12), 4.66 (1H, m, H-6), 4.72 (1H, m, H-24), 5.03, 5.20 (each 1H, both br s, H_2-26)] and an β-D-glucopyranosyl [δ 5.21 (1H, d, J=7.6 Hz, H-1′)] and an α-L-rhamnopyranosyl [δ 6.46 (1H, s like, H-1″)] moieties. The proton and carbon signals of **2** in the ^{1}H- and ^{13}C-NMR spectra were superimposable on those of ginsenoside Rg_2 (**16**),[19] except for the signals due to the side chain part (C-24—C-27), which were similar to those of floralginsenoside A[7] and notoginsenoside-C.[30] As shown in Fig. 1, the DQF COSY experiment on **1** indicated the presence of partial structures written in bold lines, and in the HMBC experiment, long-range correlations were observed between the following protons and carbons: H-13 and C-12; H-18 and C-7, 8, 14; 19-H and C-5, 9, 10; H-21 and C-17, 20, 22; H-26 and C-24, 25, 27; H-27 and C-24, 25, 26; H-1′ and C-6; H-1″ and C-2′. On the basis of this evidence, the structure of floralquinquenoside B (**2**)[31] was characterized as shown.

Floralquinquenoside C (**3**) was also obtained as an amorphous powder with negative optical rotation ($[\alpha]_D^{24}$ −13.3° in MeOH) and was shown to possess a hydroperoxide group by its positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[28] The IR spectrum of **3** showed absorption bands at 3451, 1655, and 1083 cm^{-1} assignable to hydroxyl, olefin, and ether groups. In the positive-ion FAB-MS of **3**, a quasimolecular ion peak was observed at *m/z* 839 $(M+Na)^+$, whereas the negative-ion FAB-MS showed a quasimolecular ion peak at *m/z* 815 $(M-H)^-$. The molecular formula $C_{42}H_{72}O_{15}$ of **3** was determined by HR-MS measurement. The acid hydrolysis of **3** provided D-glucose and L-rhamnose, which were identified by HPLC analysis.[1,7,8] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 2) spectra[29] of **3** showed signals due to an aglycon part [δ 0.96, 1.02, 1.30, 1.39, 1.41, 1.58, 1.59, 2.16 (3H each, all s, H_3-30, 19, 18, 29, 21, 26, 27, 28), 3.50 (1H, dd, J=4.8, 11.9 Hz, H-3), 3.94 (1H, t like, J=9.2 Hz, H-12), 4.75 (1H, m, H-6), 6.09 (1H, d, J=15.7 Hz, H-24), 6.29 (1H, ddd, J=5.5, 8.9, 15.7 Hz, H-23)], together with an β-D-glucopyranosyl [δ 5.30 (1H, d, J=7.0 Hz, H-1′)] and an α-L-rhamnopyranosyl [δ 6.54 (1H, s like, H-1″)] moieties. The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra of **3** was superimposable on those floralquinquenoside B (**2**) and ginsenoside Rg_2,[19] except for the signals due to the side chain part (C-22—C-27), which were similar to those of floralquinquenoside A (**1**), floralginsenoside B.[7] On the basis of this evidence and detail examination of DQF COSY and HMBC experiments (Fig. 1), the structure of floralquinquenoside C (**3**) was determined as shown.

Floralquinquenoside D (**4**) was also obtained as an amorphous powder with positive optical rotation ($[\alpha]_D^{25}$ +13.2° in MeOH) and was shown to possess a hydroperoxide group by its positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[28] The IR spectrum of **2** showed absorption bands at 3469, 1655, and 1076 cm^{-1} assignable to hydroxyl, olefin, and ether functions. In the positive-ion and negative-ion FAB-MS of **4**, quasimolecular ion peaks were observed at *m/z* 839 $(M+Na)^+$ and *m/z* 815 $(M-H)^-$, respectively. The HR-MS analysis revealed the molecular formula of **4** to be $C_{42}H_{72}O_{15}$. The acid hydrolysis of **4** liberated D-glucose, which was identified by HPLC analysis.[1,7,8] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[29] of **4** showed signals due to an aglycon part [δ 0.82, 0.94, 0.95, 0.99, 1.30, 1.54, 1.90 (3H each, all s, H_3-19, 30, 18, 29, 28, 21, 27), 3.38 (1H, dd, J=4.3, 11.6 Hz, H-3), 4.05 (1H, m, H-12), 4.96 (1H, dd, J=4.8, 7.9 Hz, H-24), 5.03, 5.21 (1H each, both br s, H_2-26)], together with two β-D-glucopyranosyl moieties [δ 4.93 (1H, d, J=7.7 Hz, H-1′), 5.15 (1H, d, J=7.9 Hz, H-1″)]. The proton and carbon signals due to the tetracarbocyclic moiety (C-1—C-20, C-28—C-30) including the 3- and 20-*O*-β-D-glucopyranosyl parts in the ^{1}H- and ^{13}C-NMR spectra of **4** were superimposable on those of floralginsenoside F[7] and ginsenoside-F_2,[32] whrereas the signals designated to the side chain moiety (C-20—C-27) of the aglycon part were similar to those of floralginsenoside A,[7] and notoginsenoside-C.[30] The position of the glycoside linkages were determined by a HMBC experiment, which showed long-range correlations between the following protons and carbons: H-1′ and C-3; H-1″ and C-20. Furthermore, the DQF COSY and HMBC experiments on **4** showed correlations as shown in Fig. 1. This evidence led us to formulate the structures of floralquinquenoside D (**4**)[31] as shown.

Floralquinquenoside E (**5**), obtained as an amorphous powder with negative optical rotation ($[\alpha]_D^{22}$ −1.8° in MeOH), showed absorption bands at 3433, 1651, and 1076 cm^{-1} assignable 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* 1101 $(M+Na)^+$ and *m/z* 1077 $(M-H)^-$, respectively and the fragment ion peaks were observed at *m/z* 931 $(M-C_6H_{11}O_4)^-$ in the negative-ion FAB-MS. The molecular formula $C_{53}H_{90}O_{22}$ of **5** was determined from the quasimolecular ion peak and by HR-MS measurement. The acid hydrolysis of **5** liberated D-glucose, L-rhamnose, and D-xylose.[1,7,8] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 2) spectra[29] of **5** showed signals assignable to an aglycon part [δ 0.97, 1.19, 1.36, 1.37, 1.61, 1.62, 1.67, 2.12 (3H each, all s, H_3-19, 30, 29, 18, 27, 21, 26, 28), 3.47 (1H, dd, J=4.8, 11.4 Hz, H-3), 4.17 (1H, m, H-12), 4.68 (1H, m, H-6), 5.33 (1H, m, H-24)], an β-D-xylopyranosyl [δ 4.99 (1H, d, J=7.3 Hz, H-1‴)], two β-D-glucopyranosyl [δ 5.11 (1H, d, J=7.8 Hz, H-1‴), 5.28 (1H, d, J=6.8 Hz, H-1′)], and an α-L-rhamnopyranosyl [δ 6.51 (1H, br s, H-1″)] moieties. The proton and carbon signals of the aglycon part in the ^{1}H- and ^{13}C-NMR spectra of **5** were found to be superimposable on those of protopanaxatriol 6,20-bisdesmosides, such as ginsenoside Rg_1 (**15**),[24] while the proton and carbon signals due to the 6- and 20-*O*-glycoside moieties were similar to those of ginsenoside Rg_2 (**16**)[19] and Rb_3 (**6**),[16] respectively. The position of the glycoside linkages were determined by a HMBC experiment, which showed long-range correlations between the following protons and carbons: H-1′ and C-6; H-1″ and C-2′; H-1‴ and C-20; H-1⁗ and C-6‴. Furthermore, the DQF COSY and HMBC experiments on **5** showed correlations as shown in Fig. 1. This evidence led us to formulate the structures of floralquinquenoside E (**5**) 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; EI-MS and HR-EI-MS, JEOL JMS-GC-MATE mass spectrometer; FAB-MS and HR-FAB-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; HPLC detector, Shimadzu RID-6A refractive index detector; and HPLC column, YMC-Pack ODS-A (YMC, Inc., 250×4.6 mm i.d.) and (250×20 mm i.d.) columns were used for analytical and preparative purposes, respectively.

The following experimental materials were used for chromatography: normal-phase silica gel column chromatography, Silica gel BW-200 (Fuji Silysia Chemical, Ltd., 150—350 mesh); reversed-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) (reversed 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 *Panax quinquefolium* were cultivated in Jilin province of China and collected at July, 2006. The botanical identification was undertaken by one of authors (M. Y.). A voucher of the plant is on file in our laboratory.

Isolation of Floralquinquenosides A—E (1—5) and Known Compounds from the Flower Buds of *P. quinquefolium* The Flower buds of *P. quinquefolium* (1.0 kg, Jilin province, China) were cut and extracted four times with MeOH under reflux. Evaporation of the solvent under reduced pressure provided the MeOH extract (411 g, 41.1%), which was partitioned into an EtOAc–H_2O (1 : 1, v/v) mixture to furnish an EtOAc-soluble fraction (53 g, 5.3%) and aqueous layer. The aqueous layer was extracted with *n*-BuOH to give *n*-BuOH- (308 g, 30.8%) and H_2O- (50 g, 5.0%) soluble fractions. The EtOAc-soluble fraction (46 g) was subjected to normal-phase silica gel column chromatography [1.2 kg, *n*-hexane–EtOAc (10 : 1→5 : 1→1 : 1, v/v)→$CHCl_3$–MeOH–H_2O (10 : 3 : 1→7 : 3 : 1→6 : 4 : 1, v/v)→MeOH] to give 12 fractions [Fr. 1 (0.5 g), Fr. 2 (5.6 g), Fr. 3 (8.2 g), Fr. 4 (2.5 g), Fr. 5 (0.4 g), Fr. 6 (6.3 g), Fr. 7 (1.5 g), Fr. 8 (2.9 g), Fr. 9 (4.7 g), Fr. 10 (0.9 g), Fr. 11 (8.9 g), Fr. 12 (2.0 g)]. Fraction 7 (1.5 g) was separated by reversed-phase silica gel column chromatography [50 g, MeOH–H_2O (40 : 60→50 : 50→60 : 40→70 : 30→80 : 20, v/v)→MeOH] to give 10 fractions [Fr. 7-1 (352 mg), Fr. 7-2 (28 mg), Fr. 7-3 (37 mg), Fr. 7-4 (24 mg), Fr. 7-5 (89 mg), Fr. 7-6 (113 mg), Fr. 7-7 (62 mg), Fr. 7-8 (185 mg), Fr. 7-9 (528 mg), Fr. 7-10 (54 mg)]. Fraction 7-6 (113 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give kaempferol 7-*O*-(2,3-di-*E*-*p*-coumaroyl-α-L-rhamnopyranoside) (**25**, 30 mg). Fraction 8 (2.9 g) was separated by reversed-phase silica gel column chromatography [100 g, MeOH–H_2O (40 : 60→50 : 50→60 : 40→70 : 30→80 : 20→90 : 10, v/v)→MeOH] to give 13 fractions [Fr. 8-1 (395 mg), Fr. 8-2 (113 mg), Fr. 8-3 (39 mg), Fr. 8-4 (199 mg), Fr. 8-5 (62 mg), Fr. 8-6 (91 mg), Fr. 8-7 (78 mg), Fr. 8-8 (74 mg), Fr. 8-9 (57 mg), Fr. 8-10 (95 mg), Fr. 8-11 (92 mg), Fr. 8-12 (231 mg), Fr. 8-13 (355 mg)]. Fraction 8-4 (199 mg) was purified by HPLC [[1] MeOH–H_2O (65 : 35, v/v) [2] MeCN–H_2O (22 : 78, v/v)] to give give 2 fractions [Fr. 8-4-1 (5.5 mg), Fr. 8-4-2 (38 mg)]. Fraction 8-4-2 (38 mg) was separated by sephadex LH-20 column chromatography [500 mg, $CHCl_3$–MeOH–H_2O (10 : 3 : 1, v/v)] to give floralquinquenoside A (**1**, 13 mg), kaempferol 3-*O*-α-L-rhamnopyranoside (**26**, 15 mg). Fraction 8-7 (78 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give pseudo-ginsenoside RT_5 (**20**, 33 mg). Fraction 8-8 (74 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give 24(*R*)-vina-ginsenoside R_1 (**23**, 15 mg). Fraction 9 (4.7 g) was separated by reversed-phase silica gel column chromatography [150 g, MeOH–H_2O (50 : 50→60 : 40→70 : 30→80 : 20→90 : 10, v/v)→MeOH] to give 8 fractions [Fr. 9-1 (405 mg), Fr. 9-2 (220 mg), Fr. 9-3 (2.1 g), Fr. 9-4 (170 mg), Fr. 9-5 (108 mg), Fr. 9-6 (40 mg), Fr. 9-7 (98 mg), Fr. 9-8 (1.1 g)]. Fraction 9-2 (220 mg) was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give ginsenoside Rg_2 (**16**, 18 mg). Fraction 9-3 (165 mg) was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give pseudo-ginsenoside F_{11} (**21**, 53 mg). Fraction 9-4 (170 mg) was purified by HPLC [MeOH–H_2O (65 : 35, v/v)] to give pseudo-ginsenoside Rg_2 (**16**, 23 mg) and ginsenoside F_{11} (**21**, 53 mg). Fraction 10 (0.9 g) was separated by reversed-phase silica gel column chromatography [27 g, MeOH–H_2O (40 : 60→50 : 50→60 : 40→70 : 30→80 : 20→90 : 10, v/v)→MeOH] to give 13 fractions [Fr. 10-1 (151 mg), Fr. 10-2 (36 mg), Fr. 10-3 (22 mg), Fr. 10-4 (51 mg), Fr. 10-5 (48 mg), Fr. 10-6 (55 mg), Fr. 10-7 (237 mg), Fr. 10-8 (105 mg), Fr. 10-9 (35 mg), Fr. 10-10 (50 mg), Fr. 10-11 (49 mg), Fr. 10-12 (46 mg), Fr. 10-13 (12 mg)]. Fraction 10-3 (22 mg) was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give quinquenoside L_9 (**19**, 3.4 mg). Fraction 10-6 (55 mg) was purified by HPLC [MeOH–H_2O (65 : 35, v/v)] to give ginsenoside Re (**14**, 27 mg). Fraction 10-7 (237 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give ginsenoside Rd (**7**, 16 mg) and ginsenoside I (**12**, 35 mg). Fraction 10-8 (105 mg) was purified by HPLC [MeOH–H_2O (80 : 20, v/v)] to give ginsenoside Rd (**7**, 16 mg). Fraction 11 (8.9 g) was separated by reversed-phase silica gel column chromatography [270 g, MeOH–H_2O (40 : 60→50 : 50→60 : 40→70 : 30→80 : 20→90 : 10, v/v)→MeOH] to give 15 fractions [Fr. 11-1 (1.2 g), Fr. 11-2 (282 mg), Fr. 11-3 (252 mg), Fr. 11-4 (72 mg), Fr. 11-5 (81 mg), Fr. 11-6 (719 mg), Fr. 11-7 (94 mg), Fr. 11-8 (44 mg), Fr. 11-9 (755 mg), Fr. 11-10 (498 mg), Fr. 11-11 (121 mg), Fr. 11-12 (1.6 g), Fr. 11-13 (373 mg), Fr. 11-14 (147 mg), Fr. 11-15 (2.6 g)]. Fraction 11-3 (252 mg) was purified by HPLC [MeOH–H_2O (40 : 60, v/v)] to give ginsenoside Re (**14**, 11 mg). Fraction 11-4 (72 mg) was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give ginsenoside Re (**14**, 8.0 mg). Fraction 11-5 (81 mg) was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give pseudo-ginsenoside F_{11} (**21**, 9.8 mg). Fraction 11-6 (103 mg) was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to give ginsenoside Re (**14**, 29 mg). Fraction 11-7 (94 mg) was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to give ginsenoside Re (**14**, 13 mg). Fraction 11-12 (147 mg) was purified by HPLC [MeOH–H_2O (75 : 25, v/v)] to give ginsenoside Rb_3 (**6**, 16 mg). Fraction 11-13 (167 mg) was purified by HPLC [MeOH–H_2O (75 : 25, v/v)] to give ginsenoside Rb_3 (**6**, 17 mg) and ginsenoside Rd (**7**, 30 mg). Fraction 11-14 (147 mg) was purified by HPLC [MeOH–H_2O (75 : 25, v/v)] to give ginsenoside Rd (**7**, 27 mg). The *n*-BuOH-soluble fraction (142 g) was subjected to normal-phase silica gel column chromatography [3 kg, $CHCl_3$: MeOH : H_2O (50 : 10 : 1→40 : 10 : 1→30 : 10 : 1→7 : 3 : 1→6 : 4 : 1)→MeOH] to give 7 fractions [Fr. 1 (0.4 g), Fr. 2 (1.8 g), Fr. 3 (17.1 g), Fr. 4 (2.3 g), Fr. 5 (53.9 g), Fr. 6 (61.9 g), Fr. 7 (4.4 g)]. Fraction 2 (1.8 g) was separated by reversed-phase silica gel column chromatography [55 g, MeOH : H_2O (20 : 80→30 : 70→40 : 60→50 : 50→60 : 40→70 : 30→80 : 20→MeOH→acetone)] to give 6 fractions [Fr. 2-1 (601 mg), Fr. 2-2 (186 mg), Fr. 2-3 (138 mg), Fr. 2-4 (205 mg), Fr. 2-5 (145 mg), Fr. 2-6 (210 mg)]. Fraction 2-4 (205 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give pseudo-ginsenoside F_{11} (**21**, 15 mg) and pseudo-ginsenoside RT_5 (**20**, 31 mg). Fraction 3 (17.1 g) was separated by reversed-phase silica gel column chromatography [520 g, MeOH : H_2O (50 : 50→60 : 40→70 : 30→80 : 20→90 : 10)→MeOH] to give 12 fractions [Fr. 3-1 (1.2 g), Fr. 3-2 (452 mg), Fr. 3-3 (172 mg), Fr. 3-4 (338 mg), Fr. 3-5 (1.4 g), Fr. 3-6 [= pseudo-ginsenoside F_{11} (**21**, 11 g)], Fr. 3-7 (142 mg), Fr. 3-8 (417 mg), Fr. 3-9 (387 mg), Fr. 3-10 (170 mg), Fr. 3-11 (561 mg), Fr. 3-12 (670 mg)]. Fraction 3-4 (338 mg) was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to give 24(*S*)-pseudo-ginsenoside-F_{11} (**22**, 11 mg) and Fr. 3-4-2 (310 mg). Fraction 3-4-2 (310 mg) was purified by HPLC [[1] column: Devsosil UG-5C-30, MeOH–H_2O (60 : 40, v/v) [2] MeCN : H_2O (25 : 75, v/v)] to give floralquinquenoside B (**2**, 5.0 mg), floralquinquenoside C (**3**, 17 mg), ginsenoside Rg_1 (**15**, 93 mg), ginsenoside Ia (**18**, 75 mg), and 24(*S*)-pseudo-ginsenoside F_{11} (**22**, 15 mg). Fraction 3-5 (440 mg) was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to give pseudo-ginsenoside F_{11} (**21**, 172 mg) and 24(*S*)-pseudo-ginsenoside F_{11} (**22**, 40 mg). Fraction 3-7 (180 mg) was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to give, ginsenoside-F_3 (**17**, 29 mg), ginsenoside Rg_2 (**16**, 41 mg), and pseudo-ginsenoside F_{11} (**21**, 46 mg). Fraction 3-8 (417 mg) was purified by HPLC [MeOH–H_2O (70 : 40, v/v)] to give ginsenoside Rg_2 (**16**, 97 mg). Fraction 3-9 (387 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give floralquinquenoside D (**4**, 11 mg) and ginsenoside Rg_2 (**16**, 70 mg). Fraction 3-10 (170 mg) was purified by HPLC [MeOH–H_2O (75 : 25, v/v)] to give floralquinquenoside D (**4**, 10 mg). Fraction 3-11 (561 mg) was purified by HPLC [MeOH–H_2O (80 : 20, v/v)] to give quinquenoside III (**11**, 328 mg) and pseudo-ginsenoside-RC_1 (**9**, 33 mg). Fraction 4 (2.3 g) was separated by reversed-phase silica gel column chromatography [70 g, MeOH : H_2O (50 : 50→60 : 40→70 : 30→80 : 20→90 : 10)→MeOH] to give 10 fractions [Fr. 4-1 (1.3 g), Fr. 4-2 (206 mg), Fr. 4-3 (235 mg), Fr. 4-4 (101 mg), Fr. 4-5 (303 mg), Fr. 4-6 (51 mg), Fr. 4-7 (40 mg), Fr. 4-8 (250 mg), Fr. 4-9 (21 mg), Fr. 4-10 (6.6 g)]. Fraction 4-2 (206 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give pseudo-ginsenoside F_{11} (**21**, 120 mg). Fraction 4-3 (235 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give ginsenoside Re (**14**, 52 mg). Fraction 4-5 (303 mg) was purified by HPLC [MeOH–H_2O (75 : 25, v/v)] to give quinquenoside III (**11**, 25 mg). Fraction 5 (15.5 g) was separated by reversed-phase silica gel column chromatography [46 g, MeOH : H_2O (50 : 50→60 : 40→70 : 30→80 : 20→90 : 10)→MeOH] to give 12 fractions [Fr. 5-1 (1.1 g), Fr. 5-2 (734 mg), Fr. 5-3 (345 mg), Fr. 5-4 [= pseudo-ginsenoside F_{11} (**21**, 4.3 g)], Fr. 5-5 (115 mg), Fr. 5-6 (450 mg), Fr. 5-7 (537 mg), Fr. 5-8 (502 mg), Fr. 5-9 (664 mg), Fr. 5-10 (3.94 g), Fr. 5-11 (407 mg), Fr. 5-12 (1.1 g)]. Fraction 5-2 (327 mg) was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give ginsenoside L_9 (**19**, 6.8 mg). Fraction 5-3 (345 mg) was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give pseudo-ginsenoside-RC_1 (**9**, 35 mg) and ginsenoside Re (**14**, 17 mg). Fraction 5-5

(115 mg) was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to give ginsenoside Re (**14**, 14 mg) and pseudo-ginsenoside F_{11} (**21**, 47 mg). Fraction 5-6 (450 mg) was purified by HPLC [MeOH–H_2O (65 : 35, v/v)] to give notoginsenoside-E (**13**, 145 mg) and ginsenoside I (**12**, 69 mg). Fraction 5-7 (370 mg) was purified by HPLC [MeOH–H_2O (65 : 35, v/v)] to give ginsenoside I (**12**, 37 mg) and notoginsenoside-E (**13**, 85 mg). Fraction 5-8 (313 mg) was purified by HPLC [MeOH–H_2O (70 : 30, v/v)] to give notoginsenoside-E (**13**, 9.5 mg). Fraction 5-9 (281 mg) was purified by HPLC [MeOH–H_2O (75 : 25, v/v)] to give pseudo-ginsenoside F_8 (**10**, 38.7 mg), ginsenoside Rs_1 (**8**, 43 mg), and ginsenoside Rd (**7**, 20 mg). Fraction 5-10 (414 mg) was purified by HPLC [MeOH–H_2O (80 : 20, v/v)] to give ginsenoside Rd (**7**, 211 mg). Fraction 5-11 (407 mg) was purified by HPLC [MeOH–H_2O (80 : 20, v/v)] to give ginsenoside Rb_3 (**6**, 63 mg) and ginsenoside Rd (**7**, 69 mg). Fraction 6 (20 g) was separated by reversed-phase silica gel column chromatography [58 g, MeOH : H_2O (40 : 60→50 : 50→60 : 40→70 : 30→80 : 20→90 : 10)→MeOH] to give 12 fractions [Fr. 6-1 (803 mg), Fr. 6-2 (184 mg), Fr. 6-3 (326 mg), Fr. 6-4 (245 mg), Fr. 6-5 (113 mg), Fr. 6-6 (143 mg), Fr. 6-7 (276 mg), Fr. 6-8 (1.2 g), Fr. 6-9 (3.6 g), Fr. 6-10 (12.4 g), Fr. 6-11 (341 mg), Fr. 6-12 (336 mg)]. Fraction 6-3 (106 mg) was purified by HPLC [MeOH–H_2O (35 : 65, v/v)] to give kaempferol 3-*O*-β-D-sophoroside-7-*O*-α-L-rhamnopyranoside (**24**, 61 mg). Fraction 6-5 (113 mg) was purified by HPLC [MeOH–H_2O (58 : 42, v/v)] to give floralquinquenoside E (**5**, 18 mg). Fraction 6-6 (143 mg) was purified by HPLC [MeOH–H_2O (58 : 42, v/v)] to give floralquinquenoside E (**5**, 11 mg) and ginsenoside Re (**14**, 42 mg). Fraction 6-10 (245 mg) was purified by HPLC [MeOH–H_2O (80 : 20, v/v)] to give ginsenoside Rb_3 (**6**, 60 mg). Fraction 6-11 (341 mg) was purified by HPLC [MeOH–H_2O (60 : 40, v/v)] to give ginsenoside Rb_3 (**6**, 62 mg) and ginsenoside Rd (**7**, 12 mg).

Floralquinquenoside A (**1**): A white amorphous powder; $[\alpha]_D^{23}$ +22.1° (c=0.65, MeOH); IR (KBr) ν_{max} 3415, 2934, 1655, 1076 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.84, 1.10, 1.29, 1.41, 1.57, 1.58, 1.64, 2.10 (3H each, all s, H_3-30, 19, 18, 21, 26, 27, 29, 28), 3.55 (1H, dd, J=4.5, 11.5 Hz, H-3), 3.93 (1H, m, H-12), 4.48 (1H, ddd, J=2.8, 10.5, 13.5 Hz, H-6), 5.08 (1H, d, J=7.9 Hz, H-1′), 6.08 (1H, d, J=15.9 Hz, H-24), 6.28 (1H, ddd, J=5.7, 9.0, 15.9 Hz, H-23); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 693 $[M+Na]^+$; negative-ion FAB-MS m/z 669 $[M-H]^-$; HR-FAB-MS: m/z 693.4186 (Calcd for $C_{36}H_{62}O_{11}Na$ $[M+Na]^+$, 693.4190).

Floralquinquenoside B (**2**): A white amorphous powder; $[\alpha]_D^{20}$ −16.9° (c=0.26, MeOH); IR (KBr) ν_{max} 3451, 2932, 1655, 1075 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.87, 0.90, 1.13, 1.30, 1.39, 1.86, 2.16 (3H each, all s, H_3-30, 19, 18, 21, 29, 26, 28), 3.42 (1H, dd, J=4.8, 11.0 Hz, H-3), 3.85 (1H, m, H-12), 4.66 (1H, m, H-6), 4.72 (1H, m, H-24), 5.03, 5.20 (each 1H, both s, H_2-26), 5.21 (1H, d, J=7.6 Hz, H-1′), 6.46 (1H, s like, H-1″); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 839 $[M+Na]^+$; negative-ion FAB-MS m/z 815 $[M-H]^-$; HR-FAB-MS: m/z 839.4773 (Calcd for $C_{42}H_{72}O_{15}Na$ $[M+Na]^+$, 839.4769).

Floralquinquenoside C (**3**): A white amorphous powder; $[\alpha]_D^{24}$ −13.3° (c=0.71, MeOH); IR (KBr) ν_{max} 3451, 2961, 1655, 1083 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.96, 1.02, 1.30, 1.39, 1.41, 1.58, 1.59, 2.16 (3H each, all s, H_3-30, 19, 18, 29, 21, 26, 27, 28), 3.50 (1H, dd, J=4.8, 11.9 Hz, H-3), 3.94 (1H, t, J=9.2 Hz, H-12), 4.75 (1H, m, H-6), 5.30 (1H, d, J=7.0 Hz, H-1′), 6.09 (1H, d, J=15.7 Hz, H-24), 6.29 (1H, ddd, J=5.5, 8.9, 15.7 Hz, H-23), 6.54 (1H, s like, H-1″); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 839 $[M+Na]^+$; negative-ion FAB-MS m/z 815 $[M-H]^-$, m/z 799 $[M-OH]^-$; HR-FAB-MS: m/z 839.4765 (Calcd for $C_{42}H_{72}O_{15}Na$ $[M+Na]^+$, 839.4769).

Floralquinquenoside D (**4**): A white amorphous powder; $[\alpha]_D^{25}$ +13.2° (c=0.57, MeOH); IR (KBr) ν_{max} 3469, 2961, 1655, 1076 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 600 MHz) δ: 0.82, 0.94, 0.95, 0.99, 1.30 1.54, 1.90 (3H each, all s, H_3-19, 30, 18, 29, 28, 21, 27), 3.38 (1H, dd, J=4.3, 11.6 Hz, H-3), 4.05 (1H, m, H-12), 4.96 (1H, dd, J=4.8, 7.9 Hz, H-24), 4.93 (1H, d, J=7.7 Hz, H-1′), 5.03, 5.21 (1H each, both br s, H_2-26), 5.15 (1H, d, J=7.9 Hz, H-1″); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 839 $[M+Na]^+$; negative-ion FAB-MS m/z 815 $[M-H]^-$; HR-FAB-MS: m/z 839.4774 (Calcd for $C_{42}H_{72}O_{15}Na$ $[M+Na]^+$, 839.4769).

Floralquinquenoside E (**5**): A white amorphous powder; $[\alpha]_D^{22}$ −1.8° (c=0.80, MeOH); IR (KBr) ν_{max} 3433, 2932, 1651, 1076 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.97, 1.19, 1.36, 1.37, 1.61, 1.62, 1.67, 2.12 (3H each, all s, H_3-19, 30, 29, 18, 27, 21, 26, 28), 3.47 (1H, dd, J=4.8, 11.4 Hz, H-3), 4.17 (1H, m, H-12), 4.68 (1H, m, H-6), 4.99 (1H, d, J=7.3 Hz, H-1‴), 5.11 (1H, d, J=7.8 Hz, H-1‴), 5.28 (1H, d, J=6.8 Hz, H-1′), 5.33 (1H, m, H-24), 6.51 (1H, br s, H-1″); ^{13}C-NMR data see Table 1; positive-ion FAB-MS m/z 1101 $[M+Na]^+$; negative-ion FAB-MS m/z 1077 $[M-H]^-$, m/z 931 $[M-C_6H_{11}O_4]^-$; HR-FAB-MS: m/z 1101.5828 (Calcd for $C_{53}H_{90}O_{22}Na$ $[M+Na]^+$, 1101.5821).

Acid Hydrolysis of Floralquinquenosides A (1), B (2), C (3), D (4), and E (5) A solution of **1**—**5** (1 mg each) in HCl 1.0 M (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, L-rhamnose, and D-xylose 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: 6.2 min (L-rhamnose, negative optical rotation), 7.1 min (D-xylose, positive optical rotation), 8.6 min (D-glucose, positive optical rotation), respectively.

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