Six New Dammarane-type Triterpene Saponins from the Leaves of *Panax ginseng*

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Six new minor saponins, together with known ginsenosides, were isolated from the leaves of *Panax ginseng*. The new saponins were named as ginsenoside-Rh$_5$, -Rh$_6$, -Rh$_7$ -Rh$_8$, -Rh$_9$ and -Rg$_7$, and their structures were elucidated on the basis of chemical and physicochemical evidence to be as follows: ginsenoside-Rh$_5$: 3β,6α,12β,24ξ-tetrahydroxy-dammar-20(22),25-diene 6-*O*-β-D-glucopyranoside (1), -Rh$_6$: 3β,6α,12β,20(*S*)-tetrahydroxy-25-hydroperoxy-dammar-23-ene 20-*O*-β-D-glucopyranoside (2), -Rh$_7$: 3β,7β,12β,20(*S*)-tetrahydroxy-dammar-5,24-diene 20-*O*-β-D-glucopyranoside (3), -Rh$_8$: 3β,6α,20(*S*)-trihydroxy-dammar-24-ene-12-one 20-*O*-β-D-glucopyranoside (4), -Rh$_9$: 3β,6α,20(*S*)-trihydroxy-12β,23-epoxy-dammar-24-ene 20-*O*-β-D-glucopyranoside (5) and -Rg$_7$: 3-*O*-β-D-glucopyranosyl 3β,12β,20(*S*),24(*R*)-tetrahydroxy-dammar-25-ene 20-*O*-β-D-glucopyranoside (6).

Key words *Panax ginseng*; Araliaceae; ginsenoside-Rh$_{5—9}$; ginsenoside-Rg$_7$

Panax ginseng, an ancient and famous herbal drug in traditional chinese medicines, has been used in Chinese folklore for more than 4000 years. In the course of our studies to find bioactive saponins from natural medicines, a number of dammarane-type triterpene oligoglycosides having anti-cancer, anti-arrhythmia and inhibitory effects on reducing side-effects of steroid hormones were found.[1,2] In a continuing study, further systematic research on chemical constituents from the leaves of *P. ginseng*, we now report the isolation and structural elucidation of six new saponins, together with 14 known ones among which, majoroside-F$_2$ was the first isolated from *P. ginseng*.

The 70% EtOH extract from the dried leaves of *P. ginseng* were separated by a macro-reticular resin column to give the 50% EtOH eluates which upon drying afforded the total saponins. The total saponins were chromatographed on silica gel, a reversed-phase column and finally on HPLC to afford ginsenoside-Rh$_5$ (**1**, 8 mg), -Rh$_6$ (**2**, 9 mg), -Rh$_7$ (**3**, 10 mg), -Rh$_8$ (**4**, 5 mg), -Rh$_9$ (**5**, 9 mg), -Rg$_7$ (**6**, 10 mg), majoroside-F$_2$ (**7**, 9 mg), ginsenoside-Rh$_1$ (**8**, 100 mg), chikusetsusaponin-L$_8$[3] (**9**, 15 mg), notoginsenoside-Fe[4] (**10**, 10 mg), majoroside-F$_4$[4] (**11**, 10 mg), 20(*R*)-ginsenoside-Rh$_1$[5] (**12**, 20 mg), ginsenoside-F$_1$[5] (**13**, 10 mg), -F$_2$[5] (**14**, 8 mg), -F$_3$[5] (**15**, 12 mg), -Rg$_1$[5,6] (**16**, 300 mg), -Re[5,6] (**17**, 500 mg), -Rd[5,6] (**18**, 10 mg), -Rc[5,6] (**19**, 10 mg) and -Rb$_2$[6] (**20**, 20 mg).

Ginsenoside-Rh$_5$ (**1**) was obtained as a white powder. The high-resolution FAB-MS (HR-FAB-MS) indicated that **1** has a molecular formula of $C_{36}H_{60}O_9$. In the positive-mode FAB-MS of **1**, a quasimolecular ion peak at *m/z* 659 $[M+Na]^+$ and a fragment ion peak at *m/z* 455 $[M-\text{glucosyl}-H_2O]^+$ allow only one molecule of glucose to be linked to the aglycone. On acid hydrolysis, it yielded a glucose which was identified by TLC comparison with authentic sample, suggesting **1** was a glycoside. From the ^{1}H-, ^{13}C-NMR and distortionless enhancement by polarization transfer (DEPT) spectra, **1** was proposed to be a β-D-glucopyranosyl and an aglycone with four hydroxyl groups and two double bonds. The configuration of the anomeric position was determined to be β on the basis of the coupling constant (J=8.0 Hz) of the anomeric proton signal in the ^{1}H-NMR spectrum of **1**. A set of signals at δ 106.1, 75.5, 79.7, 71.9, 78.2, and 63.1 due to β-D-glucopyranosyl were observed in the ^{13}C-NMR spectrum of **1**. The signal of C-5 at δ 61.5 is a characteristic of a protopanaxatriol-type aglycone, suggesting **1** was a monoglucoside whose sapogenol moiety was a protopanaxatriol-type triterpene with variations in its side-chain. The β-D-glucopyranosyl bonding to C-6 of the aglycone was characterized from heteronuclear multiple bond spectroscopy (HMBC) experiment. A long-range correlation was observed between the anomeric proton signal at δ 5.05 and the C-6 signal at δ 80.1. Furthermore, the ^{13}C-NMR signals of **1** were found to be superimposable on those of ginsenoside-Rh$_1$ (**8**) except for the signals due to the side-chain part (C-22—C-27) of the aglycone which showed a signal of a terminal double bond at δ 149.9 and 110.0, and two olefinic carbon signals at δ 142.4 and 122.2. The structure of the side-chain part of the sapogenol moiety was elucidated by ^{13}C–^{1}H shift correlation spectroscopy (COSY), ^{1}H–^{1}H COSY and HMBC experiments of **1**. In the HMBC spectrum, a methyl proton signal at δ 1.83 showed long-range correlations between δ 51.0 (C-17), δ 142.4, and 122.2. So this methyl signal can be assigned to the proton of C-21, and the two olefinic carbon signals can be assigned for C-20 and C-22, respectively. Similarly, the HMBC spectrum also revealed long-range correlations between the following protons and carbons: H-23 and C-20, 22, 24; H-27 and C-24, 25, 26 (Fig. 1). In addition, in the ^{1}H–^{1}H COSY spectrum, the signals at δ 2.41, 2.55 (H-23) showed a correlation with each other, and the correlations between H-23 with δ 5.69 (t like, J=7.5 Hz, H-22) and δ 4.37 (dd, J=3.5, 8.5 Hz, H-24). The stereochemistry of the double bond at C-20 (22) was proposed to be (*E*) since the signal for C-21 was observed at δ 13.2 in the ^{13}C-NMR spectrum of **1**, while the methyl carbon of a (*Z*)-type structure is usually observed at about δ 20—30.[7,8] From the above results, the structure of **1** was determined as 3β,6α,12β,24ξ-tetrahydroxy-dammar-20 (22), 25-diene 6-*O*-β-D-glucopyranoside. It is a new saponin and named as ginsenoside-Rh$_5$.

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Ginsenoside-Rh_6 (**2**) was isolated as a white powder. The molecular formula of $C_{36}H_{62}O_{11}$ for **2** was clarified by HR-FAB-MS measurement. On acid hydrolysis, it yielded a glucose detected by TLC comparison with authentic sample, and an aglycone. Compound **2** was shown to possess a hydroperoxyl group by its positive response to the ferrous thiocyanate reagent.[9] The ^{1}H-NMR spectrum of **2** showed an anomeric proton signal of the β-D-glucopyranosyl moiety at δ 5.22 (d, J=7 Hz, H-1′) and two olefinic proton signals in a disubstituted E-double bond at δ 6.06 (d, J=16 Hz, H-24) and 6.19 (m, H-23). The ^{13}C-NMR signals of **2** were similar to those of ginsenoside-F_1 (**13**) except for the signals due to the side-chain part (C-22—C-27) of the aglycone. The structure of the side-chain part of the aglycone of **2** could be determined by ^{13}C–^{1}H COSY, ^{1}H–^{1}H COSY and HMBC experiments. In the HMBC spectrum, a methyl proton signal at δ 1.62 showed long-range correlations with ^{13}C-NMR signals at δ 52.2 (C-17), 83.1 (C-20) and 39.7 (C-22), so this methyl proton signal can be assigned to H-21. Furthermore other long-range correlations were also observed between the following protons and carbons: H-22 (δ 2.74, 3.06, dd, J=6, 14 Hz)/C-20, 23, 24; H-24 (δ 6.06, d, J=16.0 Hz)/C-22, 23, 25, 26, 27; H-26, 27/C-24, 25 (Fig. 1). In addition, in the ^{1}H–^{1}H COSY spectrum of **2**, the signal at δ 6.06 (H-24) coupled with that of H-23, and both of them coupled with the signals of H-22. So the structure of the side-chain in **2** was elucidated as shown in Fig. 1. This conclusion was also supported by comparison of the ^{13}C-NMR data of **2** with those of notoginsenoside-E which is a protopanaxadiol-type saponin with changes in the side-chain of aglycone.[10] The β-D-glucopyranosyl was suggested to link to C-20 of the aglycone by the interpretation of the HMBC spectrum which showed a long-range correlation between the anomeric proton and C-20. Based on these findings, compound **2** was established as 3β,6α,12β,20(*S*)-tetrahydroxy-25-hydroperoxy-dammar-23-ene 20-*O*-β-D-glucopyranoside and named as ginsenoside-Rh_6.

Ginsenoside-Rh_7 (**3**) was also obtained as a white powder. Here again, the molecular formula $C_{36}H_{60}O_9$ of **3** was clarified from its HR-FAB-MS. In the FAB-MS, a quasimolecular

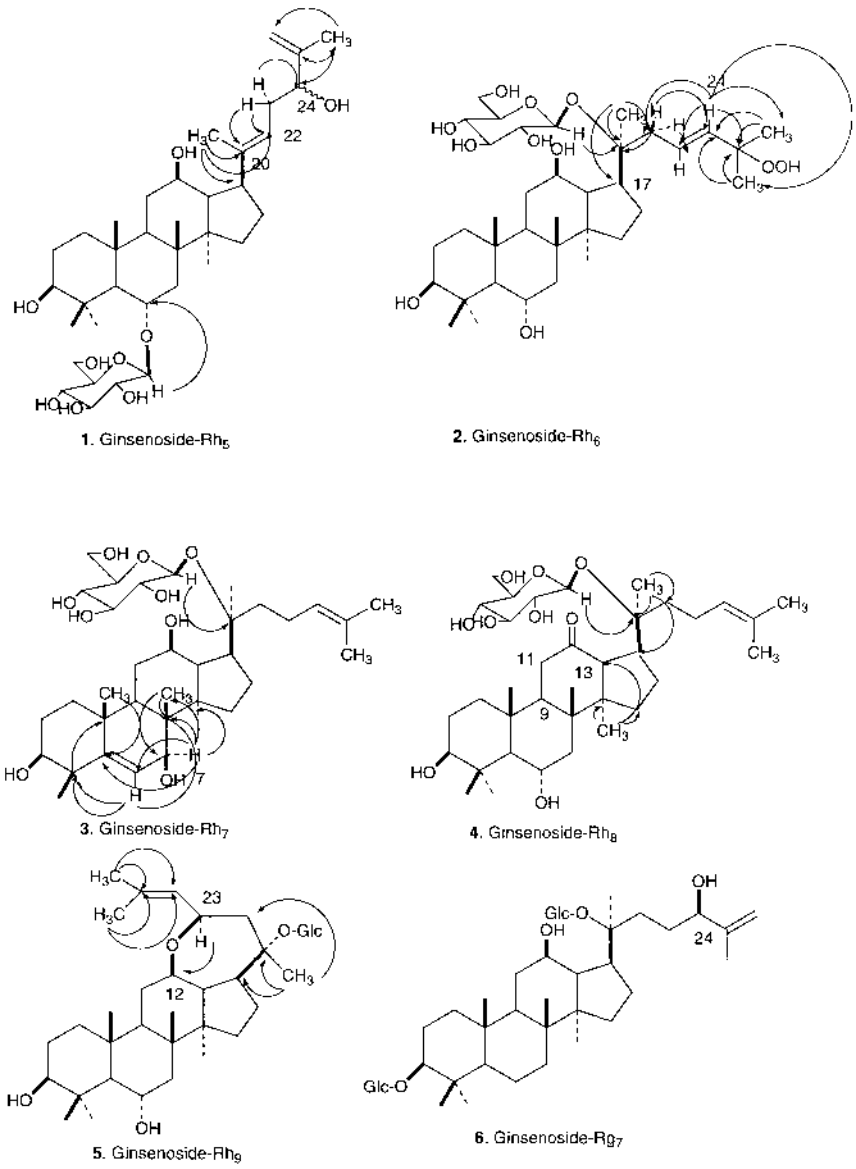
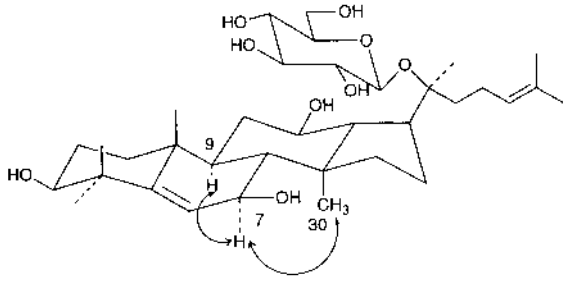


Fig. 1. The Structures of Ginsenosides **1**—**6** and Long-Range Correlations in the HMBC Spectra of **1**—**5**

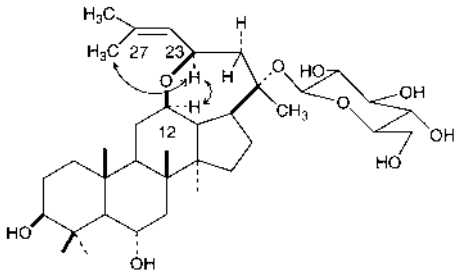
ion peak at *m/z* 659 $[M+Na]^+$ and a fragment ion peak at *m/z* 455 $[M-glucosyl-H_2O]^+$ was observed. The acid hydrolysis of **3** liberated a glucose which was identified by TLC comparison with authentic sample. The ^{1}H-NMR spectrum of **3** showed a signal due to the anomeric proton of the β-D-glucopyranosyl moiety at δ 5.23 (d, J=7.5 Hz), two olefinic proton signals in two trisubstituted double bonds at δ 5.93 (d, J=1.5 Hz, H-6) and 5.27 (dd-like, H-24) and three methine proton signals bearing three hydroxy functions at δ 3.50 (dd, J=4.5, 11.5 Hz, H-3), 4.74 (br s, H-7) and 4.15 (m, H-12). The carbon signals in the ^{13}C-NMR spectrum of **3** were similar to those of ginsenoside-F_1 (**13**), except for the signals due to the B-ring part of the aglycone moiety. The panel structure of this part in **3** was characterized by the HMBC experiment which showed long-range correlations between the following protons and carbons: H-7 (δ 4.74)/C-5, 6, 8, 14, 18; H-6 (δ 5.93)/C-4, 8, 10 (Fig. 1). The configuration of C-7 of the aglycone can be determined by rotating frame Overhauser enhancement spectroscopy (ROESY) spectrum; ROE correlations were observed between H-7 and H-9, H-30 (Fig. 2). Consequently, the structure of ginsenoside-Rh_7 was determined as shown in Fig. 1.

Ginsenoside-Rh_8 (**4**) was obtained as a white powder. The HR-FAB-MS analysis revealed a molecular formula of $C_{36}H_{60}O_9$ for **4**. The ^{13}C-NMR spectrum of **4** showed a carbonyl carbon signal at δ 211.2 and a set of signals at δ 98.5, 75.7, 78.2, 71.9, 78.0, and 63.0 due to a β-D-glucopyranosyl , indicating that **4** is a glucoside. The anomeric carbon signal of **4** appeared at unusually high field (δ 98.5), indicating that **4** must be a β-D-glucopyranoside of a tertiary alcohol. This was also supported by the presence of a signal at δ 81.3 due to a quaternary carbon bearing an oxygen function. In comparison of the carbon resonances attributable to the aglycone moiety of **4** with those of chikusetsusaponin-LT_8,[11] the signal at δ 211.2 was assigned to C-12. In the ^{1}H–^{1}H COSY spectrum of **4**, correlations between H-9 and H-11, H-13 and H-17 were observed. In addition, by the aid of ^{13}C–^{1}H COSY and HMBC spectra of **4**, all the signals due to aglycone protons were definitively assigned. On the basis of this evidence, the structure of **4** was elucidated as 3β,6α,20(*S*)-trihydroxydammar-24-ene-12-one 20-*O*-β-D-glucopyranoside. It is a new compound and named as ginsenoside-Rh_8.

Ginsenoside-Rh_9 (**5**) was obtained as a white powder. The molecular formula $C_{36}H_{60}O_9$ was clarified from the HR-FAB-MS of **5**. The ^{13}C- and ^{1}H-NMR spectra of **5** indicated that **5** was a glucoside. By comparison of the ^{13}C-NMR signals of **5** with those of ginsenoside-La,[12] the signals of **5** were found to be composed of signals due to C-12, -17, -20—-27, and a glucopyranosyl attached to C-20 of the aglycone of ginsenoside-La and resonances due to C-1—-11, -13—-16, and the other methyl groups of **13**, suggesting **5** has the same aglycone part as in ginsenoside-La. In the ^{1}H–^{1}H COSY spectrum of **5**, the signal at δ 4.81 (t, J=8.5, H-23) correlated with signals at δ 5.53 (br d, J=8 Hz, H-24), 2.23 (dd, J=16, 9.5 Hz, H-22), and 2.80 (br d, J=16 Hz, H-22); in addition the signal at δ 3.64 (m, H-12) correlated with signals at δ 2.08 (m, H-11) and 1.60 (t, J=16 Hz, H-13) supporting the same result. By observation of the cross peaks correlated with the 8 methyls in the HMBC spectrum, the panel structure of **5** was further confirmed. The long-range correlation between the signal at δ 4.81 (1H, t, J=8.5 Hz, H-23) and the signal at δ 79.8 (C-12), indicated the presence of an ether linkage between C-12 and C-23. The configurations of C-20 and C-23 were determined by ROESY spectrum. The ROE correlations between H-23 and H-12, H-27, indicated the configurations of C-20 and C-23 were both β. From the above findings, **5** was identified as 3β,6α,20(*S*)-trihydroxy-12β,23-epoxy-dammar-24-ene 20-*O*-β-D-glucopyranoside. **5** is a new compound and named as ginsenoside-Rh_9.



3. Ginsenoside-Rh_7



5. Ginsenoside-Rh_9

Fig. 2. ROE Correlations in the ROESY Spectra of **3** and **5**

Ginsenoside-Rg_7 (**6**) was obtained as a white powder. On acid hydrolysis, **6** yielded a sugar which was identified as a glucose by TLC comparison with authentic sample, suggesting **6** was a glycoside. Its FAB-MS revealed a molecular ion at *m/z* 800 $[M]^+$. The ^{13}C-NMR spectrum showed two sets of signals at δ 107.0, 75.8, 78.8, 72.0, 78.7, 63.2, and δ 98.4, 75.4, 79.0, 71.8, 78.4, 63.1, which were due to β-D-glucopyranosyl units. The aglycone of **6** was elucidated by detailed analysis of its ^{13}C-NMR data. A comparison of the ^{13}C-NMR spectrum of **6** with that of majoroside-F_2 (**7**),[13] showed a good agreement for all carbon signals due to the aglycone and sugar moieties, except for relatively significant upfield shifts of the C-24 and C-26 signals by δ=−0.4 and −0.9 ppm, respectively (δ 75.8 (C-24), δ 109.3 (C-26) in compound **7**), on going from **6** to **7**. This indicated that **6** is the C-24 epimer of **7**. In their HPLC behavior, they showed different retention times (**6**; 43 min, **7**: 33 min), suggesting **6** should be a stereoisomer of **7**. In previous studies, C-24 epimeric mixtures of dammarane saponins having similar side-chain structure named majoroside F_1 and vina-ginsenoside-R_9 were isolated and their ^{13}C-NMR data were established.[14] Based on the ^{13}C-NMR assignment for majoroside-F_1, the signals appearing at lower field than those of the corresponding signals of vina-ginsenoside-R_9 were ascribed to

the 24(*R*) isomer. Compound **6** was therefore deduced to be the corresponding 24(*R*) counterpart of **7** and was formulated as 3-*O*-*β*-D-glucopyranosyl 3*β*,12*β*,20(*S*),24(*R*)-tetrahydroxy-dammar-25-ene 20-*O*-*β*-D-glucopyranoside, which is a new compound and named as ginsenoside-Rg_7. The 14 known saponins (**7**—**20**) were identified by comparison of their spectral data with literature values.[3—6)]

Experimental

General Procedures Optical rotations were determined with a Carlo Erba 1106 digital polarimeter. NMR spectra were taken on a JEOL *α*500 in C_5D_5N at 25°C, TMS as an internal standard. Mass spectra were recorded with a JEOL JMS-SX 102A mass spectrometer. For HPLC, a C18 column (Waters) was used.

Extraction and Separation of Saponins The air-dried leaves of *Panax ginseng* (3.5 kg), collected in Heilongjiang province, China in October 1995, were identified by Professor Ying-Jie Chen and extracted twice with 70% ethanol and the combined extracts were concentrated *in vacuum*. The 70% EtOH extract was subjected to a macro-reticular absorption resin (D 101, 1 kg, supplied by Tianjin insecticide manufacture) column by eluting with water to remove impurities, and then eluting with 50% ethanol to give the saponin fraction, which was dried with a spray-drier (equipment) to afford the total crude saponins (100 g). The total saponins (100 g) were subjected to chromatography on a silica gel column (1.5 kg) and eluted in a stepwise manner with $CHCl_3$–MeOH mixture [30 : 1 (100×250 ml), 20 : 1 (50×250 ml), 10 : 1 (50×250 ml), 10 : 2 (100×250 ml), 10 : 3 (100×250 ml), 10 : 4 (100×250 ml), 10 : 5 (100×250 ml)] to give 600 fractions (each of 250 ml).

The fractions from No.166—176 ($CHCl_3$–MeOH, 10 : 1) were collected and separated by using low-pressure Lobar column chromatography (Lichroprep RP-18, UV 203 nm detection) to furnish **8**, **12**, and the other fractions 166-2 and 166-3. The fraction 166-2 was rechromatographed by RP-HPLC on C18 column with MeOH–H_2O (7 : 3) as eluate, (flow rate: 2 ml/min; RI detector) to afford **1**, **2** and **3**. The fraction 166-3 was rechromatographed on HPLC with MeOH–H_2O (6 : 4) as eluate (flow rate: 2 ml/min; RI detector) to afford **4** and **5**. Each fraction from No. 198—201, No. 242—250, No. 310—320 was rechromatographed on HPLC with MeOH–H_2O (7 : 3) as eluate to afford compounds **13** from No. 198—201, **9**, **14**, **15** from No. 242—250 and compound **16** from No. 310—320.

The fractions from No. 336 to No. 339 ($CHCl_3$–MeOH, 10 : 3) were combined and rechromatographed on HPLC with MeOH–H_2O (7 : 3) as eluate (flow rate; 2 ml/min; RI detector) to afford **6** and **7** (t_R value of **6** is 43 min; t_R of **7** is 33 min). In the same manner, fractions 386—396 was chromatographed to give compound **17**, fractions 416—422 to give **18**, fractions 465—469 to give **10**, **11**, **19**, and **20**.

Ginsenoside-Rh_5 (1) A white powder, $[\alpha]_D^{21}$ +20.8° (*c*=0.1, MeOH). HR-FAB-MS (*m/z*): Calcd for $C_{36}H_{60}O_9Na$ $[M+Na]^+$: 659.4135. Found: 659.4163. ^{1}H-NMR δ (ppm): 0.84, 1.06, 1.24, 1.62, 1.83, 1.88, 2.09 (3H each, all s, H-30, 19, 18, 29, 21, 27, 28), 2.41, 2.55 (1H each, m, H-23), 3.54 (1H, dd, *J*=5, 11.5 Hz, H-3), 3.95 (1H, m, H-12), 4.37 (1H, dd, *J*=3.5, 8.5 Hz, H-24), 4.47 (1H, dd, *J*=3, 10.5 Hz, H-6), 5.28, 4.98 (1H each, both br s, H-26), 5.69 (1H, t like, *J*=7.5 Hz, H-22), 5.05 (1H, d, *J*=8.0 Hz, H-1′), 4.12 (1H, t, *J*=8 Hz, H-2′), 4.27 (1H, t-like, *J*=8.5 Hz, H-3′), 4.23 (1H, dd, *J*=8.5 Hz, H-4′), 4.39 (1H, dd, *J*=5.5, 11.0 Hz, H-6′), 4.56 (1H, dd, *J*=2.5, 12 Hz, H-6′). ^{13}C-NMR data are given in Tables 1 and 2.

Ginsneoside-Rh_6 (2) A white powder, $[\alpha]_D^{21}$ +21.8° (*c*=0.1, MeOH). HR-FAB-MS (*m/z*): Calcd for $C_{36}H_{62}O_{11}Na$ $[M+Na]^+$: 693.4190. Found : 693.4194. ^{1}H-NMR δ (ppm): 0.91, 1.06, 1.15, 1.47, 1.59, 1.62, 1.88, 2.01 (3H each, all s, H-30, 19, 18, 29, 21, 27, 28), 1.30 (1H, d, *J*=10 Hz, H-5), 2.74, 3.06 (1H each, both dd, *J*=6, 14 Hz, H-22), 3.52 (1H, dd, *J*=4, 11.5 Hz, H-3), 4.02 (1H, m, H-12), 4.42 (1H, dt, *J*=3.5, 10 Hz, H-6), 6.06 (1H, d, *J*=16 Hz, H-24), 6.19 (1H, m, H-23), 5.22 (1H, d, *J*=7.0 Hz, H-1′). ^{13}C-NMR data are given in Tables 1 and 2.

Ginsneoside-Rh_7 (3) A white powder, $[\alpha]_D^{21}$ +30.1° (*c*=0.1, MeOH). HR-FAB-MS (*m/z*): Calcd for $C_{36}H_{60}O_9Na$ $[M+Na]^+$: 659.4135. Found : 659.4175. ^{1}H-NMR δ (ppm): 1.13, 1.24, 1.33, 1.36, 1.45, 1.59, 1.61, 1.66 (3H each, all s, H-30, 19, 18, 29, 28, 26, 27, 21), 3.50 (1H, dd, *J*=4.5, 11.5 Hz, H-3), 4.15 (1H, m, H-12), 4.74 (1H, br. s, H-7), 5.27 (1H, dd, H-24), 5.93 (1H, d, *J*=1.5 Hz, H-6), 5.23 (1H, d, *J*=7.5 Hz, H-1′), 4.05 (1H, t, *J*=8 Hz, H-2′), 4.27 (1H, t, *J*=9.0 Hz, H-3′), 4.14 (1H, t like, *J*=9.0 Hz, H-4′), 4.02 (1H, m, H-5′), 4.35 (1H, dd, *J*=5.5, 11.5 Hz, H-6′), 4.52 (1H, dd, *J*=2.0, 11.5 Hz, H-6′). ^{13}C-NMR data are given in Tables 1 and 2.

Ginsenoside-Rh_8 (4) A white powder, HR-FAB-MS (*m/z*): Calcd for $C_{36}H_{60}O_9Na$ $[M+Na]^+$: 659.4135. Found: 659.4146. ^{1}H-NMR δ (ppm): 0.93, 1.02, 1.45, 1.46, 1.58, 1.62, 1.64, 1.98 (each 3H, all s, H-30, 19, 29, 18, 21, 26, 27, 28), 1.95 (1H, m, H-9), 1.93, 2.40 (each 1H, m, H-11), 2.93 (1H, td, *J*=10, 5 Hz, H-17), 3.51 (1H, dd, *J*=10.5, 5 Hz, H-3) , 3.69 (1H, d, *J*=10 Hz, H-13). ^{13}C-NMR data are given in Tables 1 and 2.

Table 1. ^{13}C-NMR Data of the Aglycones of **1**—**6** (in C_5D_5N)

Carbon No.	**1**	**2**	**3**	**4**	**5**	**6**
1	39.5	39.4	39.8	40.5	39.6	39.2
2	28.0	28.2	27.2	27.9	28.1	26.8
3	78.6	78.5	77.6	78.2	78.4	88.8
4	40.2	40.4	42.7	40.4	40.4	39.7
5	61.5	61.8	147.5	61.5	61.9	56.4
6	80.1	67.7	127.4	67.7	67.7	18.3
7	45.4	47.4	71.2	47.0	47.5	35.1
8	41.4	41.2	42.4	41.9	40.9	40.0
9	50.5	49.8	47.5	54.4	50.3	50.2
10	39.8	39.4	38.4	39.0	39.4	37.0
11	32.6	31.0	33.3	40.3	30.1	30.9
12	72.6	70.5	69.8	211.2	79.8	70.3
13	50.6	49.2	50.6	56.1	49.3	49.4
14	50.7	51.5	51.0	56.0	51.2	51.5
15	32.5	30.7	34.5	32.3	32.5	31.1
16	26.8	26.4	28.4	24.6	25.5	26.8
17	51.0	52.2	51.1	42.6	46.9	52.4
18	17.4	17.6	10.8	17.8	16.5	16.3
19	17.7	17.5	20.4	17.5	16.8	15.9
20	142.4	83.1	83.5	81.3	81.9	83.3
21	13.2	23.3	22.5	22.6	24.6	22.8
22	122.2	39.7	36.5	39.5	51.8	32.8
23	35.3	126.5	23.3	24.0	72.5	31.1
24	75.2	138.1	126.0	125.8	129.2	76.2
25	149.9	81.3	130.9	130.9	131.4	149.4
26	110.0	25.2	25.8	25.8	25.7	110.2
27	18.5	25.4	17.8	17.6	17.7	18.5
28	31.8	32.0	29.1	31.8	31.9	28.2
29	16.4	16.5	23.5	16.4	17.7	16.8
30	16.8	17.2	18.2	17.1	17.1	17.3

Table 2. ^{13}C-NMR Data of the Sugar Part of **1**—**6** (in C_5D_5N)

Carbon No.	**1**	**2**	**3**	Carbon No.	**4**	**5**	**6**
6-Glc				3-Glc			
1	106.1			1			107.0
2	75.5			2			75.8
3	79.7			3			78.8
4	71.9			4			72.0
5	78.2			5			78.7
6	63.1			6			63.2
20-Glc				20-Glc			
1		98.3	98.4	1	98.5	99.3	98.4
2		75.3	75.2	2	75.7	75.4	75.4
3		78.9	79.3	3	78.2	79.0	79.0
4		71.6	71.7	4	71.9	72.0	71.8
5		78.3	78.4	5	78.0	78.2	78.4
6		63.0	62.9	6	63.0	63.1	63.1

Ginsenoside-Rh_9 (5) A white powder, HR-FAB-MS (*m/z*): Calcd for $C_{36}H_{60}O_9Na$ $(M+Na)^+$: 659.4135. Found: 659.4180. ^{1}H-NMR δ (ppm): 1.02, 1.06, 1.09, 1.45, 1.50, 1.67, 1.80, 1.98 (each 3H, all s, H-19, 30, 18, 29, 21, 26, 27, 28), 1.60 (1H, t, *J*=16 Hz, H-13), 2.08 (2H, m, H-11), 2.23 (1H, dd, *J*=16, 9.5 Hz, H-22), 2.80 (1H, br d, *J*=16 Hz, H-22), 3.64 (1H, m, H-12), 4.81 (1H, t, *J*=8.5 Hz, H-23), 5.53 (1H, br d, *J*=8 Hz, H-24), 5.12 (1H, d, *J*=8 Hz, H-1′). ^{13}C-NMR data are given in Tables 1 and 2.

Ginsenoside-Rg_7 (6) A white powder, ^{1}H-NMR δ: 5.22 (1H, d, *J*=7.9 Hz, H″-1 of Glc), 4.93 (1H, d, *J*=7.3 Hz, H′-1of another Glc). ^{13}C-NMR data are given in Tables 1 and 2. FAB-MS (*m/z*): 823 $[M+Na]^+$, 800 $[M]^+$, 642 $[M+Na-glc-H_2O]^+$, 420 $[M-2glc-3H_2O]^+$.

Acid Hydrolysis A solution of compounds **1**—**5** (a few milligrams) in MeOH–HCl (1 : 1) was placed in a capillary and the capillary was sealed.

After heating at 80° for 4 h, the solution was subjected to silica gel TLC, together with the standard samples, using *n*-BuOH–AcOH–H_2O (5 : 1 : 4, upper layer) and $CHCl_3$–MeOH–H_2O (16 : 9 : 2) as the developing solvents and using *O*-phthalic acid-aniline as the detection reagent. Only glucose was detected from compounds **1**—**5**.

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