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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_1 (**1**), ginsenoside Re (**2**), ginsenoside Rc (**3**), ginsenoside Rb_1 (**4**), ginsenoside Rb_2 (**5**), ginsenoside Rd (**6**), ginsenoside Rg_3 (**7**), ginsenoside F_2 (**8**), ginsenoside Rb_3 (**9**), and ginsenoside Rd_2 (**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® RP-C_{18} (5 μ, 10 × 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 (Silica gel 60, 70 - 230 mesh, Merck Co., Germany). Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} and RP-18 F_{254s} (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 μm, Merck Co., Germany). Low pressure liquid chromatography was carried out over a Lobar®-A glass prepacked column (Lichroprep® Si 60, Lichroprep® RP-18, 240 × 10 mm, 40 - 63 μm, Merck Co., Germany), a FMI QSY-0 pump (Fluid metering, Inc., USA), and a Duramat® 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), $CHCl_3$ (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_2O (70 : 30) and a RP-18 column chromatography (MeOH-H_2O = 60 : 40) to give six fractions (R1 - R7). The R1 fraction (700.0 mg) was subjected to RP-18 column chromatography (MeOH-H_2O = 60 : 40) and LiChroprep silica Lobar®-A columns ($CHCl_3$-MeOH-H_2O = 6 : 3 : 0.1), and purified by semi-preparative HPLC (CH_3CN-H_2O = 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_2O = 70 : 30), and purified using semi-preparative HPLC (MeOH-H_2O = 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®-A RP-18 (MeOH-H_2O = 75 : 25), and purified using semi-preparative HPLC (MeOH-H_2O = 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®-A (MeOH-H_2O = 55 : 45), and purified using semi-preparative HPLC (MeOH-H_2O = 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®-A (MeOH-H_2O = 65 : 35), and purified using semi-preparative HPLC (MeOH-H_2O = 65 : 35) to afford **9** (5.0 mg, 0.014% w/w) and **10** (5.0 mg, 0.014% w/w).

Ginsenoside Rg_1 (**1**) – Colorless gum; $[\alpha]_D$: +15.0 (*c* = 0.22, MeOH); ESI-MS: *m/z* 823 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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'-1), 5.16 (1H, d, *J* = 7.0 Hz, H"-1); ^{13}C-NMR (125 MHz, C_5D_5N): δ 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'-1), 75.4 (C'-2), 80.1 (C'-3), 71.6 (C'-4), 79.6 (C'-5), 63.0 (C'-6), 98.2 (C"-1), 75.1 (C"-2), 79.3 (C"-3), 70.1 (C"-4), 78.2 (C"-5), 62.9 (C"-6).

Ginsenoside Re (**2**) – Colorless gum; $[\alpha]_D$: –10.2 (*c* = 0.10, MeOH); ESI-MS: *m/z* 969 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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'-1), 5.62 (1H, d, *J* = 7.5 Hz, H"-1), 1.58 (1H, d, *J* = 7.0 Hz, H-6"), 5.23 (1H, d, *J* = 7.5 Hz, H"'-1); ^{13}C-NMR (125 MHz, C_5D_5N): δ 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'-1), 79.1 (C'-2), 78.0 (C'-3), 72.1 (C'-4), 78.0 (C'-5), 63.0 (C'-6), 101.8 (C"-1), 72.1 (C"-2), 72.1 (C"-3), 73.8 (C"-4), 69.3 (C"-5), 18.7 (C"-6), 98.2 (C"'-1), 74.9 (C"'-2), 78.8 (C"'-3), 71.3 (C"'-4), 77.8 (C"'-5), 62.8 (C"'-6).

Ginsenoside Rc (**3**) – Colorless gum; $[\alpha]_D$: +5.2 (*c* = 0.14, MeOH); ESI-MS: *m/z* 1101 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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'-1), 5.16 (1H, d, *J* = 7.5 Hz, H"-1), 5.38 (1H, d, *J* = 7.5 Hz, H"'-1), 5.58 (1H, s, H""-1); ^{13}C-NMR (125 MHz, C_5D_5N): δ 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'-1), 83.1 (C'-2), 77.8 (C'-3), 71.5 (C'-4), 77.8 (C'-5), 62.8 (C'-6), 106.0 (C"-1), 76.8 (C"-2), 78.7 (C"-3), 71.5 (C"-4), 78.0 (C"-5), 62.6 (C"-6), 98.0 (C"'-1), 74.9 (C"'-2), 78.0 (C"'-3), 71.5 (C"'-4), 76.3 (C"'-5), 68.4 (C"'-6), 110.0 (C""-1), 83.3 (C""-2), 78.9 (C""-3), 85.8 (C""-4), 62.5 (C""-5).

Ginsenoside Rb_1 (**4**) – Colorless gum; $[\alpha]_D$: +15.2 (*c* = 0.15, MeOH); ESI-MS: *m/z* 1131 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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'-1), 5.16 (1H, d, *J* = 7.0 Hz, H"-1), 5.18 (1H, d, *J* = 7.0 Hz, H"'-1), 5.39 (1H, d, *J* = 7.0 Hz, H""-1); ^{13}C-NMR (125 MHz, C_5D_5N): δ 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'-1), 83.1 (C'-2), 78.8 (C'-3),

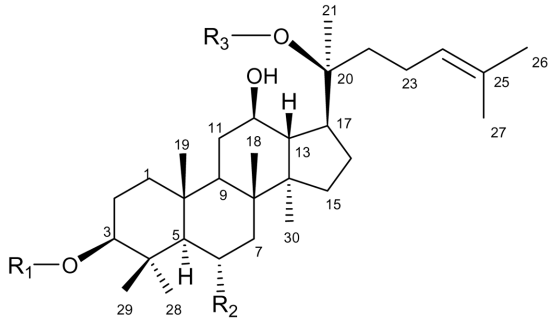
71.5 (C'-4), 78.0 (C'-5), 62.6 (C'-6), 106.0 (C"-1), 76.8 (C"-2), 78.7 (C"-3), 71.5 (C"-4), 78.0 (C"-5), 62.7 (C"-6), 98.0 (C"'-1), 74.9 (C"'-2), 78.0 (C"'-3), 71.5 (C"'-4), 76.7 (C"'-5), 70.1 (C"'-6), 105.0 (C""-1), 74.9 (C""-2), 78.8 (C""-3), 71.5 (C""-4), 78.0 (C""-5), 62.6 (C""-6).

Ginsenoside Rb_2 (**5**) – Colorless gum; $[\alpha]_D$: +11.0 (c = 0.10, MeOH); ESI-MS: *m/z* 1101 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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), 5.38 (1H, d, J = 7.0 Hz, H""-1); ^{13}C-NMR (125 MHz, C_5D_5N): δ 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; $[\alpha]_D$: +13.0 (c = 0.25, MeOH); ESI-MS: *m/z* 969 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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): δ 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_3 (**7**) – Colorless gum; $[\alpha]_D$: +22.0 (c = 0.20, MeOH); ESI-MS: *m/z* 807 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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, 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): δ 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_2 (**8**) – Colorless gum; $[\alpha]_D$: +7.5 (c = 0.15, MeOH); ESI-MS: *m/z* 807 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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): δ 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



	R_1	R_2	R_3
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**.

(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_3 (**9**) – Colorless gum; $[\alpha]_D$: +17.0 (c = 0.10, MeOH); ESI-MS: *m/z* 1101 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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): δ 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_2 (**10**) - Colorless gum; $[\alpha]_D$: +18.0 (c = 0.15, MeOH); ESI-MS: *m/z* 939 $[M + Na]^+$; ^{1}H-NMR (500 MHz, C_5D_5N): δ 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 = 7.5Hz, H'''-1); ^{13}C-NMR (125 MHz, C_5D_5N): δ 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 ^{1}H-NMR spectrum showed eight methyl groups [δ 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 [δ 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 [δ 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 [δ 78.6 (C-3), 78.1 (C-6), 70.1 (C-12), 83.2 (C-20)], eight methylene carbons [δ 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 [δ 61.3 (C-5), 49.9 (C-9), 49.1 (C-13), 51.4 (C-17)], four quaternary carbons [δ 40.3 (C-4), 39.6 (C-8), 39.5 (C-10), 51.3 (C-14)] and two olefinic carbons [δ 125.9 (C-24), 130.8 (C-25)]. These spectral data suggested that **1** was protopanaxatriol dammarane type saponin (Tanaka and Yahara, 1978). The ^{1}H- and ^{13}C-NMR spectra exhibited two anomeric protons and carbons of sugars [δ_H 5.00 (1H, d, J = 7.0 Hz, H'-1), 5.16 (1H, d, J = 7.0 Hz, H''-1), δ_C 105.9 (C'-1), 98.2 and (C''-1)]. The down field shifts of C-6 and C-20 [δ 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_1.

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 ^{1}H- and ^{13}C-NMR spectra of **2** were similar to those of **1**, but three anomeric signals of sugar were shown at δ_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 δ_C 101.8 (C'-1), 101.8 (C''-1), 98.2 (C'''-1). The signals at δ_H 1.58 (d, J = 7.0 Hz) and δ_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 [δ 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 δ_H 3.27 (1H, m, H-3), 3.98 (1H, m, H-12) and δ_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 δ_H 4.98 (d, J = 7.5 Hz, H'-1), 5.16 (d, J = 7.5 Hz, H''-1), 5.38 (d, J = 7.5 Hz, H'''-1), and 5.58 (s, H''''-1) and δ_C 105.0 (C'-1), 106.0 (C''-1), 98.0 (C'''-1), and 110.0 (C''''-1), respectively. The anomeric proton signal at δ 5.58 (s, H''''-1) indicated to be a L-arabinose (Adinolfi *et al*., 1988; Sanada *et al*., 1974a). The down field shifts of C-3 and C-20 [δ 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 δ 4.98 (d, J = 7.0 Hz, H'-1), 5.16 (d, J = 7.0 Hz, H''-1), 5.18 (d, J = 7.0 Hz, H'''-1), and 5.39 (d, J = 7.0 Hz, H''''-1). 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_1.

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 δ 5.38 (d, J = 7.0 Hz, H''''-1) 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_2.

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 δ_H 4.95 (d, J = 7.0 Hz, H'-1), 5.19 (d, J = 7.0 Hz, H''-1), 5.35 (d, J = 7.0 Hz, H'''-1) and δ_C 105.0 (C'-1), 106.0 (C''-1), 98.2 (C'''-1). 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 α 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 δ_H 4.92 (d, J = 7.5 Hz, H'-1), 5.19 (d, J = 8.0 Hz, H''-1) and δ_C 104.3 (C'-1), 98.7 (C''-1). The down field shift of C-3 [δ 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_3.

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 [δ 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_2.

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 δ_H 5.39 (d, J = 7.5 Hz, H''''-1), δ_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_3.

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 δ_H 5.01 (d, J = 7.0 Hz, H'-1), 5.14 (d, J = 7.0 Hz, H''-1), 4.71 (d, J = 7.5 Hz, H'''-1) and δ_C 105.0 (C'-1), 98.6 (C''-1), 107.4 (C'''-1). 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_2.

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