

## Ginsenosides from the Roots of Korean Cultivated-Wild Ginseng

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**Abstract** – Column chromatographic separation of 70% EtOH extract of the roots of Korean cultivated-wild ginseng led to the isolation of ten ginsenosides (**1** - **10**). The isolated compounds were identified as ginsenoside Rg<sub>1</sub> (**1**), ginsenoside Re (**2**), ginsenoside Rc (**3**), ginsenoside Rb<sub>1</sub> (**4**), ginsenoside Rb<sub>2</sub> (**5**), ginsenoside Rd (**6**), ginsenoside Rg<sub>3</sub> (**7**), ginsenoside F<sub>2</sub> (**8**), ginsenoside Rb<sub>3</sub> (**9**), and ginsenoside Rd<sub>2</sub> (**10**) by physicochemical and spectroscopic methods. The compounds (**1** - **10**) were for the first time isolated from the roots of Korean cultivated-wild ginseng.

**Keywords** – Korean cultivated-wild ginseng, ginsenoside

### Introduction

The roots of *Panax ginseng* (Araliaceae) have been used as a tonic and as a remedy for a variety of pathological conditions for centuries. Most studies of *P. ginseng* investigated the ginsenoside saponins (Park *et al.*, 1998; Washida *et al.*, 2003; Yoshikawa *et al.*, 2007). To date, more than 30 ginsenosides have been isolated from *Panax* species (Park, 1996). Although some pharmacological studies of Korean cultivated-wild ginseng, such as antioxidant (Kim and Kim, 2006) and antitumor effects (Kim *et al.*, 2004) have been described, there have been no studies of the ginsenoside constituents of Korean cultivated-wild ginseng (Jangnoisam). We have reported cytotoxic polyacetylenes from Korean cultivated-wild ginseng (Yang *et al.*, 2008).

In continuing study on this source, we have isolated ten saponins (**1** - **10**) from the 70% EtOH extract of the roots of Korean cultivated-wild ginseng. Their structures were determined by physicochemical and spectroscopic methods.

### Experimental

**Chemical and instrument** – The optical rotations were determined using a Jasco P-1020 polarimeter (Jasco Co., Japan). The NMR spectra were recorded on a Bruker

Biospin Avance 500 (Bruker Co., German), and a Varian Unity INOVA 500 NB NMR spectrometer (Varian Co., USA). The semi-preparative HPLC was carried out over a Gemini<sup>®</sup> RP-C<sub>18</sub> (5  $\mu$ , 10  $\times$  250 mm, Phenomenex Co., USA) column using a 306 pump (Gilson Co., France) and a RI-71 detector (Shodex Co., Japan). Open column chromatography was carried out over silica gel 60, 70 - 230 mesh, Merck Co., Germany). Thin-layer chromatography (TLC) was performed on silica gel 60 F<sub>254</sub> and RP-18 F<sub>254s</sub> (Merck Co., Germany). The packing material of the molecular sieve column chromatography was Sephadex LH-20 (Pharmacia Co., Sweden). The packing material of the open column chromatography was silica gel 60 RP-18 (40 - 63  $\mu$ m, Merck Co., Germany). Low pressure liquid chromatography was carried out over a Lobar<sup>®</sup>-A glass prepacked column (Lichroprep<sup>®</sup> Si 60, Lichroprep<sup>®</sup> RP-18, 240  $\times$  10 mm, 40 - 63  $\mu$ m, Merck Co., Germany), a FMI QSY-0 pump (Fluid metering, Inc., USA), and a Duramat<sup>®</sup> 80 pump (CFG Prominent Co., Germany).

**Plant material** – The roots of Korean cultivated-wild ginseng (35.0 g) were provided from the Korea Insam Association in July 2006.

**Extraction and Isolation** – The roots of Korean cultivated-wild ginseng (35.0 g) were refluxed three times with 70% EtOH. The resulting 70% EtOH extract (8.0 g) was partitioned by solvent to give *n*-hexane (200.0 mg), CHCl<sub>3</sub> (90.0 mg) and *n*-BuOH (1.6 g) soluble fractions.

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The *n*-BuOH fraction (1.6 g) was chromatographed over a Sephadex LH-20 using MeOH-H<sub>2</sub>O (70 : 30) and a RP-18 column chromatography (MeOH-H<sub>2</sub>O = 60 : 40) to give six fractions (R1 - R7). The R1 fraction (700.0 mg) was subjected to RP-18 column chromatography (MeOH-H<sub>2</sub>O = 60 : 40) and LiChroprep silica Lobar<sup>®</sup>-A columns (CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O = 6 : 3 : 0.1), and purified by semi-preparative HPLC (CH<sub>3</sub>CN-H<sub>2</sub>O = 30 : 70) to afford **1** (40.0 mg, 0.11% w/w) and **2** (30.0 mg, 0.085% w/w). The R2 fraction (460.0 mg) was subjected to RP-18 column chromatography (MeOH-H<sub>2</sub>O = 70 : 30), and purified using semi-preparative HPLC (MeOH-H<sub>2</sub>O = 60 : 40) to afford **3** (98.0 mg, 0.28% w/w), **4** (170.0 mg, 0.48% w/w) and **5** (35.0 mg, 0.1% w/w). The R3 fraction (50.0 mg) was subjected to LiChroprep Lobar<sup>®</sup>-A RP-18 (MeOH-H<sub>2</sub>O = 75 : 25), and purified using semi-preparative HPLC (MeOH-H<sub>2</sub>O = 75 : 25) to afford **6** (25.0 mg, 0.07% w/w). The R4 fraction (150.0 mg) was subjected to LiChroprep RP-18 Lobar<sup>®</sup>-A (MeOH-H<sub>2</sub>O = 55 : 45), and purified using semi-preparative HPLC (MeOH-H<sub>2</sub>O = 55 : 45) to afford **7** (5.0 mg, 0.014% w/w) and **8** (5.0 mg, 0.014% w/w). The R5 fraction (70.0 mg) was subjected to LiChroprep RP-18 Lobar<sup>®</sup>-A (MeOH-H<sub>2</sub>O = 65 : 35), and purified using semi-preparative HPLC (MeOH-H<sub>2</sub>O = 65 : 35) to afford **9** (5.0 mg, 0.014% w/w) and **10** (5.0 mg, 0.014% w/w).

**Ginsenoside Rg<sub>1</sub> (1)** – Colorless gum; [ $\alpha$ ]<sub>D</sub>: +15.0 (*c* = 0.22, MeOH); ESI-MS: *m/z* 823 [M + Na]<sup>+</sup>; <sup>1</sup>H-NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  0.79 (3H, s, H-18), 1.02 (3H, s, H-19), 1.14 (3H, s, H-30), 1.59 (3H, s, H-26), 1.57 (3H, s, H-27), 1.56 (3H, s, H-21), 1.54 (3H, s, H-28), 2.06 (3H, s, H-29), 3.57 (1H, m, H-3), 4.51 (1H, m, H-6), 3.98 (1H, m, H-12), 5.00 (1H, d, *J* = 7.0 Hz, H<sup>'</sup>-1), 5.16 (1H, d, *J* = 7.0 Hz, H<sup>''</sup>-1); <sup>13</sup>C-NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  39.4 (C-1), 27.6 (C-2), 78.6 (C-3), 40.3 (C-4), 61.3 (C-5), 78.1 (C-6), 45.1 (C-7), 39.6 (C-8), 49.9 (C-9), 39.5 (C-10), 30.6 (C-11), 70.1 (C-12), 49.1 (C-13), 51.3 (C-14), 30.6 (C-15), 26.5 (C-16), 51.4 (C-17), 17.7 (C-18), 17.5 (C-19), 83.2 (C-20), 22.2 (C-21), 36.1 (C-22), 23.1 (C-23), 125.9 (C-24), 130.8 (C-25), 25.7 (C-26), 17.1 (C-27), 31.7 (C-28), 16.3 (C-29), 17.5 (C-30), 105.9 (C<sup>'</sup>-1), 75.4 (C<sup>'</sup>-2), 80.1 (C<sup>'</sup>-3), 71.6 (C<sup>'</sup>-4), 79.6 (C<sup>'</sup>-5), 63.0 (C<sup>'</sup>-6), 98.2 (C<sup>''</sup>-1), 75.1 (C<sup>''</sup>-2), 79.3 (C<sup>''</sup>-3), 70.1 (C<sup>''</sup>-4), 78.2 (C<sup>''</sup>-5), 62.9 (C<sup>''</sup>-6).

**Ginsenoside Re (2)** – Colorless gum; [ $\alpha$ ]<sub>D</sub>: -10.2 (*c* = 0.10, MeOH); ESI-MS: *m/z* 969 [M + Na]<sup>+</sup>; <sup>1</sup>H-NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  0.94 (3H, s, H-18), 0.95 (3H, s, H-19), 1.16 (3H, s, H-30), 1.39 (3H, s, H-26), 1.58 (3H, s, H-27), 1.58 (3H, s, H-21), 1.58 (3H, s, H-28), 2.09 (3H, s, H-29), 3.57 (1H, m, H-3), 4.51 (1H, m, H-6), 3.98 (1H, m, H-12), 5.16 (1H, d, *J* = 7.5 Hz, H<sup>'</sup>-1), 5.62 (1H, d,

*J* = 7.5 Hz, H<sup>''</sup>-1), 1.58 (1H, d, *J* = 7.0 Hz, H-6<sup>''</sup>), 5.23 (1H, d, *J* = 7.5 Hz, H<sup>'''</sup>-1); <sup>13</sup>C-NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  39.3 (C-1), 27.7 (C-2), 78.5 (C-3), 39.3 (C-4), 60.8 (C-5), 74.5 (C-6), 45.9 (C-7), 41.1 (C-8), 49.5 (C-9), 39.6 (C-10), 30.7 (C-11), 70.1 (C-12), 49.0 (C-13), 51.3 (C-14), 30.9 (C-15), 26.6 (C-16), 51.6 (C-17), 17.7 (C-18), 17.2 (C-19), 83.2 (C-20), 22.2 (C-21), 36.0 (C-22), 23.1 (C-23), 125.9 (C-24), 130.8 (C-25), 25.7 (C-26), 17.4 (C-27), 32.1 (C-28), 17.2 (C-29), 17.7 (C-30), 101.8 (C<sup>'</sup>-1), 79.1 (C<sup>'</sup>-2), 78.0 (C<sup>'</sup>-3), 72.1 (C<sup>'</sup>-4), 78.0 (C<sup>'</sup>-5), 63.0 (C<sup>'</sup>-6), 101.8 (C<sup>''</sup>-1), 72.1 (C<sup>''</sup>-2), 72.1 (C<sup>''</sup>-3), 73.8 (C<sup>''</sup>-4), 69.3 (C<sup>''</sup>-5), 18.7 (C<sup>''</sup>-6), 98.2 (C<sup>'''</sup>-1), 74.9 (C<sup>'''</sup>-2), 78.8 (C<sup>'''</sup>-3), 71.3 (C<sup>'''</sup>-4), 77.8 (C<sup>'''</sup>-5), 62.8 (C<sup>'''</sup>-6).

**Ginsenoside Rc (3)** – Colorless gum; [ $\alpha$ ]<sub>D</sub>: +5.2 (*c* = 0.14, MeOH); ESI-MS: *m/z* 1101 [M + Na]<sup>+</sup>; <sup>1</sup>H-NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  0.85 (3H, s, H-18), 0.96 (3H, s, H-19), 0.97 (3H, s, H-30), 1.02 (3H, s, H-26), 1.25 (3H, s, H-27), 1.60 (3H, s, H-21), 1.61 (3H, s, H-28), 1.64 (3H, s, H-29), 3.27 (1H, m, H-3), 3.98 (1H, m, H-12), 4.98 (1H, d, *J* = 7.5 Hz, H<sup>'</sup>-1), 5.16 (1H, d, *J* = 7.5 Hz, H<sup>''</sup>-1), 5.38 (1H, d, *J* = 7.5 Hz, H<sup>'''</sup>-1), 5.58 (1H, s, H<sup>'''</sup>-1); <sup>13</sup>C-NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  39.1 (C-1), 26.6 (C-2), 88.9 (C-3), 39.6 (C-4), 56.3 (C-5), 18.3 (C-6), 35.1 (C-7), 39.9 (C-8), 50.1 (C-9), 36.8 (C-10), 30.7 (C-11), 70.1 (C-12), 49.5 (C-13), 51.3 (C-14), 30.8 (C-15), 26.6 (C-16), 51.6 (C-17), 17.5 (C-18), 16.2 (C-19), 83.3 (C-20), 22.4 (C-21), 36.0 (C-22), 23.3 (C-23), 125.9 (C-24), 130.9 (C-25), 25.7 (C-26), 17.8 (C-27), 28.0 (C-28), 16.5 (C-29), 17.3 (C-30), 105.0 (C<sup>'</sup>-1), 83.1 (C<sup>'</sup>-2), 77.8 (C<sup>'</sup>-3), 71.5 (C<sup>'</sup>-4), 77.8 (C<sup>'</sup>-5), 62.8 (C<sup>'</sup>-6), 106.0 (C<sup>''</sup>-1), 76.8 (C<sup>''</sup>-2), 78.7 (C<sup>''</sup>-3), 71.5 (C<sup>''</sup>-4), 78.0 (C<sup>''</sup>-5), 62.6 (C<sup>''</sup>-6), 98.0 (C<sup>'''</sup>-1), 74.9 (C<sup>'''</sup>-2), 78.0 (C<sup>'''</sup>-3), 71.5 (C<sup>'''</sup>-4), 76.3 (C<sup>'''</sup>-5), 68.4 (C<sup>'''</sup>-6), 110.0 (C<sup>'''</sup>-1), 83.3 (C<sup>'''</sup>-2), 78.9 (C<sup>'''</sup>-3), 85.8 (C<sup>'''</sup>-4), 62.5 (C<sup>'''</sup>-5).

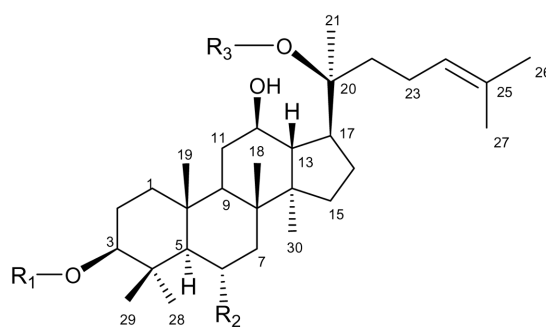
**Ginsenoside Rb<sub>1</sub> (4)** – Colorless gum; [ $\alpha$ ]<sub>D</sub>: +15.2 (*c* = 0.15, MeOH); ESI-MS: *m/z* 1131 [M + Na]<sup>+</sup>; <sup>1</sup>H-NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  0.78 (3H, s, H-18), 0.96 (3H, s, H-19), 0.96 (3H, s, H-30), 1.10 (3H, s, H-26), 1.25 (3H, s, H-27), 1.59 (3H, s, H-21), 1.61 (3H, s, H-28), 1.62 (3H, s, H-29), 3.20 (1H, m, H-3), 3.95 (1H, m, H-12), 4.98 (1H, d, *J* = 7.0 Hz, H<sup>'</sup>-1), 5.16 (1H, d, *J* = 7.0 Hz, H<sup>''</sup>-1), 5.18 (1H, d, *J* = 7.0 Hz, H<sup>'''</sup>-1), 5.39 (1H, d, *J* = 7.0 Hz, H<sup>'''</sup>-1); <sup>13</sup>C-NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  39.1 (C-1), 26.6 (C-2), 88.9 (C-3), 39.6 (C-4), 56.3 (C-5), 18.6 (C-6), 35.1 (C-7), 39.9 (C-8), 50.1 (C-9), 36.8 (C-10), 30.7 (C-11), 70.1 (C-12), 49.3 (C-13), 51.3 (C-14), 30.8 (C-15), 26.6 (C-16), 51.6 (C-17), 16.2 (C-18), 15.9 (C-19), 83.4 (C-20), 22.6 (C-21), 36.1 (C-22), 23.1 (C-23), 125.8 (C-24), 131.0 (C-25), 25.8 (C-26), 17.8 (C-27), 28.0 (C-28), 16.5 (C-29), 17.3 (C-30), 105.3 (C<sup>'</sup>-1), 83.1 (C<sup>'</sup>-2), 78.8 (C<sup>'</sup>-3),

71.5 (C'-4), 78.0 (C'-5), 62.6 (C'-6), 106.0 (C''-1), 76.8 (C''-2), 78.7 (C''-3), 71.5 (C''-4), 78.0 (C''-5), 62.7 (C''-6), 98.0 (C'''-1), 74.9 (C'''-2), 78.0 (C'''-3), 71.5 (C'''-4), 76.7 (C'''-5), 70.1 (C'''-6), 105.0 (C''''-1), 74.9 (C''''-2), 78.8 (C''''-3), 71.5 (C''''-4), 78.0 (C''''-5), 62.6 (C''''-6).

**Ginsenoside Rb<sub>2</sub> (5)** – Colorless gum;  $[\alpha]_D^{25}$ : +11.0 ( $c = 0.10$ , MeOH); ESI-MS:  $m/z$  1101  $[M + Na]^+$ ;  $^1H$ -NMR (500 MHz,  $C_5D_5N$ ):  $\delta$  0.78 (3H, s, H-18), 0.95 (3H, s, H-19), 0.95 (3H, s, H-30), 1.05 (3H, s, H-26), 1.24 (3H, s, H-27), 1.58 (3H, s, H-21), 1.60 (3H, s, H-28), 1.62 (3H, s, H-29), 3.21 (1H, m, H-3), 3.95 (1H, m, H-12), 4.85 (1H, d,  $J = 7.0$  Hz, H'-1), 4.95 (1H, d,  $J = 7.0$  Hz, H''-1), 5.11 (1H, d,  $J = 7.0$  Hz, H'''-1);  $^{13}C$ -NMR (125 MHz,  $C_5D_5N$ ):  $\delta$  39.1 (C-1), 26.5 (C-2), 89.1 (C-3), 39.6 (C-4), 56.4 (C-5), 18.3 (C-6), 35.1 (C-7), 39.9 (C-8), 50.1 (C-9), 36.8 (C-10), 30.7 (C-11), 70.1 (C-12), 49.3 (C-13), 51.3 (C-14), 30.7 (C-15), 26.6 (C-16), 51.6 (C-17), 16.2 (C-18), 15.9 (C-19), 83.5 (C-20), 22.2 (C-21), 36.3 (C-22), 23.1 (C-23), 125.8 (C-24), 131.0 (C-25), 25.8 (C-26), 17.8 (C-27), 28.0 (C-28), 16.5 (C-29), 17.3 (C-30), 105.0 (C'-1), 83.0 (C'-2), 78.1 (C'-3), 71.5 (C'-4), 78.1 (C'-5), 62.6 (C'-6), 105.9 (C''-1), 76.9 (C''-2), 79.0 (C''-3), 71.5 (C''-4), 78.7 (C''-5), 62.8 (C''-6), 98.0 (C'''-1), 74.9 (C'''-2), 78.7 (C'''-3), 71.5 (C'''-4), 76.6 (C'''-5), 69.1 (C'''-6), 104.5 (C''''-1), 72.0 (C''''-2), 73.9 (C''''-3), 68.5 (C''''-4), 65.5 (C''''-5).

**Ginsenoside Rd (6)** – Colorless gum;  $[\alpha]_D^{25}$ : +13.0 ( $c = 0.25$ , MeOH); ESI-MS:  $m/z$  969  $[M + Na]^+$ ;  $^1H$ -NMR (500 MHz,  $C_5D_5N$ ):  $\delta$  0.79 (3H, s, H-18), 0.97 (3H, s, H-19), 0.99 (3H, s, H-30), 1.05 (3H, s, H-26), 1.23 (3H, s, H-27), 1.59 (3H, s, H-21), 1.59 (3H, s, H-28), 1.62 (3H, s, H-29), 3.21 (1H, m, H-3), 3.95 (1H, m, H-12), 4.95 (1H, d,  $J = 7.0$  Hz, H'-1), 5.19 (1H,  $J = d, 7.0$  Hz, H''-1), 5.35 (1H, d,  $J = 7.0$  Hz, H'''-1);  $^{13}C$ -NMR (125 MHz,  $C_5D_5N$ ):  $\delta$  39.1 (C-1), 26.7 (C-2), 88.9 (C-3), 39.6 (C-4), 56.4 (C-5), 18.5 (C-6), 35.2 (C-7), 40.0 (C-8), 50.2 (C-9), 36.9 (C-10), 30.8 (C-11), 70.1 (C-12), 49.4 (C-13), 51.4 (C-14), 30.8 (C-15), 26.7 (C-16), 51.7 (C-17), 15.9 (C-18), 16.3 (C-19), 83.3 (C-20), 22.4 (C-21), 36.0 (C-22), 23.1 (C-23), 125.9 (C-24), 131.0 (C-25), 25.8 (C-26), 16.6 (C-27), 28.0 (C-28), 17.3 (C-29), 17.8 (C-30), 105.0 (C'-1), 83.3 (C'-2), 78.1 (C'-3), 71.6 (C'-4), 78.1 (C'-5), 62.8 (C'-6), 106.0 (C''-1), 77.0 (C''-2), 79.1 (C''-3), 71.6 (C''-4), 78.1 (C''-5), 62.8 (C''-6), 98.2 (C'''-1), 75.0 (C'''-2), 78.1 (C'''-3), 71.6 (C'''-4), 78.1 (C'''-5), 62.6 (C'''-6).

**Ginsenoside Rg<sub>3</sub> (7)** – Colorless gum;  $[\alpha]_D^{25}$ : +22.0 ( $c = 0.20$ , MeOH); ESI-MS:  $m/z$  807  $[M + Na]^+$ ;  $^1H$ -NMR (500 MHz,  $C_5D_5N$ ):  $\delta$  0.81 (3H, s, H-18), 0.97 (3H, s, H-19), 1.14 (3H, s, H-30), 1.50 (3H, s, H-26), 1.60 (3H, s, H-27), 1.60 (3H, s, H-21), 1.60 (3H, s, H-28), 2.10 (3H, s,



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
1	H	O-Glu	Glu
2	H	O-Glu (2→1) Rha.	Glu
3	Glu (1→2) Glu	H	Glu (6→1) Ara (fu)
4	Glu (1→2) Glu	H	Glu (6→1) Glu
5	Glu (1→2) Glu	H	Glu (6→1) Ara (py)
6	Glu (1→2) Glu	H	Glu
7	Glu (1→2) Glu	H	H
8	Glu	H	Glu
9	Glu (1→2) Glu	H	Glu (6→1) Xyl
10	Glu	H	Glu (6→1) Ara (py)

**Fig. 1.** Structures of the compounds 1 - 10.

H-29), 3.47 (1H, m, H-3), 3.86 (1H, m, H-12), 4.92 (1H, d,  $J = 7.5$  Hz, H'-1), 5.19 (1H, d,  $J = 8.0$  Hz, H''-1), 5.35 (1H, m, H-24);  $^{13}C$ -NMR (125 MHz,  $C_5D_5N$ ):  $\delta$  39.5 (C-1), 25.0 (C-2), 83.7 (C-3), 40.1 (C-4), 61.9 (C-5), 18.2 (C-6), 36.6 (C-7), 40.7 (C-8), 50.4 (C-9), 41.7 (C-10), 32.5 (C-11), 70.6 (C-12), 49.7 (C-13), 51.9 (C-14), 31.4 (C-15), 26.2 (C-16), 52.0 (C-17), 17.9 (C-18), 17.6 (C-19), 75.6 (C-20), 22.5 (C-21), 45.4 (C-22), 23.7 (C-23), 126.5 (C-24), 131.4 (C-25), 27.1 (C-26), 18.0 (C-27), 28.2 (C-28), 17.2 (C-29), 17.6 (C-30), 104.3 (C'-1), 80.3 (C'-2), 79.7 (C'-3), 72.8 (C'-4), 79.2 (C'-5), 63.8 (C'-6), 98.7 (C''-1), 76.5 (C''-2), 80.2 (C''-3), 72.2 (C''-4), 78.7 (C''-5), 63.4 (C''-6).

**Ginsenoside F<sub>2</sub> (8)** – Colorless gum;  $[\alpha]_D^{25}$ : +7.5 ( $c = 0.15$ , MeOH); ESI-MS:  $m/z$  807  $[M + Na]^+$ ;  $^1H$ -NMR (500 MHz,  $C_5D_5N$ ):  $\delta$  0.97 (3H, s, H-18), 1.12 (3H, s, H-19), 1.14 (3H, s, H-30), 1.41 (3H, s, H-26), 1.68 (3H, s, H-27), 1.68 (3H, s, H-21), 1.81 (3H, s, H-28), 2.13 (3H, s, H-29), 3.50 (1H, m, H-3), 3.93 (1H, m, H-12), 4.72 (1H, d,  $J = 7.0$  Hz, H'-1), 5.29 (1H, d,  $J = 7.0$  Hz, H''-1);  $^{13}C$ -NMR (125 MHz,  $C_5D_5N$ ):  $\delta$  39.8 (C-1), 26.2 (C-2), 89.7 (C-3), 40.1 (C-4), 55.1 (C-5), 18.1 (C-6), 36.2 (C-7), 40.7 (C-8), 50.2 (C-9), 40.4 (C-10), 32.6 (C-11), 69.9 (C-12), 48.7 (C-13), 52.1 (C-14), 31.7 (C-15), 26.2 (C-16), 52.1

(C-17), 17.4 (C-18), 17.6 (C-19), 83.6 (C-20), 23.4 (C-21), 36.2 (C-22), 23.4 (C-23), 126.8 (C-24), 131.2 (C-25), 27.5 (C-26), 18.0 (C-27), 28.2 (C-28), 18.0 (C-29), 17.8 (C-30), 102.4 (C'-1), 74.8 (C'-2), 78.8 (C'-3), 72.7 (C'-4), 79.0 (C'-5), 63.6 (C'-6), 102.2 (C''-1), 74.6 (C''-2), 79.8 (C''-3), 71.5 (C''-4), 79.0 (C''-5), 61.3 (C''-6).

**Ginsenoside Rb<sub>3</sub> (9)** – Colorless gum;  $[\alpha]_D^{25}$ : +17.0 ( $c=0.10$ , MeOH); ESI-MS:  $m/z$  1101  $[M + Na]^+$ ;  $^1H$ -NMR (500 MHz,  $C_5D_5N$ ):  $\delta$  0.82 (3H, s, H-18), 0.97 (3H, s, H-19), 0.97 (3H, s, H-30), 1.11 (3H, s, H-26), 1.29 (3H, s, H-27), 1.63 (3H, s, H-21), 1.65 (3H, s, H-28), 1.67 (3H, s, H-29), 3.31 (1H, m, H-3), 3.98 (1H, m, H-12), 4.93 (1H, d,  $J=7.0$  Hz, H'-1), 5.14 (1H, d,  $J=7.0$  Hz, H''-1), 5.34 (1H, d,  $J=7.0$  Hz, H'''-1), 5.39 (1H, d,  $J=7.5$  Hz, H''''-1);  $^{13}C$ -NMR (125 MHz,  $C_5D_5N$ ):  $\delta$  39.7 (C-1), 27.1 (C-2), 89.4 (C-3), 40.1 (C-4), 56.9 (C-5), 18.9 (C-6), 36.6 (C-7), 40.5 (C-8), 50.7 (C-9), 37.4 (C-10), 31.1 (C-11), 69.6 (C-12), 49.9 (C-13), 51.8 (C-14), 28.5 (C-15), 26.2 (C-16), 52.1 (C-17), 17.0 (C-18), 16.7 (C-19), 83.9 (C-20), 22.8 (C-21), 37.4 (C-22), 23.7 (C-23), 126.4 (C-24), 131.5 (C-25), 26.2 (C-26), 17.8 (C-27), 28.5 (C-28), 18.9 (C-29), 18.3 (C-30), 105.0 (C'-1), 83.9 (C'-2), 78.4 (C'-3), 72.6 (C'-4), 78.1 (C'-5), 65.9 (C'-6), 106.5 (C''-1), 77.2 (C''-2), 78.5 (C''-3), 72.1 (C''-4), 78.7 (C''-5), 63.4 (C''-6), 98.6 (C'''-1), 75.4 (C'''-2), 79.6 (C'''-3), 70.6 (C'''-4), 76.6 (C'''-5), 63.2 (C'''-6), 105.5 (C''''-1), 74.5 (C''''-2), 77.6 (C''''-3), 69.6 (C''''-4), 68.9 (C''''-5).

**Ginsenoside Rd<sub>2</sub> (10)** - Colorless gum;  $[\alpha]_D^{25}$ : +18.0 ( $c=0.15$ , MeOH); ESI-MS:  $m/z$  939  $[M + Na]^+$ ;  $^1H$ -NMR (500 MHz,  $C_5D_5N$ ):  $\delta$  0.84 (3H, s, H-18), 0.96 (3H, s, H-19), 0.98 (3H, s, H-30), 1.01 (3H, s, H-26), 1.31 (3H, s, H-27), 1.63 (3H, s, H-21), 1.65 (3H, s, H-28), 1.67 (3H, s, H-29), 3.38 (1H, m, H-3), 3.95 (1H, m, H-12), 5.01 (1H, d,  $J=7.0$  Hz, H'-1), 5.14 (1H, d,  $J=7.0$  Hz, H''-1), 4.71 (1H, d,  $J=7.5$  Hz, H'''-1);  $^{13}C$ -NMR (125 MHz,  $C_5D_5N$ ):  $\delta$  40.1 (C-1), 26.2 (C-2), 89.2 (C-3), 39.7 (C-4), 56.9 (C-5), 18.9 (C-6), 35.6 (C-7), 40.5 (C-8), 50.7 (C-9), 36.6 (C-10), 30.4 (C-11), 70.6 (C-12), 49.9 (C-13), 51.8 (C-14), 28.6 (C-15), 26.6 (C-16), 52.1 (C-17), 16.7 (C-18), 16.4 (C-19), 83.9 (C-20), 23.7 (C-21), 37.4 (C-22), 22.5 (C-23), 126.4 (C-24), 131.5 (C-25), 27.1 (C-26), 18.3 (C-27), 31.0 (C-28), 17.8 (C-29), 17.2 (C-30), 105.0 (C'-1), 75.4 (C'-2), 78.8 (C'-3), 71.5 (C'-4), 72.6 (C'-5), 63.6 (C'-6), 98.6 (C''-1), 76.2 (C''-2), 79.2 (C''-3), 72.6 (C''-4), 74.5 (C''-5), 68.9 (C''-6), 107.4 (C'''-1), 72.0 (C'''-2), 73.9 (C'''-3), 79.6 (C'''-4), 65.9 (C'''-5).

## Results and Discussion

The structures of the compounds **1 - 10** were identified

by comparison of their spectral data with those reported in the literatures. The isolated dammarane type ginsenosides (**1 - 10**) were first reported from the Korean cultivated-wild ginseng.

Compound **1** was obtained as a colorless gum. The ESI-MS spectrum of **1** showed a quasimolecular ion peak at  $m/z$  823  $[M + Na]^+$ . The  $^1H$ -NMR spectrum showed eight methyl groups [ $\delta$  0.79 (3H, s, H-18), 1.02 (3H, s, H-19), 1.14 (3H, s, H-30), 1.59 (3H, s, H-26), 1.57 (3H, s, H-27), 1.56 (3H, s, H-21), 1.54 (3H, s, H-28), and 2.06 (3H, s, H-29)], and three oxygenated protons [ $\delta$  3.57 (1H, m, H-3), 4.51 (1H, m, H-6), 3.98 (1H, m, H-12)]. The  $^{13}C$ -NMR spectrum showed eight methyl carbons [ $\delta$  17.7 (C-18), 17.5 (C-19), 17.5 (C-30), 25.7 (C-26), 17.1 (C-27), 22.2 (C-21), 31.7 (C-28), and 16.3 (C-29)], four oxygenated carbons [ $\delta$  78.6 (C-3), 78.1 (C-6), 70.1 (C-12), 83.2 (C-20)], eight methylene carbons [ $\delta$  39.4 (C-1), 27.6 (C-2), 45.1 (C-7), 30.6 (C-11), 30.6 (C-15), 26.5 (C-16), 36.1 (C-22), 23.1 (C-23)], four methine carbons [ $\delta$  61.3 (C-5), 49.9 (C-9), 49.1 (C-13), 51.4 (C-17)], four quaternary carbons [ $\delta$  40.3 (C-4), 39.6 (C-8), 39.5 (C-10), 51.3 (C-14)] and two olefinic carbons [ $\delta$  125.9 (C-24), 130.8 (C-25)]. These spectral data suggested that **1** was protopanaxatriol dammarane type saponin (Tanaka and Yahara, 1978). The  $^1H$ - and  $^{13}C$ -NMR spectra exhibited two anomeric protons and carbons of sugars [ $\delta_H$  5.00 (1H, d,  $J=7.0$  Hz, H'-1), 5.16 (1H, d,  $J=7.0$  Hz, H''-1),  $\delta_C$  105.9 (C'-1), 98.2 and (C''-1)]. The down field shifts of C-6 and C-20 [ $\delta$  78.1 (C-6), 83.2 (C-20)] suggested that the positions of D-glucoses were at C-6 and C-20. Based on the above consideration and a comparison with the data in the literature (Chen *et al.*, 1981), the structure of **1** was identified as ginsenoside Rg<sub>1</sub>.

Compound **2** was obtained as a colorless gum. The ESI-MS spectrum of **2** showed a quasimolecular ion peak at  $m/z$  969  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **2** were similar to those of **1**, but three anomeric signals of sugar were shown at  $\delta_H$  5.16 (d,  $J=7.5$  Hz, H'-1), 5.62 (d,  $J=7.5$  Hz, H''-1), 5.23 (d,  $J=7.5$  Hz, H'''-1), and  $\delta_C$  101.8 (C'-1), 101.8 (C''-1), 98.2 (C'''-1). The signals at  $\delta_H$  1.58 (d,  $J=7.0$  Hz) and  $\delta_C$  18.7 suggested to be the presence of the L-rhamnose (Sanada *et al.*, 1974b). The down field shift of C-6 and C-20 [ $\delta$  74.5 (C-6), 83.2 (C-20)] suggested that the positions of two D-glucoses and a L-rhamnose were at C-6 and at C-20, respectively. Based on the above consideration and a comparison with the data in the literatures (Sanada *et al.*, 1974b; Tanaka and Yahara, 1978), the structure of **2** was identified as ginsenoside Re.

Compound **3** was obtained as a colorless gum. The

ESI-MS spectrum of **3** showed a quasimolecular ion peak at  $m/z$  1101  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **3** were similar to those of **1** and **2**, but oxygenated protons and carbons signals of **3** were exhibited at  $\delta_H$  3.27 (1H, m, H-3), 3.98 (1H, m, H-12) and  $\delta_C$  88.9 (C-3), 70.1 (C-12), and 83.3 (C-20). These spectral data suggested that **3** was protopanaxadiol dammarne type saponin (Morita *et al.*, 1986). Four anomeric signals in the  $^1H$ - and  $^{13}C$ -NMR spectra were shown at  $\delta_H$  4.98 (d,  $J=7.5$  Hz, H<sup>-1</sup>), 5.16 (d,  $J=7.5$  Hz, H<sup>-1</sup>), 5.38 (d,  $J=7.5$  Hz, H<sup>-1</sup>), and 5.58 (s, H<sup>-1</sup>) and  $\delta_C$  105.0 (C<sup>-1</sup>), 106.0 (C<sup>-1</sup>), 98.0 (C<sup>-1</sup>), and 110.0 (C<sup>-1</sup>), respectively. The anomeric proton signal at  $\delta$  5.58 (s, H<sup>-1</sup>) indicated to be a L-arabinose (Adinolfi *et al.*, 1988; Sanada *et al.*, 1974a). The down field shifts of C-3 and C-20 [ $\delta$  88.9 (C-3), 83.3 (C-20)] suggested that the position of sugars were at C-3 and C-20. Based on the above consideration and a comparison with the data in the literature (Sanada *et al.*, 1974a), the structure of **3** was identified as ginsenoside Rc.

Compound **4** was obtained as a colorless gum. The ESI-MS spectrum of **4** showed a quasimolecular ion peak at  $m/z$  1131 ( $[M + Na]^+$ ). The  $^1H$ - and  $^{13}C$ -NMR spectra of **4** were similar to those of **3**, but four anomeric proton signals of sugars in the  $^1H$ -NMR spectrum were shown at  $\delta$  4.98 (d,  $J=7.0$  Hz, H<sup>-1</sup>), 5.16 (d,  $J=7.0$  Hz, H<sup>-1</sup>), 5.18 (d,  $J=7.0$  Hz, H<sup>-1</sup>), and 5.39 (d,  $J=7.0$  Hz, H<sup>-1</sup>). Based on the above consideration and a comparison with the data in the literature (Chen *et al.*, 1981), the structure of **4** was identified as ginsenoside Rb<sub>1</sub>.

Compound **5** was obtained as a colorless gum. The ESI-MS spectrum of **5** showed a quasimolecular ion peak at  $m/z$  1101  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **5** were similar to of **3**, but the proton signal at  $\delta$  5.38 (d,  $J=7.0$  Hz, H<sup>-1</sup>) suggested L-arabinose (Yoshikawa *et al.*, 1993). Based on the above consideration and a comparison with the data in the literatures (Sanada *et al.*, 1974a; Morita *et al.*, 1986), the structure of **5** was determined to be ginsenoside Rb<sub>2</sub>.

Compound **6** was obtained as a colorless gum. The ESI-MS spectrum of **6** showed a quasimolecular ion peak at  $m/z$  969  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **6** were similar to those of **4**, but three anomeric signals of sugars were shown at  $\delta_H$  4.95 (d,  $J=7.0$  Hz, H<sup>-1</sup>), 5.19 (d,  $J=7.0$  Hz, H<sup>-1</sup>), 5.35 (d,  $J=7.0$  Hz, H<sup>-1</sup>) and  $\delta_C$  105.0 (C<sup>-1</sup>), 106.0 (C<sup>-1</sup>), 98.2 (C<sup>-1</sup>). Based on the above consideration and a comparison with the data in the literature (Tanaka and Yahara, 1978), the structure of **6** was identified as ginsenoside Rd.

Compound **7** was obtained as a colorless gum. The  $\alpha$  value was +22.0 ( $c=0.20$ , MeOH). The ESI-MS spectrum

of **7** showed a quasimolecular ion peak at  $m/z$  807  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **7** were similar to those of **6**, but two anomeric signals of sugars were shown at  $\delta_H$  4.92 (d,  $J=7.5$  Hz, H<sup>-1</sup>), 5.19 (d,  $J=8.0$  Hz, H<sup>-1</sup>) and  $\delta_C$  104.3 (C<sup>-1</sup>), 98.7 (C<sup>-1</sup>). The down field shift of C-3 [ $\delta$  83.7 (C-3)] suggested that the position of sugars were at C-3. Based on the above consideration and a comparison with the data in the literatures (Kasai *et al.*, 1983; Kitagawa *et al.*, 1983), the structure of **7** was identified as ginsenoside Rg<sub>3</sub>.

Compound **8** was obtained as a colorless gum. The ESI-MS spectrum of **8** showed a quasimolecular ion peak at  $m/z$  807  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **8** were similar to those of **7**, but the down field shift of C-3 and C-20 [ $\delta$  89.7 (C-3) and 83.6 (C-20)] suggested that the positions of sugars were at C-3 and C-20. Based on the above consideration and a comparison with the data in the literature (Yahara *et al.*, 1976), the structure of **8** was identified as ginsenoside F<sub>2</sub>.

Compound **9** was obtained as a colorless gum. The ESI-MS spectrum of **9** showed a quasimolecular ion peak at  $m/z$  1101  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **9** were similar to those of **6**, but the anomeric signal of D-xylose was shown at  $\delta_H$  5.39 (d,  $J=7.5$  Hz, H<sup>-1</sup>),  $\delta_C$  105.5. Based on the above consideration and a comparison with the data in the literatures (Tanaka and Yahara, 1978; Sanada and Shoji, 1978), the structure of **9** was identified as ginsenoside Rb<sub>3</sub>.

Compound **10** was obtained as a colorless gum. The ESI-MS spectrum of **10** showed a quasimolecular ion peak at  $m/z$  939  $[M + Na]^+$ . The  $^1H$ - and  $^{13}C$ -NMR spectra of **10** were similar to those of **5**, but only three anomeric signals of sugar were shown at  $\delta_H$  5.01 (d,  $J=7.0$  Hz, H<sup>-1</sup>), 5.14 (d,  $J=7.0$  Hz, H<sup>-1</sup>), 4.71 (d,  $J=7.5$  Hz, H<sup>-1</sup>) and  $\delta_C$  105.0 (C<sup>-1</sup>), 98.6 (C<sup>-1</sup>), 107.4 (C<sup>-1</sup>). Based on the above consideration and a comparison with the data in the literature (Koizumi *et al.*, 1982), the structure of **10** was determined to ginsenoside Rd<sub>2</sub>.

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