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STRUCTURES OF DAMMARANE-TYPE TRITERPENE TRIGLYCOSIDES FROM THE FLOWER BUDS OF *PANAX GINSENG*[1]

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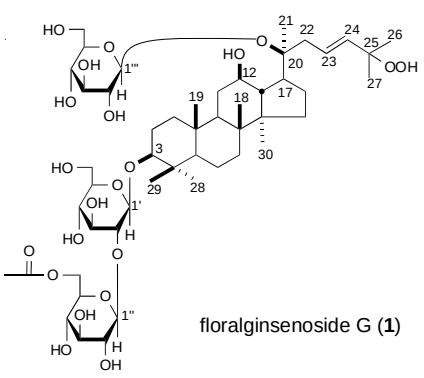
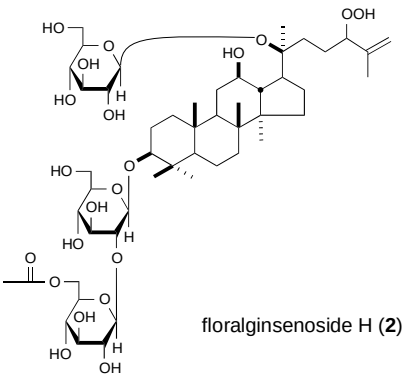
Abstract —New dammarane-type triterpene triglycosides, floralginsenosides G, H, I, J, K, La, and Lb, were isolated from the flower buds of *Panax ginseng* C. A. MEYER together with ten known dammarane-type triterpene oligoglycosides. The structures of new compounds were elucidated on the basis of chemical and physicochemical evidence.

During the course of our studies on bioactive constituents of medicinal flowers,[2,3] we have previously reported the isolation and structure elucidation of six dammarane-type triterpene diglycosides named floralginsenosides A, B, C, D, E, and F with a hydroperoxide group from the flower buds of *Panax* (*P.*) *ginseng* C. A. MEYER (Araliaceae) together with ten known dammarane-type triterpene oligoglycosides.[4] As a continuing study, we further isolated seven new dammarane-type triterpene triglycosides termed floralginsenosides G (**1**), H (**2**), I (**3**), J (**4**), K (**5**), La (**6**), and Lb (**7**) from ginseng flower. This paper deals with the isolation and structure elucidation of new dammarane-type triterpene triglycosides (**1**–**7**).[5]
The *n*-butanol-soluble portion, which was obtained by *n*-butanol–water partition of the methanolic extract from the flower buds of *P. ginseng* cultivated in Jilin province of China, was subjected to normal-phase silica gel column chromatography to give nine fractions as shown in the previous paper.[4] Fractions 3–8 were separated by reversed-phase silica gel column chromatography followed by HPLC to afford floralginsenosides G (**1**, 0.0028%, from the dried flower buds), H (**2**, 0.0017%), I (**3**, 0.0063%), J (**4**, 0.0047%), K (**5**, 0.0037%), La (**6**, 0.0036%), and Lb (**7**, 0.0016%) together with ginsenoside Re (**9**,[6] 2.69%), pseudo-ginsenoside-RS_1 (**10**,[6] 0.0036%), vina-ginsenoside-R4 (**11**,[7] 0.017%), notoginsenoside-E (**12**,[8] 0.090%), majoroside F_6 (**13**,[9] 0.0032%), ginsenoside I (**14**,[8] 0.057%), ginsenoside Rd (**15**,[10] 1.23%), ginsenoside Rc (**16**,[11] 0.19%), ginsenoside Rb_1 (**17**,[12] 0.36%), and ginsenoside Rb_2 (**18**,[11] 0.48%).



floralginsenoside G (**1**)



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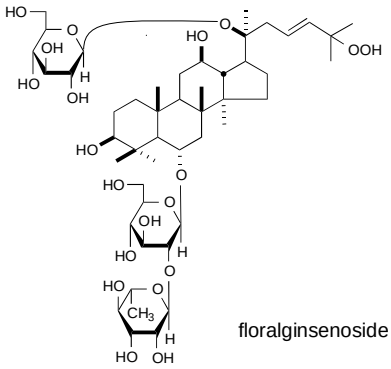
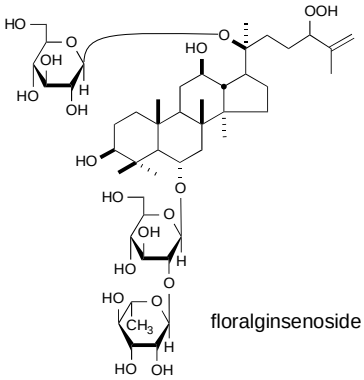
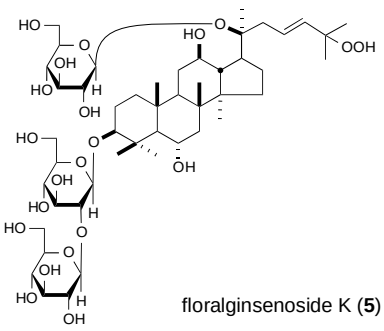


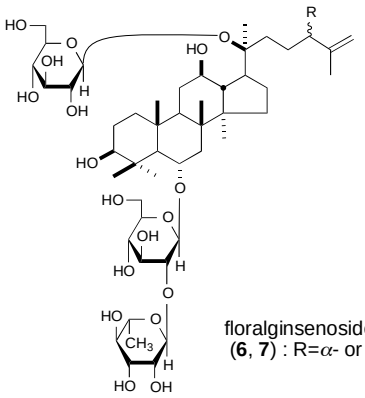
floralginsenoside I (**3**)



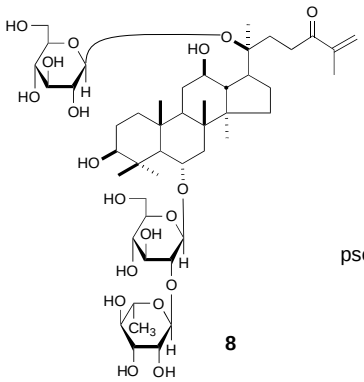
floralginsenoside J (**4**)



floralginsenoside K (**5**)



floralginsenosides La, Lb (**6**, **7**) : R=α- or β-OH



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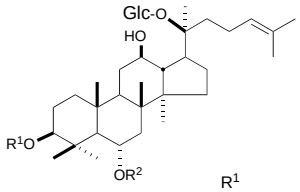
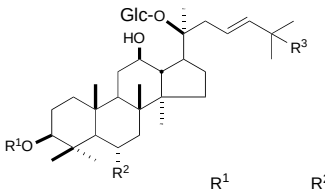
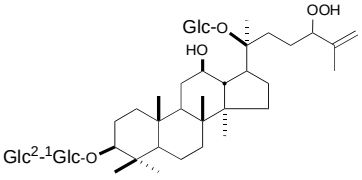


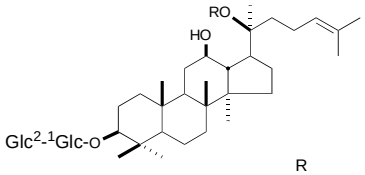
	R^1	R^2
ginsenoside Re (**9**):	H	$Glc^{2\text{-}1}Rha$
pseudo-ginsenoside-RS_1 (**10**):	H	$Glc^{2\text{-}1}Rha^{6\text{-}Ac}$
vina-ginsenoside-R4 (**11**):	$Glc^{2\text{-}1}Glc$	H



	R^1	R^2	R^3
notoginsenoside-E (**12**):	$Glc^{2\text{-}1}Glc$	H	OOH
majoroside F_6 (**13**):	Glc	$O\text{-}Glc^{2\text{-}1}Rha$	OH



ginsenoside I (**14**)



	R
ginsenoside Rd (**15**):	Glc
ginsenoside Rc (**16**):	$Glc^{6\text{-}1}Ara(f)$
ginsenoside Rb_1 (**17**):	$Glc^{6\text{-}1}Glc$
ginsenoside Rb_2 (**18**):	$Glc^{6\text{-}1}Ara(p)$

Glc: β-D-glucopyranosyl,
Ara(f): α-L-arabinofuranosyl,
Ara(p): α-L-arabinopyranosyl,
Rha: α-L-rhamnopyranosyl

Chart 1

Structures of Floralginsenosides

Floralginsenosides G (**1**) and H (**2**) were isolated as an amorphous powder with positive optical rotation (**1**: $[\alpha]_D^{22}$ +20.3°; **2**: $[\alpha]_D^{26}$ +25.5° in MeOH). Both compounds (**1**, **2**) were shown to possess a hydroperoxide residue by the positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[13,14] The IR spectra of **1** and **2** showed absorption bands (**1**: 1718, 1655, 1252 cm^{-1}; **2**: 1736, 1655, 1252 cm^{-1}) assignable to ester and olefin functions in addition to strong absorption bands (**1**: 3415, 1078 cm^{-1}; **2**: 3415, 1078 cm^{-1}) suggestive of a glycoside structure. The negative-ion FAB-MS spectra of **1** and **2** exhibited a common pseudomolecular ion peak at *m/z* 1019 $(M\text{-}H)^-$ in addition to fragment ion peaks at

m/z 1003 $(M\text{-}OH)^-$, *m/z* 977 $(M\text{-}C_2H_3O)^-$, *m/z* 961 $(M\text{-}C_2H_3O_2)^-$, and *m/z* 839 $(M\text{-}C_6H_{11}O_5)^-$, while the positive-ion FAB-MS spectra of **1** and **2** showed a common pseudomolecular ion peak at *m/z* 1043 $(M+Na)^+$. High-resolution MS analysis of the pseudomolecular ion peak $(M+Na)^+$ revealed the common molecular formula of **1** and **2** to be $C_{50}H_{84}H_{21}$. Acid hydrolysis of **1** and **2** with 1.0 M aqueous hydrochloric acid (HCl) liberated D-glucose, which was identified by HPLC analysis using an optical rotation detector.[15] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra of **1** and **2**, which were assigned by various NMR experiments,[16] showed signals due to an aglycon part [**1**: δ 0.90, 0.91, 1.03, 1.15, 1.34, 1.58, 1.59, 1.60 (3H each, all s, 30, 19, 18, 29, 28, 26, 27, 21-H_3), 3.29 (1H, dd, *J*=4.3, 11.7 Hz, 3-H), 4.00 (1H, m, 12-H), 6.03 (1H, d, *J*=15.9 Hz, 24-H), 6.20 (1H, ddd, *J*=6.2, 8.6, 15.9 Hz, 23-H); **2**: δ 0.87, 0.94, 0.99, 1.13, 1.35, 1.61, 1.92 (3H each, all s, 19, 30, 18, 29, 28, 21, 27-H_3), 3.28 (1H, dd, *J*=4.3, 11.7 Hz, 3-H), 4.10 (1H, m, 12-H), 4.74 (1H, dd-like, *J*=*ca*. 5, 8 Hz, 24-H), 5.07, 5.23 (each 1H, both br s, 26-H_2)], an acetyl group [**1**: δ 2.05 (3H, s), 4.78 (1H, dd, *J*=4.9, 11.7 Hz), 4.93 (1H, dd, *J*=2.2, 11.7 Hz) (6"-H_2); **2**: δ 2.04 (3H, s), 4.77 (1H, dd, *J*=4.9, 11.9 Hz), 4.92 (1H, br d, *J*=*ca*. 12 Hz) (6"-H_2)], and three β-D-glucopyranosyl moieties [**1**: δ 4.90 (1H, d, *J*=7.6 Hz, 1'-H), 5.30 (1H, d, *J*=7.6 Hz, 1"-H), 5.20 (1H, d, *J*=7.6 Hz, 1'"-H); **2**: δ 4.89 (1H, d, *J*=7.8 Hz, 1'-H), 5.29 (1H, d, *J*=7.8 Hz, 1"-H), 5.15 (1H, d, *J*=8.1 Hz, 1'"-H)]. The proton and carbon signals in the ^{1}H- and ^{13}C-NMR spectra of **1** and **2** were superimposable on those of notoginsenoside-E (**12**)[8] and ginsenoside I (**14**),[8] respectively, expect for the signals due to the 6"-acetyl group of the terminal glucopyranosyl moiety. The position of the acetyl group in **1** and **2** was clarified by a HMBC experiment, which showed long-range correlation between the 6"-proton and acetyl carbonyl carbon. Furthermore, respective comparison of the ^{13}C-NMR data of **1** and **2** with those of **12** and **14** indicated the presence of an acetylation shift at the 6"-position of **1** and **2**. Finally, alkaline hydrolysis of **1** and **2** with 5% aqueous KOH–50% aqueous 1,4-dioxane (1:1) yielded **12** and **14**, respectively. On the basis of this evidence and detail examination of ^{1}H-^{1}H COSY and HMBC experiments (Figure 1), the structures of floralginsenosides G (**1**) and H (**2**)[17] were determined as shown.

Floralginsenosides I (**3**) and J (**4**) were also isolated as an amorphous powder with negative and positive optical rotation (**3**: $[\alpha]_D^{24}$ -4.7°; **4**: $[\alpha]_D^{26}$ +2.8° in MeOH) and showed positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[13,14] The IR spectra of **3** and **4** showed absorption bands assignable to hydroxyl and olefin functions (**3**: 3547, 1655 cm^{-1}; **4**: 3433, 1655 cm^{-1}). The common molecular formula $C_{48}H_{82}O_{20}$ of **3** and **4** were determined from the quasimolecular ion peaks [*m/z* 977 $(M-H)^-$ and *m/z* 1001 $(M+Na)^+$] in the negative-ion and positive-ion FAB-MS and by high-resolution MS measurement. Their negative-ion FAB-MS spectrum showed fragment ion peaks at *m/z* 961 $(M\text{-}OH)^-$ and *m/z* 797 $(M\text{-}OH\text{-}C_6H_{11}O_5)^-$. The acid hydrolysis of **3** and **4** liberated D-glucose and L-rhamnose, which were identified by HPLC analysis using an optical rotation detection.[15] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[16] of **3** and **4** showed signals due to an aglycon part [**3**: δ 0.91, 1.05, 1.25, 1.38, 1.55, 1.58, 1.59, 2.08 (3H each, all s, 30, 19, 18, 29, 21, 26, 27, 28-H_3), 3.46 (1H, dd, *J*=4.9, 11.7 Hz, 3-H), 3.96 (1H, m, 12-H), 4.96 (1H, br dd, *J*=*ca*. 4, 11 Hz, 6-H), 6.07 (1H, d, *J*=15.8 Hz, 24-H), 6.22 (1H, ddd, *J*=6.6, 8.1, 15.8 Hz, 23-H); **4**: δ 0.79 1.00, 1.17, 1.35, 1.58, 1.86, 2.07 (3H each, all s, 30, 19, 18, 29, 21, 27, 28-H_3), 3.45 (1H, dd, *J*=4.9, 11.5 Hz, 3-H), 4.08 (1H, m, 12-H), 4.32 (1H, m, 6-H), 4.69 (1H, dd-like, *J*=*ca*. 5, 8 Hz, 24-H), 5.01, 5.20 (each 1H, both br s, 26-H_2)], two β-D-glucopyranosyl moieties [**3**: δ

5.25 (1H, d, *J*=6.9 Hz, 1'-H), 5.18 (1H, d, *J*=7.8 Hz, 1'"-H); **4**: δ 5.24 (1H, d-like, *J*=*ca*. 7 Hz, 1'-H), 5.18 (1H, d, *J*=7.8 Hz, 1'"-H)], and an α-L-rhamnopyranosyl moiety [**3**: δ 6.44 (1H, br s, 1"-H); **4**: δ 6.42 (1H, br s, 1"-H)]. The proton and carbon signals due to the tetracarbocyclic moieties (1-C–20-C, 28-C–30-C) including the 6- and 20-*O*-glycosidic parts in the ^{1}H- and ^{13}C-NMR spectra of **3** and **4** were superimposable on those of ginsenoside Re,[6] whereas the signals due to the side chain parts (20-C–27-C) of **3** and **4** were similar to those of **1** and **2**, respectively. As shown in Figure 1, the structures of **3** and **4** were clarified by means of ^{1}H-^{1}H COSY and HMBC experiments. Namely, the ^{1}H-^{1}H COSY experiments on **3** and **4** indicated the presence of partial structures written in bold lines and the connectivities of the quaternary carbon and positions of the glycoside linkages in **3** and **4** were elucidated by HMBC experiment, which showed long-range correlations between the following protons and carbons; **3**, **4**: 5-H and 6-C; 6-H and 6-C; 11-H and 12-C; 13-H and 13-C; 18-H and 7, 8, 14-C; 19-H and 5, 10-C; 28-H and 3, 4, 5, 29-C; 29-H and 3, 4, 5, 28-C; 30-H and 8, 13, 14-C; 1'-H and 6-C; 1"-H and 2'-C; 1"'-H and 20-C; **3**: 22-H and 20-C; 24-H and 22, 26, 27-C; 26-H and 24, 25, 27-C; 27-H and 24, 25, 26-C; **4**: 26-H and 24, 27-C; 27-H and 24, 25, 26-C. Treatment of **4** with pyridine yielded the enone derivative (**8**), whose molecular formula $C_{48}H_{80}O_{19}$ was determined from the negative-ion and positive-ion FAB-MS [*m/z* 959 $(M-H)^-$, *m/z* 983 $(M+Na)^+$] and by high-resolution MS measurement. Although the proton and carbon signals due to the tetracarbocyclic part including the 6- and 20-glycoside moieties in the ^{1}H- and ^{13}C-NMR (Table 1) spectra[16] of **8** was superimposable on those of **4**, while the signals due to the side chain part of **8** resembled those of notoginsenoside-B[18] and vina-ginsenoside R_{25}.[19] On the basis of those findings and the alkaline degradation mechanisms of the hydroperoxide group,[20] the structure of **8** was clarified. Consequently, the structures of floralginsenosides I (**3**) and J (**4**)[17] were characterized as shown.

Floralginsenoside K (**5**), obtained as an amorphous powder with positive optical rotation ($[\alpha]_D^{26}$ +13.5° in MeOH), showed the positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent.[13,14] In the IR spectrum of **5**, absorption bands were observed at 3433 and 1655 cm^{-1} assignable to hydroxyl and olefin functions. The molecular formula $C_{48}H_{82}O_{21}$ was determined from the pseudo molecular ion peaks [*m/z* 993 $(M-H)^-$ and *m/z* 1017 $(M+Na)^+$] in the negative-ion and positive-ion FAB-MS and by high-resolution MS measurement. The acid hydrolysis of **5** liberated D-glucose.[15] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[16] of **5** showed signals due to an aglycon part [δ 0.94, 0.99, 1.13, 1.52, 1.57, 1.58, 1.59, 2.00 (3H each, all s, 19, 30, 18, 29, 27, 26, 21, 28-H_3), 3.38 (1H, dd, *J*=4.6, 11.6 Hz, 3-H), 4.00 (1H, m, 12-H), 4.33 (1H, m, 6-H), 6.03 (1H, d, *J*=16.0 Hz, 24-H), 6.21 (1H, ddd, *J*=6.5, 8.1, 15.5 Hz, 23-H)] together with three β-D-glucopyranosyl moieties [δ 4.96 (1H, d, *J*=7.4 Hz, 1'-H), 5.20 (1H, d, *J*=7.7 Hz, 1"'-H), 5.38 (1H, d, *J*=7.6 Hz, 1"-H)]. The proton and carbon signals due to the tetracarbocyclic part in the ^{1}H- and ^{13}C-NMR spectra of **5** were similar to those of vina-ginsenoside-R4,[7] whereas the signals due to the side chain part resembled those of **1** and **3**. The ^{1}H-^{1}H COSY experiment on **5** indicated the presence of partial structures written in bold lines and the HMBC experiment showed long-range correlations as shown in Figure 1. This evidence led us to formulate the structure of floralginsenoside K (**5**) as shown.

Floralginsenosides La (**6**) and Lb (**7**), obtained as an amorphous powder (**6**: $[\alpha]_D^{27}$ +2.3°; **7**: $[\alpha]_D^{26}$ -7.5° in MeOH), showed absorption bands due to hydroxyl and olefin function in the IR spectra (**6**: 3415 and

1655 cm^{-1}; **7**: 3451 and 1655 cm^{-1}). The common molecular formula $C_{48}H_{82}O_{19}$ was determined from the negative-ion and positive-ion FAB-MS data [*m/z* 961 $(M-H)^-$ and *m/z* 985 $(M+Na)^+$] and by high-resolution MS measurement. The acid hydrolysis of **6** and **7** liberated D-glucose and L-rhamnose.[15] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[16] of **6** and **7** showed signals due to an aglycon part [**6**: δ 0.94, 0.97, 1.18, 1.35, 1.58, 1.88, 2.06 (3H each, all s, 30, 19, 18, 29, 21, 27, 28-H_3), 3.44 (1H, dd, *J*=4.6, 11.5 Hz, 3-H), 4.08 (1H, m, 12-H), 4.40 (1H, m, 24-H), 4.66 (1H, dd, *J*=3.2, 10.4 Hz, 6-H), 4.89, 5.25 (each 1H, both br s, 26-H_2); **7**: δ 0.83, 0.90, 1.11, 1.30, 1.50, 1.88, 2.05 (3H each, all s, 30, 19, 18, 29, 21, 27, 28-H_3), 3.39 (1H, dd, *J*=4.9, 11.7 Hz, 3-H), 3.92 (1H, m, 12-H), 4.32 (1H, m, 24-H), 4.62 (1H, dd, *J*=3.4, 10.4 Hz, 6-H), 4.86, 5.22 (each 1H, both s, 26-H_2)] together with two β-D-glucopyranosyl moieties [**6**: δ 5.16 (1H, d, *J*=7.8 Hz, 1"'-H), 5.22 (1H, d, *J*=6.6 Hz, 1'-H); **7**: δ 5.15 (1H, d, *J*=7.6 Hz, 1"'-H), 5.20 (1H, d, *J*=6.9 Hz, 1'-H)] and an α-L-rhamnopyranosyl moiety [**6**: δ 6.41 (1H, s, 1"-H); **7**: δ 6.40 (1H, s, 1"-H)]. The proton and carbon signals due to the tetracarbocyclic moiety including the 6- and 20-*O*-glucoside parts in the ^{1}H- and ^{13}C-NMR spectra of **6** and **7** were similar to those of **3**, **4**, and **8**, while the signals due to the side chain parts of **6** and **7** were superimposable on those of majoroside F_1 (24*R*)[21] and majoroside F_2 (24*S*),[21] respectively.[22] On the basis of this evidence and the ^{1}H-^{1}H COSY and HMBC experiments (Figure 1), **6** and **7** were found to be stereoisomeric at the 24-position with each other. Finally, reduction of the enone **8** with sodium borohydride ($NaBH_4$) provided **6** and **7** in a 2:1 ratio. Consequently, the structures of floralginsenosides La (**6**)[17] and Lb (**7**)[17] were elucidated to be as shown.

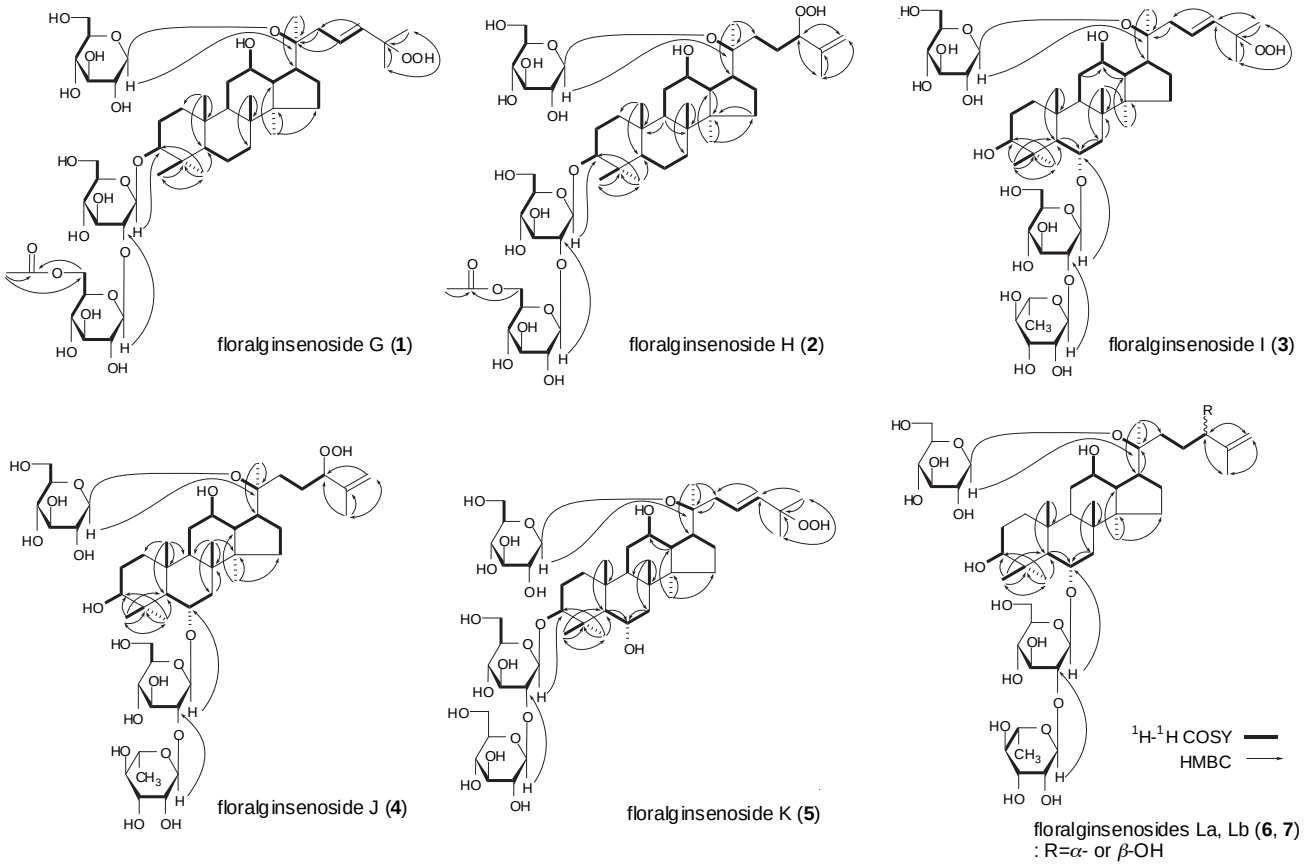


Figure 1. Significant ^{1}H-^{1}H COSY and HMBC Correlations for Floralginsenosides (**1**—**7**)

Table 1. ^{13}C-NMR Data for Floralginsenosides G (**1**), H (**2**), I (**3**), J (**4**), K (**5**), La (**6**), and Lb (**7**) and **8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
C-1	39.3	39.3	39.5	39.5	39.3	39.5	39.2	39.2	C-1'	105.0	104.9	101.8	101.8	105.3	101.8	101.7	101.7
C-2	26.9	26.4	27.8	27.8	26.8	27.8	27.6	27.5	C-2'	84.3	84.3	79.6	79.4	83.6	79.3	79.3	79.2
C-3	89.3	89.3	78.8	78.8	90.0	78.5	78.2	78.4	C-3'	78.1	78.1	78.0	78.2	78.1	78.8	78.6	78.3
C-4	39.9	39.8	40.3	40.0	40.7	40.0	39.8	39.8	C-4'	71.6	71.8	72.9	72.8	72.0	72.7	72.4	72.4
C-5	56.6	56.6	60.9	61.0	61.9	60.9	60.7	60.6	C-5'	78.0	78.0	78.2	78.3	78.5	78.2	78.4	78.1
C-6	18.6	18.6	74.7	74.8	67.6	74.7	74.4	74.3	C-6'	63.0	63.0	63.1	63.3	63.0	63.2	62.9	62.7
C-7	35.2	35.2	46.0	45.9	47.6	45.9	45.8	45.8	C-1''	106.2	106.1	101.9	101.9	106.1	101.8	101.8	101.7
C-8	40.2	40.1	41.3	41.3	41.3	41.2	41.0	41.0	C-2''	76.8	76.8	72.4	72.5	77.0	72.3	72.3	72.1
C-9	50.2	50.3	49.7	49.6	49.8	49.6	49.3	49.4	C-3''	78.9	79.1	72.3	72.4	78.1	72.3	72.1	72.2
C-10	37.1	37.0	39.8	39.8	38.9	39.7	39.5	39.5	C-4''	71.2	71.1	74.2	74.3	71.8	74.2	74.0	74.0
C-11	31.1	30.9	31.1	31.2	31.1	31.1	30.9	30.7	C-5''	75.5	75.5	69.5	69.5	78.2	69.5	69.3	69.3
C-12	70.5	70.3	70.3	70.4	70.5	70.4	70.1	70.1	C-6''	64.8	64.8	18.7	18.8	63.1	18.7	18.6	18.6
C-13	49.7	49.7	49.0	49.3	49.4	49.0	48.8	48.9	C-1'''	98.4	98.3	98.1	98.4	98.4	98.3	98.2	97.9
C-14	51.6	51.5	51.6	51.6	51.5	51.5	51.3	51.3	C-2'''	75.3	75.2	75.2	75.4	75.3	75.2	75.2	74.9
C-15	30.7	31.2	30.7	30.8	30.7	30.7	30.7	30.6	C-3'''	78.2	78.2	79.4	78.8	78.9	79.0	78.7	79.1
C-16	26.5	26.8	26.8	26.6	26.5	26.7	26.7	26.4	C-4'''	71.8	71.6	71.7	71.8	71.8	71.7	71.5	71.4
C-17	52.3	51.9	52.2	52.3	52.3	52.1	52.2	52.0	C-5'''	78.6	78.6	78.5	78.5	78.1	78.2	78.2	78.1
C-18	16.1	16.0	17.3	17.4	17.6	17.3	17.0	17.0	C-6'''	63.1	63.1	63.1	63.1	63.0	63.1	63.1	62.8
C-19	17.2	16.3	17.3	17.6	17.3	17.5	17.4	17.1	$\underline{C}H_3CO$	20.9	20.9						
C-20	83.2	83.2	83.2	83.1	83.2	83.5	83.0	82.9	$CH_3\underline{C}O$	171.0	171.0						
C-21	23.3	22.6	22.6	23.3	23.3	22.8	22.6	21.8									
C-22	39.9	32.9	32.9	39.5	39.8	32.4	32.5	32.6									
C-23	126.7	22.6	26.7	126.7	126.6	30.3	30.9	29.8									
C-24	138.1	90.0	90.0	138.2	138.1	75.7	76.1	202.3									
C-25	81.3	145.9	146.1	81.4	81.3	*	*	144.2									
C-26	25.3	113.5	113.2	25.3	25.4	109.9	110.1	123.7									
C-27	25.5	17.6	17.8	25.5	25.3	18.5	18.2	17.6									
C-28	28.1	28.1	32.2	32.2	31.5	32.2	32.0	32.0									
C-29	16.5	16.5	17.6	17.6	16.8	17.5	17.5	17.3									
C-30	16.4	17.4	17.1	17.2	17.4	17.3	16.6	17.5									

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

*: overlapped in solvent

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.

Isolation of Floralginsenosides (1–7)

The dried flower buds of *Panax ginseng* (1.0 kg), which was cultivated in Jilin province of China at 2004 and presented from Koshiro Co. Ltd. (Osaka), 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 [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 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 3-11 (0.28 g) was purified by prep. HPLC [MeOH–H_2O (65:35, v/v)] to give fraction 3-11-5 (0.02 g), and floralginsenoside G (**1**, 11 mg, 0.0017%). Fraction 3-11-5 (0.02 g) was further separated by prep. HPLC [MeOH–H_2O (65:35, v/v)] to give floralginsenosides H (**2**, 8 mg, 0.0012%). Fraction 3-12 (0.15 g) was separated by prep. HPLC [MeOH–H_2O (70:30, v/v)] to give **2** (11 mg, 0.0016%). Fraction 4 (13.6 g) was separated by reversed-phase silica gel column chromatography [400 g, MeOH–H_2O (30:70–40:60–50:50–60:40–70:30–80:20–90:10, v/v)–MeOH] to furnish ten fractions [Fr. 4-

1 (0.34 g), Fr. 4-2 (0.42 g), Fr. 4-3 (0.31 g), Fr. 4-4 (0.16 g), Fr. 4-5 (1.16 g), Fr. 4-6 (0.08 g), Fr. 4-7 (0.19 g), Fr. 4-8 (1.63 g), Fr. 4-9 (0.58 g), Fr. 4-10 (6.61 g)]. Fraction 4-4 (0.31 g) was purified by prep. HPLC [MeOH–H_2O (40:60, v/v)] to give floralginsenosides I (**3**, 13 mg, 0.0020%), and J (**4**, 17 mg, 0.0024%). Fraction 4-5 (0.23 g) was purified by prep. HPLC [MeOH–H_2O (55:45, v/v)] to give ginsenoside Re (**9**, 56 mg, 0.041 %). Fraction 4-7 (0.19 g) was purified by prep. HPLC [MeOH–H_2O (60:40, v/v)] to give pseudo-ginsenoside-RS_1 (**10**, 25 mg, 0.0036%). Fraction 4-8 (0.19 g) was separated by prep. HPLC [MeOH–H_2O (65:35, v/v)] to give notoginsenoside-E (**12**, 32 mg, 0.039%), ginsenoside I (**14**, 9 mg, 0.010%). Fraction 4-9 (0.14 g) was purified by prep. HPLC [MeOH–H_2O (65:35, v/v)] to give **12** (26 mg, 0.0016%), **14 (**13 mg, 0.0081%**)**. Fraction 4-10 (0.20 g) was purified by prep. HPLC [MeOH–H_2O (75:25, v/v)] to give ginsenoside Rd (**15**, 115 mg, 0.57%). Fraction 5 (55.0 g) was separated by reversed-phase silica gel column chromatography [400 g, MeOH–H_2O (40:60–50:50–60:40–70:30–80:20–90:10, v/v)–MeOH] to furnish ten fractions [Fr. 5-1 (5.30 g), Fr. 5-2 (3.31 g), Fr. 5-3 (1.15 g), Fr. 5-4 (32.3 g), Fr. 5-5 (0.38 g), Fr. 5-6 (0.68 g), Fr. 5-7 (1.10 g), Fr. 5-8 (0.17 g), Fr. 5-9 (0.71 g), Fr. 5-10 (10.7 g)]. Fraction 5-3 (0.13 g) was purified by prep. HPLC [MeOH–H_2O (50:50, v/v)] to give **9** (84 mg, 0.10%). Fraction 5-4 (0.10 g) was purified by prep. HPLC [MeOH–H_2O (50:50, v/v)] to give **9** (53 mg, 2.4%). Fraction 5-5 (0.17 g) was purified by prep. HPLC [MeOH–H_2O (60:40, v/v)] to give floralginsenoside K (**5**, 11 mg, 0.0037%), **9** (13 mg, 0.0043 %), and vina-ginsenoside-R4 (**11**, 48 mg, 0.017%). Fraction 5-6 (0.16 g) was separated by prep. HPLC [MeOH–H_2O (60:40, v/v)] to give **12** (48 mg, 0.029%), and **14** (20 mg, 0.012**%)**. Fraction 5-7 (0.13 g) was purified by prep. HPLC [MeOH–H_2O (65:35, v/v)] to give **14** (19 mg, 0.024%). Fraction 5-8 (0.17 g) was purified by prep. HPLC [MeOH–H_2O (70:30, v/v)] to give **12** (35 mg, 0.0051%), **14** (14 mg, 0.0020%) and ginsenoside Rc (**16**, 19 mg, 0.0028%). Fraction 5-9 (0.15 g) was purified by prep. HPLC [MeOH–H_2O (75:25, v/v)] to give **16** (65 mg, 0.045%), ginsenoside Rb_2 (**18**, 27 mg, 0.019%), and **15** (15 mg, 0.010%). Fraction 6 (15.9 g) was separated by reversed-phase silica gel column chromatography [500 g, MeOH–H_2O (40:60–50:50–60:40–70:30–80:20–90:10, v/v)–MeOH] to furnish twelve fractions [Fr. 6-1 (0.08 g), Fr. 6-2 (1.14 g), Fr. 6-3 (0.14 g), Fr. 6-4 (0.65 g), Fr. 6-5 (0.39 g), Fr. 6-6 (0.20 g), Fr. 6-7 (0.67 g), Fr. 6-8 (1.42 g), Fr. 6-9 (0.49 g), Fr. 6-10 (9.90 g), Fr. 6-11 (1.63 g), Fr. 6-12 (0.68 g)]. Fraction 6-5 (0.39 g) was purified by prep. HPLC [MeOH–H_2O (40:60, v/v)] to give **3** (15 mg, 0.0022%). Fraction 6-7 (0.17 g) was purified by prep. HPLC [MeOH–H_2O (55:45, v/v)] to give **9** (58 mg, 0.0033 %). Fraction 6-10 (0.47 g) was purified by prep. HPLC [MeOH–H_2O (75:25, v/v)] to give Fr. 6-10-1 (0.11 g), and **18** (84 mg, 0.26%). Fraction 6-10-1 was further separated by prep. HPLC [MeCN–H_2O (33:67, v/v)] to give ginsenosides Rb_1 (**17**, 19 mg, 0.060%), **16** (49 mg, 0.15%) and **18** (23 mg, 0.070%). Fraction 6-11 (0.32 g) was purified by prep. HPLC [MeOH–H_2O (75:25, v/v)] to give Ft. 6-11-1 (93 mg), and **15** (32 mg, 0.049%). Fraction 6-11-1 (0.09 g) was separated by prep. HPLC [MeCN–H_2O (33:67, v/v)] to give **18** (55 mg, 0.085%). Fraction 7 (12.1 g) was separated by reversed-phase silica gel column chromatography [400 g, MeOH–H_2O (40:60–50:50–60:40–70:30, v/v)–MeOH] to furnish twelve fractions [Fr. 7-1 (0.70 g), Fr. 7-2 (0.12 g), Fr. 7-3 (0.17 g), Fr. 7-4 (0.19 g), Fr. 7-5 (0.19 g), Fr. 7-6 (0.60 g), Fr. 7-7 (1.14 g), Fr. 7-8 (0.53 g), Fr. 7-9 (1.43 g), Fr. 7-10 (5.15 g), Fr. 7-11 (0.19 g), Fr. 7-12 (0.48 g)]. Fraction 7-3 (0.17 g) was purified by prep. HPLC [MeCN–H_2O (1:5, v/v)] to give floralginsenosides La (**6**, 26 mg, 0.0038%), **4** (16

mg, 0.0023%) and Lb (**7**, 10 mg, 0.0016%). Fraction 7-4 (0.19 g) was purified by prep. HPLC [MeCN–H_2O (1:5, v/v)] to give majoroside F_6 (**13**, 22 mg, 0.0032%), and **3** (15 mg, 0.0021%). Fraction 7-9 (0.35 g) was purified by prep. HPLC [MeCN–H_2O (33:67, v/v)] to give **17** (221 mg, 0.30%), and **18** (49 mg, 0.067%). Fraction 7-11 (0.19 g) was purified by prep. HPLC [MeOH–H_2O (80:20, v/v)] to give **15** (33 mg, 0.0048%). Fraction 8 (5.9 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 twelve fractions [Fr. 8-1 (0.99 g), Fr. 8-2 (0.19 g), Fr. 8-3 (0.04 g), Fr. 8-4 (0.04 g), Fr. 8-5 (0.11 g), Fr. 8-6 (0.02 g), Fr. 8-7 (0.03 g), Fr. 8-8 (0.11 g), Fr. 8-9 (0.92 g), Fr. 8-10 (0.67 g), Fr. 8-11 (0.64 g), Fr. 8-12 (1.10 g)]. Fraction 8-10 (0.17 g) was purified by prep. HPLC [MeOH–H_2O (50:50, v/v)] to give **9** (54 mg, 0.029%).

Floralginsenoside G **(1):** a white amorphous powder, $[\alpha]_D^{22}$ +20.3° (*c*=0.14, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{50}H_{84}O_{21}Na$ $(M+Na)^+$: 1043.5403. Found: 1043.5406. IR (KBr) 3415, 2941, 1718, 1655, 1252, 1078 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 600 MHz) δ 0.90, 0.91, 1.03, 1.15, 1.34, 1.58, 1.59, 1.60 (3H each, all s, 30, 19, 18, 29, 28, 26, 27, 21-H_3), 3.29 (1H, dd, *J*=4.3, 11.7 Hz, 3-H), 4.00 (1H, m, 12-H), 4.90 (1H, d, *J*=7.6 Hz, 1'-H), 5.20 (1H, d, *J*=7.6 Hz, 1"'-H), 5.30 (1H, d, *J*=7.6 Hz, 1"-H), 6.03 (1H, d, *J*=15.9 Hz, 24-H), 6.20 (1H, ddd, *J*=6.2, 8.6, 15.9 Hz, 23-H). ^{13}C-NMR (pyridine-d_5, 150 MHz) δc: give in Table 1. Positive-ion FAB-MS *m/z* 1043 $(M+Na)^+$. Negative-ion FAB-MS *m/z* 1019 $(M-H)^-$, 1003 $(M-OH)^-$, 977 $(M-C_2H_3O)^-$, 961 $(M-C_2H_3O_2)^-$, 839 $(M-OH-C_6H_{11}O_5)^-$.

Floralginsenoside H **(2):** a white amorphous powder, $[\alpha]_D^{26}$ +25.5° (*c*=0.52, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{50}H_{84}O_{21}Na$ $(M+Na)^+$: 1043.5403. Found: 1043.5406. IR (KBr) 3415, 2945, 1736, 1655, 1252, 1078 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ 0.87, 0.94, 0.99, 1.13, 1.35, 1.61, 1.92 (3H each, all s, 19, 30, 18, 29, 28, 21, 27-H_3), 3.28 (1H, dd, *J*=4.3, 11.7 Hz, 3-H), 4.10 (1H, m, 12-H), 4.74 (1H, dd-like, *J*=*ca*. 5, 8 Hz, 24-H), 4.89 (1H, d, *J*=7.8 Hz, 1'-H), 5.15 (1H, d, *J*=8.1 Hz, 1"'-H), 5.07, 5.23 (each 1H, both br s, 26-H_2), 5.29 (1H, d, *J*=7.8 Hz, 1-H"). ^{13}C-NMR (pyridine-d_5, 125 MHz) δc: give in Table 1. Positive-ion FAB-MS *m/z* 1043 $(M+Na)^+$. Negative-ion FAB-MS *m/z* 1019 $(M-H)^-$, 1003 $(M-OH)^-$, 977 $(M-C_2H_3O)^-$, 961 $(M-C_2H_3O_2)^-$, 839 $(M-OH-C_6H_{11}O_5)$.

Floralginsenoside I (**3**): a white amorphous powder, $[\alpha]_D^{24}$ +4.7° (*c*=0.55, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{48}H_{82}O_{20}Na$ $(M+Na)^+$: 1001.5297. Found: 1001.5305. IR (KBr) 3547, 2961, 1655, 1076 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ 0.91, 1.05, 1.25, 1.38, 1.55, 1.58, 1.59, 2.08 (3H each, all s, 30, 19, 18, 29, 21, 26, 27, 28-H_3), 3.46 (1H, dd, *J*=4.9, 11.7 Hz, 3-H), 3.96 (1H, m, 12-H), 4.96 (1H, br dd, *J*=*ca*. 4, 11 Hz, 6-H), 5.18 (1H, d, *J*=7.8 Hz, 1"'-H), 5.25 (1H, d, *J*=6.9, 1'-H), 6.07 (1H, d, *J*=15.8 Hz, 24-H), 6.22 (1H, ddd, *J*=6.6, 8.1, 15.8 Hz, 23-H), 6.44 (1H, s, 1"-H). ^{13}C-NMR (pyridine-d_5, 125 MHz) δc: give in Table 1. Positive-ion FAB-MS *m/z* 1001 $(M+Na)^+$. Negative-ion FAB-MS *m/z* 977 $(M-H)^-$, 961 $(M-OH)^-$, 797 $(M-OH-C_6H_{11}O_5)^-$.

Floralginsenoside J (**4**): a white amorphous powder, $[\alpha]_D^{26}$ -2.8° (*c*=0.63, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{48}H_{82}O_{20}Na$ $(M+Na)^+$: 1001.5297. Found: 1001.5294. IR (KBr) 3433, 2934, 1655, 1076 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ 0.79 1.00, 1.17, 1.35, 1.58, 1.86, 2.07 (3H each, all s, 30, 19, 18, 29, 21, 27, 28-H_3), 3.45 (1H, dd, *J*=4.9, 11.5 Hz, 3-H), 4.08 (1H, m, 12-H), 4.32

(1H, m, 6-H), 4.69 (1H, dd-like, *J*=*ca*. 5, 8 Hz, 24-H), 5.01, 5.20 (each 1H, both br s, 26-H_2), 5.18 (1H, d, *J*=7.8 Hz, 1"'-H), 5.24 (1H, dd-like, *J*=*ca*. 7 Hz, 1'-H), 6.42 (1H, br s, 1"-H); ^{13}C-NMR (pyridine-d_5, 125 MHz) δc: give in Table 1. Positive-ion FAB-MS *m/z* 1001 $(M+Na)^+$. Negative-ion FAB-MS *m/z* 977 $(M-H)^-$, 961 $(M-OH)^-$, 781 $(M-OOH-C_6H_{11}O_5)^-$.

Floralginsenoside K (**5**): a white amorphous powder, $[\alpha]_D^{26}$ +13.5° (*c*=0.58, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{48}H_{82}O_{21}Na$ $(M+Na)^+$: 1017.5246. Found: 1017.5252. IR (KBr) 3433, 2943, 1655, 1078 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 600 MHz) δ 0.94, 0.99, 1.13, 1.52, 1.57, 1.58, 1.59, 2.00 (3H each, all s, 19, 30, 18, 29, 27, 26, 21, 28-H_3), 3.45 (1H, dd, *J*=4.9, 11.5 Hz, 3-H), 4.08 (1H, m, 12-H), 4.32 (1H, m, 6-H), 4.69 (1H, dd-like, *J*=*ca*. 5, 8 Hz, 24-H), 4.96 (1H, d, *J*=7.4 Hz, 1'-H), 5.01, 5.20 (each 1H, both br s, 26-H_2), 5.20 (1H, d, *J*=7.7 Hz, 1"'-H), 5.38 (1H, d, *J*=7.6 Hz, 1"-H). ^{13}C-NMR (pyridine-d_5, 150 MHz) δc: give in Table 1. Positive-ion FAB-MS *m/z* 1017 $(M+Na)^+$. Negative-ion FAB-MS *m/z* 993 $(M-H)^-$, 977 $(M-OH)^-$, 813 $(M-OH-C_6H_{11}O_5)^-$;

Floralginsenoside La (**6**): a white amorphous powder, $[\alpha]_D^{27}$ +2.3° (*c*=0.12, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{48}H_{82}O_{19}Na$ $(M+Na)^+$: 985.5348. Found: 985.5341. IR (KBr): 3415, 2361, 1655, 1076 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 500 MHz) δ 0.94, 0.97, 1.18, 1.35, 1.58, 1.88, 2.06 (3H each, all s, 30, 19, 18, 29, 21, 27, 28-H_3), 3.44 (1H, dd, *J*=4.6, 11.5 Hz, 3-H), 4.08 (1H, m, 12-H), 4.40 (1H, m, 24-H), 4.66 (1H, dd, *J*=3.2, 10.4 Hz, 6-H), 4.89, 5.25 (each 1H, both br s, 26-H_2), 5.16 (1H, d, *J*=7.8 Hz, 1"'-H), 5.22 (1H, d, *J*=6.6 Hz, 1'-H), 6.41 (1H, s, 1"-H). ^{13}C-NMR (pyridine-d_5, 125 MHz) δc: give in Table 1. Positive-ion FAB-MS *m/z* 985 $(M+Na)^+$. Negative-ion FAB-MS *m/z* 961 $(M-H)^-$, 781 $(M-C_6H_{12}O_6)^-$.

Floralginsenoside Lb **(7):** a white amorphous powder, $[\alpha]_D^{26}$ -7.5° (*c*=0.45, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{48}H_{82}O_{19}Na$ $(M+Na)^+$: 985.5348. Found: 985.5355. IR (KBr): 3451, 2361, 1655, 1074 cm^{-1}. ^{1}H-NMR (pyridine-d_5, 600 MHz) δ 0.83, 0.90, 1.11, 1.30, 1.50, 1.88, 2.05 (3H each, all s, 30, 19, 18, 29, 21, 27, 28-H_3), 3.39 (1H, dd, *J*=4.9, 11.7, 3-H), 3.92 (1H, m, 12-H), 4.32 (1H, m, 24-H), 4.62 (1H, dd, *J*=3.4, 10.4, 6-H), 4.86, 5.22 (each 1H, both s, 26-H_2), 5.15 (1H, d, *J*=7.6 Hz, 1"'-H), 5.20 (1H, d, *J*=6.9 Hz, 1'-H), 6.40 (1H, s, 1"-H). ^{13}C-NMR (pyridine-d_5, 150 MHz) δc: give in Table 1. Positive-ion FAB-MS: *m/z* 985 $(M+Na)^+$. Negative-ion FAB-MS: *m/z* 961 $(M-H)^-$, 781 $(M-C_6H_{12}O_6)^-$.

Acid Hydrolysis of Floralginsenosides G (1), H (2), I (3), J (4), K (5), La (6) and Lb (7).

A solution of **1**–**7** (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, 250 mm × 4.6 mm i.d. (Tokyo Kasei Co., Ltd., Tokyo, Japan); detection, optical mobile phase, MeCN–H_2O (75:25, v/v); flow rate 0.80 ml/min; column temperature, room tempereture. Identification of D-glucose, L-rhamnose 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), 8.6 min (D-glucose, positive optical rotation), respectively.

Alkaline hydrolysis of floralginsenosides G (1), H (2).

A solution of floralginsenosides (**1** and **2**: 2 mg each) in 50% aqueous 1,4-dioxane (1.0 mL) was treated with 10% aqueous KOH (1.0 mL) and the whole was stirred at 37 °C for 1 h. After removal of the solvent from a part (0.1 mL) of the reaction mixture under reduced pressure, the residue was dissolved in $(CH_2)_2Cl_2$ (1.0 mL) and the solution was treated with *p*-nitrobenzyl-*N*,*N*'-diisopropylisourea (1 mg), then the whole was stirred at 80°C for 1 h. The reaction mixture was subjected to HPLC analysis [column: COSMOSIL 5C_{18}-MS-II, 250 0 4.6 mm i.d.; mobile phase: MeOH–H_2O (70:30, v/v); detection: UV (254 nm); flow rate: 1.00 mL/min] to identify the *p*-nitrobenzylester of acetic acid (t_R 5.3 min). The rest of each reaction was neutralized with DOWEX HCR W2 (H^+ form) and the resin was removed by filtration. Evaporation of the solvent from the filtrate under reduced pressure yielded a product, which was subjected to HPLC analysis [column: COSMOSIL 5C_{18}-MS-II, 250 × 4.6 mm i.d.; mobile phase: MeOH–H_2O (70:30, v/v); detection: RI; flow rate: 1.00 ml/min] to identify notoginsenoside-E (**12**, from **1**) or ginsenoside I (**14**, from **2**).

Treatment of 4 with pyridine. A solution of **4** (15 mg) in pyridine (0.6 mL) was permitted to stand for 2 d at 40°C. Removal of the solvent from the reaction solution under reduced pressure gave **8** (15 mg).

8: a white amorphous powder, $[\alpha]_D^{26}$ -7.2° (*c*=0.45, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{48}H_{80}O_{19}Na$ $(M+Na)^+$: 983.5192. Found: 983.5187. IR (KBr): 3451, 2930, 1745, 1677, 1074 cm^{-1}; ^{1}H-NMR (pyridine-d_5, 600 MHz) δ 0.86, 0.89, 1.07, 1.28, 1.44, 1.77, 2.03 (3H each, all s, 30, 19, 18, 29, 21, 27, 28-H_3), 3.39w (1H, dd, *J*=4.8, 11.7 Hz, 3-H), 4.02 (1H, m, 12-H), 4.60 (1H, dd, *J*=3.4, 12.4 Hz, 6-H), 5.08 (1H, d, *J*=7.8 Hz, 1"'-H), 5.16 (1H, dd, *J*=6.9 Hz, 1'-H), 5.59, 6.14 (each 1H, both s, H_2-26), 6.43 (1H, s, 1"-H). ^{13}C-NMR (pyridine-d_5, 150 MHz) δc: give in Table 1. Positive-ion FAB-MS: *m/z* 983 $(M+Na)^+$. Negative-ion FAB-MS: *m/z* 959 $(M-H)^-$, 797 $(M-C_6H_{11}O_5)^-$.

$NaBH_4$ Reduction of 8. A solution of **8** (4.0 mg) in MeOH (2.0 ml) was treated with $NaBH_4$ (2.5 mg) and $CeCl_3 \cdot 7H_2O$ (4.0 mg) and the whole mixture was stirred at room temperature for 2 h. After treatment of the reaction mixture with acetone (6.0 ml), the whole was evaporation under reduced pressure to give a residue. The residue was purified with silica gel column chromatography [0.5 g, $CHCl_3$-MeOH-H_2O (10:3:1–65:35:10, lower layer, v/v/v)] to give a mixture of **6** and **7** (3.8 mg, ca 2:1), which was separated by HPLC [COSMOSIL 5C_{18}-MS-II, (250 × 4.6 mm i.d.), MeCN–H_2O (1:5, v/v)]. Compounds **6** and **7** were identified with authentic samples by HPLC and ^{1}H-NMR.

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22 The stereostructure of the 24-hydroxyl group was reported to be capable of determination by comparison of ^{13}C-NMR data,[21] and the signals due to the side chain part (20-C–27-C) in the ^{13}C-NMR spectra of **6** and **7** were conformity with those of the 24(*R*)- and 24(*S*)-compounds, respectively. However, the differences of the chemical shifts between the 24(*R*)- and 24(*S*)-compounds were found to be very small, so that we did not adapt the rule to **6** and **7**.