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Identification of Dammarane-type Triterpenoid Saponins from the Root of *Panax ginseng*

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Abstruct – The root of *Panax ginseng*, is a Korea traditional medicine, which is used in both raw and processed forms due to their different pharmacological activities. As part of a continued chemical investigation of ginseng, the focus of this research is on the isolation and identification of compounds from *Panax ginseng* root by open column chromatography, medium pressure liquid chromatography, semi-preparative-high performance liquid chromatography, Fast atom bombardment mass spectrometric, and nuclear magnetic resonance. Dammarane-type triterpenoid saponins were isolated from *Panax ginseng* root by open column chromatography, medium pressure liquid chromatography, and semi-preparative-high performance liquid chromatography. Their structures were identified as protopanaxadiol ginsenosides [gypenoside-V (**1**), ginsenosides-Rb1 (**2**), -Rb2 (**3**), -Rb3 (**4**), -Rc (**5**), and -Rd (**6**)], protopanaxatriol ginsenosides [20(*S*)-notoginsenoside-R2 (**7**), notoginsenoside-Rt (**8**), 20(*S*)-*O*-glucoginsenoside-Rf (**9**), 6-*O*-[α-L-rhamnopyranosyl(1 → 2)-β-D-glucopyranosyl]-20-*O*-β-D-glucopyranosyl-3β,12β, 20(*S*)-dihydroxy-dammar-25-en-24-one (**10**), majoroside-F6 (**11**), pseudoginsenoside-Rt3 (**12**), ginsenosides-Re (**13**), -Re5 (**14**), -Rf (**15**), -Rg1 (**16**), -Rg2 (**17**), and -Rh1 (**18**), and vinaginsenoside-R15 (**19**)], and oleanene ginsenosides [calenduloside-B (**20**) and ginsenoside-Ro (**21**)] through the interpretation of spectroscopic analysis. The configuration of the sugar linkages in each saponin was established on the basic of chemical and spectroscopic data. Among them, compounds **1**, **8**, **10**, **11**, **12**, **19**, and **20** were isolated for the first time from *P. ginseng* root.

Keywords – *Panax ginseng*, Ginsenoside, Dammarane-type triterpenoid, Saponin

Introduction

Panax ginseng (Araliaceae) is a traditional medicinal plant that has been used therapeutically for thousands of years in East Asia. The name "*Panax*" means "all healing" or "all cure", which describes the traditional belief that ginseng can heal all aspects of the body.[1] The name "*ginseng*" is derived from Chinese word "Jin-chen", meaning human body-shaped root.[2] Ginseng, notably the root of *P. ginseng*, is the most valuable of all medicinal plants in Korea, China, and Japan.[3,4] Ginseng can be commonly classified into Korean ginseng (*P. ginseng*), Chinese ginseng (*P. notoginseng*), and American ginseng (*P. quinquefolium*).[5]

Ginseng has been used as an adaptogenic agent and is known to have a positive effect on inflammation and aging, immune-modulating functions, the central nervous system, cardiovascular system, diabetes, and cancer, as well as having antioxidant, hypotensive, antitumor, cognitive, sedative, and analgesic benefits.[6-12] Saponins are the major constituents of ginseng.[13-15] To date, approximately 70 kinds of saponins have been isolated from ginseng and named as ginsenosides. Most of the aglycone moieties of ginsenosides are protopanaxadiol (PPD) and protopanaxatriol (PPT).[16-17] The algycone of ginsenoside Ro is an oleanolic acid.[18,19]

As part of a continued chemical investigation of ginseng, the focus of this research is on the isolation and identification of compounds from ginseng by open column chromatography (CC), medium pressure liquid chromatography (MPLC), semi-preparative-high performance liquid chromatography (SemiPrep-HPLC), fast atom bombardment mass spectrometry (FAB-MS), and nuclear magnetic resonance (NMR).

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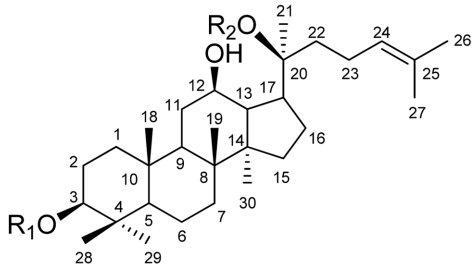
Experimental

Plant materials – Dried and powdered white ginseng (*P. ginseng*) collected from Geumsan (2010), was supplied by Korea Food Research Institute, Sungnam, Republic of Korea.

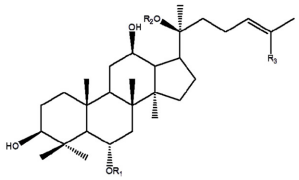
Reagents and instruments – Solvents such as ethanol (EtOH), *n*-hexane, chloroform ($CHCl_3$), ethyl acetate (EtOAc), and *n*-butanol (*n*-BuOH) (SamChun Pure Chemical Co., Pyeongtaek, Korea) were used in the MPLC mobile phase. HPLC-grade acetonitrile (ACN) and water were purchased from J.T. Baker (Phillipsburg, NJ, USA). Pyridine was used as NMR solution. All other solvents were analytical grade. EI-MS was conducted with a Jeol JMS-600W (Tokyo, Japan) mass spectrometer, and FAB-MS was performed with a Jeol JMS-AX505WA mass spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AVANCE 500 NMR (Bremen, Germany) spectrometer using tetramethyl silane (TMS) as the internal standard. Chemical shifts are reported in parts per million (δ), and coupling constants (*J*) are expressed in Hertz. An Eyela rotary evaporator system (Tokyo, Japan) under reflux *in vacuo* was used for evaporation. Thin layer chromatography (TLC) was conducted with Kiesel gel 60 F_{254} (Art. 5715, Merck Co., Darmstadt, Germany) plates (silica gel, 0.25 mm layer thickness), and compounds were visualized by spraying with 10% H_2SO_4 in methanol (MeOH), followed by heating to 100 °C. CC was conducted with a LiChroprep RP-18 (40 - 63 μm, Merck Co., Germany) and Sephadex LH-20 (100 - 100G; Sigma-Aldrich Co., USA). MPLC (Biotage, Uppsala, Sweden) equipped with cartridges (KP-SIL, 39 × 225 mm) was used. SemiPrep-HPLC was carried out on an Agilent series 1260 separation system (Santa Clara, CA, USA) with fraction collector, 1260 Quat pump VL, a 1260 Variable Wavelength Detector, and an Eclipse XDB-C_{18} SemiPreparative column (5 μm, 150 × 9.4 mm), at an elution flow rate of 1.0 mL/min. Gas chromatography (GC) (HP 5890 series II, Hewlett-Packard, Avondale, PA) using a HP-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness; Agilent, J&W Scientific, Folsom, CA) [column temperature: 230 °C; detector temperature: 200°C; injector temperature: 200 °C; He gas flow rate: 1 mL/min] was used for sugar determination.

Extraction and isolation – Dried and powdered white ginseng (7.0 kg) was extracted with EtOH (21 L × 3) under reflux, and the extracts were combined and evaporated, leaving a brown residue (139 g). The residue was dissolved in water (7 L) and partitioned successively with *n*-hexane (7 L × 3), $CHCl_3$ (7 L × 3), EtOAc (7 L × 3), and *n*-BuOH (7 L × 3) to give the *n*-hexane (50 g), $CHCl_3$ (11 g), EtOAc (11 g), and *n*-BuOH (50 g) fractions. The *n*-BuOH fraction of white ginseng (WGB) was subjected to MPLC eluted with a $CHCl_3$/MeOH gradient (100:0 → 0:100). Fractions were combined according to their TLC behavior in order to obtain 13 fractions (WGB 1 → WGB 13). Fraction WGB 2 (2 g, Ve/Vt = 0.11, where Ve refers to the volume of eluent for the corresponding fraction and Vt represents the total elution volume) was repeatedly chromatographed on an MPLC eluted with $CHCl_3$/MeOH (80:20 → 0:100) eluent (1,408 mL) to obtain 5 fractions (WGB 2.1 - 2.5). WGB 2.5 (1.1 g, Ve/Vt = 0.47) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) eluent (2,370 mL) to obtain 7 fractions (WGB 2.5.1 - 2.5.7). WGB 2.5.4 (70 mg, Ve/Vt = 0.01) was further fractionated by SemiPrep-HPLC eluted with ACN/water (20:80 → 0:100) to yield 9 additional fractions (WGB 2.5.4.1 - 2.5.4.9) including compound **8** (WGB 2.5.4.7, 3 mg) (Table 2). WGB 2.5.3 (100 mg, Ve/Vt = 0.01) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:2 → 1:0) to yield 4 additional fractions (WGB 2.5.3.1 - 2.5.3.4) including compound **12** (WGB 2.5.3.2, 3 mg). Fraction WGB 4 (8 g, Ve/Vt = 0.15) was repeatedly chromatographed on an MPLC eluted with $CHCl_3$/MeOH (100:0 → 0:100) eluent (1,254 mL) to obtain 7 fractions (WGB 4.1 - 4.7). WGB 4-4 (250 mg, Ve/Vt = 0.05) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:2 → 1:0) eluent (286 mL) to obtain 13 fractions (WGB 4.4.1 - 4.4.13). WGB 4-4-9

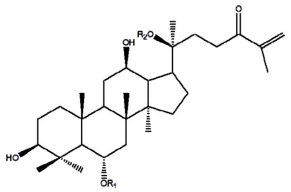


Gypenoside-V (**1**)	R_1: Glc2 → Glc	R_2: Glc6 → Rha
Ginsenoside-Rb1 (**2**)	R_1: Glc2 → Glc	R_2: Glc6 → Glc
Ginsenoside-Rb2 (**3**)	R_1: Glc2 → Glc	R_2: Glc6 → Ara
Ginsenoside-Rb3 (**4**)	R_1: Glc2 → Glc	R_2: Glc6 → Xyl
Ginsenoside-Rc (**5**)	R_1: Glc2 → Glc	R_2: Glc6 → Ara(f)
Ginsenoside-Rd (**6**)	R_1: Glc2 → Glc	R_2: Glc

Fig. 1. Chemical structures of PPD types.

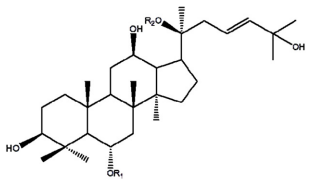


20(*S*)-Notoginsenoside-R2 (**7**)	R_1: Glc2 → Xyl	R_2: H	R_3: CH_3
Notoginsenoside-Rt (**8**)	R_1: Glc6 → OAc	R_2: Glc	R_3: CH_3
20(*S*)-*O*-Glucoginsenoside-Rf (**9**)	R_1: Glc2 → Glc	R_2: Glc	R_3: CH_3
Pseudoginsenoside-RT3 (**12**)	R_1: Xyl	R_2: Glc	R_3: CH_3
Ginsenoside-Re (**13**)	R_1: Glc2 → Rha	R_2: Glc	R_3: CH_3
Ginsenoside-Re5 (**14**)	R_1: Glc2 → Glc	R_2: H	R_3: CH_2OH
Ginsenoside-Rf (**15**)	R_1: Glc2 → Glc	R_2: H	R_3: CH_3
Ginsenoside-Rg1 (**16**)	R_1: Glc	R_2: Glc	R_3: CH_3
Ginsenoside-Rg2 (**17**)	R_1: Glc2 → Rha	R_2: H	R_3: CH_3
Ginsenoside-Rh1 (**18**)	R_1: Glc	R_2: H	R_3: CH_3



6-*O*-[*α*-L-Rhamnopyranosyl(1→2)-β-D-glucopyranosyl]-20-*O*-β-D-glucopyranosyl-3β,12β,20(*S*)-dihydroxy-dammar-25-en-24-one (**10**)

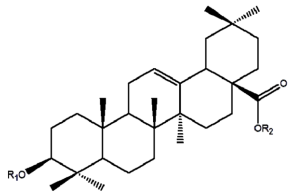
R_1: Glc2 → Rha R_2: Glc



Majotoside-F6 (**11**)	R_1: Glc2 → Rha	R_2: Glc
Vinaginsenoside-R15 (**19**)	R_1: Glc	R_2: Glc

Fig. 2. Chemical structures of PPT types.

(180 mg, Ve/Vt = 0.08) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) eluent (462 mL) to obtain 21 fractions (WGB 4.4.9.1 - 4.4.9.21). WGB 4.4.9.5 (70 mg, Ve/Vt = 0.01) was further fractionated by SemiPrep-HPLC eluted with ACN/water (20:80 → 0:100) to yield 9 additional fractions (WGB 4.4.9.5.1 - 4.4.9.5.8) including compound **14** (WGB 4.4.9.5.2, 3 mg). The combined fractions (WGB 4.5, 4.6 and 4.7; 3 g, Ve/Vt = 0.42) were separated on an MPLC eluted with $CHCl_3$/MeOH (90:10 → 0:100) eluent (748 mL) to obtain 6 fractions (WGB 4.5.1 - 4.5.6). WGB 4.5.6 (350 mg, Ve/Vt = 0.15) was separated a Sephadex LH-20 column (φ 1.0 × 32 cm) eluted with 70% MeOH eluent (580 mL) to obtain 3 fractions (WGB 4.5.6.1 - 4.5.6.3). WGB 4.5.6.2 (50 mg, Ve/Vt = 0.66) was separated



Calenduloside-B (**20**)	R_1: Glc4 → Gal	R_2: Glc
Ginsenoside-Ro (**21**)	R_1: GlcUA2 → Glc	R_2: Glc

Fig. 3. Chemical structures of oleanene types.

a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) eluent (420 mL) to obtain 10 fractions (WGB 4.5.6.2.1 - 4.5.6.2.10) including compound **1** (WGB 4.5.6.2.10, 2.5 mg). WGB 4.5.2 (920 mg, Ve/

Vt = 0.12) was separated on an MPLC eluted with $CHCl_3$/MeOH (75:25 → 100:0) eluent (2,948 mL) to obtain 6 fractions (WGB 4.5.2.1 - 4.5.2.6). WGB 4.5.2.6 (340 mg, Ve/Vt = 0.57) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) to yield 6 additional fractions (WGB 4.5.2.6.1 - 4.5.2.6.6) including compound **11** (WGB 4.5.2.6.2, 2.5 mg). WGB 4.4 (0.5 g, Ve/Vt = 0.1) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:2 → 1:0) eluent (286 mL) to obtain 13 fractions (WGB 4.4.1 - 4.4.13) including compounds **16** (WGB 4.4.7, 10 mg) and **17** (WGB 4.4.9, 2 mg). WGB 4.4.11 (30 mg, Ve/Vt = 0.12) was further fractionated by LiChroprep RP18 column (φ 1.0 × 32 cm) to yield 5 additional fractions (WGB 4.4.11.1 - 4.4.11.5) including compound **19** (WGB 4.4.11.2, 1 mg). Fraction WGB 5 (8 g, Ve/Vt = 0.15) was repeatedly chromatographed on an MPLC eluted with $CHCl_3$/MeOH (100:0 → 0:100) eluent (2,222 mL) to obtain 9 fractions (WGB 5.1 - 5.9). WGB 5.3 (100 mg, Ve/Vt = 0.04) was further fractionated by SemiPrep-HPLC eluted with ACN/water (20:80 → 0:100) to yield 3 additional fractions (WGB 5.3.1 - 5.3.3) including compound **18** (WGB 5.3.3, 3 mg) (Table 2). WGB 5.6 (450 mg, Ve/Vt = 0.09) was repeatedly chromatographed on an MPLC eluted with $CHCl_3$/MeOH (80:20 → 70:30) eluent (1,892 mL) to obtain 9 fractions (WGB 5.6.1 - 5.6.9). WGB 5.6.4 (220 mg, Ve/Vt = 0.12) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) to yield 7 additional fractions (WGB 5.6.4.1 - 5.6.4.7). WGB 5.6.4.4 (450 mg, Ve/Vt = 0.09) was repeatedly chromatographed on an MPLC eluted with $CHCl_3$/MeOH (80:20 → 70:30) to obtain 6 fractions (WGB 5.6.4.4.1 - 5.6.4.4.6) including compounds **21** (WGB 5-6-4-4-3, 2.5 mg). WGB 5.8 (3.1 g, Ve/Vt = 0.24) was further chromatographed on an MPLC eluted with $CHCl_3$/MeOH (80:20 → 0:100) eluent (3,960 mL) to obtain 7 additional fractions (WGB 5.8.1 - 5.8.7) including compounds **3** (WGB 5.8.6, 4.5 mg) and **7** (WGB 5.8.4, 2.5 mg). WGB 5.8.5 (1.3 g, Ve/Vt = 0.17) was chromatographed on an MPLC eluted with $CHCl_3$/MeOH (80:20 → 60:40) eluent (3,080 mL) to obtain 4 additional fractions (WGB 5.8.5.1 - 5.8.5.4) including compound **5** (WGB 5.8.5.4, 10.5 mg). WGB 5.8.5.2 (105 mg, Ve/Vt = 0.16) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) to yield 11 additional fractions (WGB 5.8.5.2.1 - 5.8.5.2.11) including compounds **6** (WGB 5.8.5.2.10, 12.5 mg), **13** (WGB 5.8.5.2.4, 25.5 mg), and **15** (WGB 5.8.5.2.8, 12.5 mg). WGB 5.8.7 (24 mg, Ve/Vt = 0.15) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) to yield 9 additional fractions (WGB 5.8.7.1 - 5.8.7.9) including compound **10** (WGB 5.8.7.8, 2.1 mg). Fraction 10 (7 g) was repeatedly chromatographed on an MPLC eluted with $CHCl_3$/MeOH (100:0 → 0:100) eluent (3,300 mL) to obtain 5 fractions (WGB 10.1 - 10.5). WGB 10.5 (2.7 g, Ve/Vt = 0.47) was chromatographed on an MPLC eluted with $CHCl_3$/MeOH (70:30 → 0:100) eluent (1,694 mL) to obtain 5 additional fractions (WGB 10.5.1 - 10.5.5) including compound **2** (WGB 10.5.2, 4.5 mg). The combined fractions (WGB 10.5.3 and 10.5.4; 2.7 g, Ve/Vt = 0.47) were chromatographed on an MPLC eluted with $CHCl_3$/MeOH (45:55→ 0:100) eluent (5,280 mL) to obtain 5 additional fractions (WGB 10.5.3.1 - 10.5.3.5) including compound **4** (WGB 10.5.3.2, 3.5 mg). WGB 10.5.3.5 (420 mg, Ve/Vt = 0.63) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) to yield 11 additional fractions (WGB 10.5.3.5.1 - 10.5.3.5.11) including compound **20** (WGB 4.5.2.6.2, 1.2 mg). Fraction WGB 11 (3 g, Ve/Vt = 0.11) was separated a Sephadex LH-20 column (φ 2.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) eluent (418 mL) to obtain 4 fractions (WGB 11.1 - 11.4). WGB 11.2 (520 mg, Ve/Vt = 0.42) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:1 → 1:0) to yield 4 fractions (WGB 11.2.1 - 11.2.4). WGB 11.2.4 (370 mg, Ve/Vt = 0.14) was separated a LiChroprep RP18 column (φ 1.0 × 32 cm) eluted with MeOH/water (1:3 → 1:0) to yield 7 additional fractions (WGB 11.2.4.1 - 11.2.4.7) including compound **9** (WGB 11.2.4.7, 1.5 mg).

Compound **1**; White amorphous powder; TLC (Rf = 0.28, $CHCl_3$:MeOH:water = 60:40:2); IR (KBr): ν_{max} 3355 and 1071 (hydroxyl groups and glycosidic linkage) cm^{-1}; FAB-MS: *m/z* 1,115 $[M+Na]^+$; ^1H- and ^{13}C-NMR (500 MHz, pyridine) data: Table 1.

Compound **8**; White amorphous powder; TLC (Rf = 0.81, $CHCl_3$:MeOH:H_2O = 60:40:2); IR (KBr): ν_{max} 3355 and 1073 (hydroxyl groups and glycosidic linkage) cm^{-1}; FAB-MS: *m/z* 865 $[M+Na]^+$; ^1H- and ^{13}C-NMR (500 MHz, pyridine) data: Table 1.

Compound **10**; White amorphous powder; TLC (Rf = 0.17, $CHCl_3$:MeOH:water = 70:30:2); IR (KBr): ν_{max} 3344 and 1071 (hydroxyl groups and glycosidic linkage) cm^{-1}; FAB-MS: *m/z* 983 $[M+Na]^+$; ^1H- and ^{13}C-NMR (500 MHz, pyridine) data: Table 1.

Compound **11**; White amorphous powder; TLC (Rf = 0.33, $CHCl_3$:MeOH:water = 60:40:2); IR (KBr): ν_{max} 3348 and 1071 (hydroxyl groups and glycosidic linkage) cm^{-1}; FAB-MS: *m/z* 985 $[M+Na]^+$; ^1H- and ^{13}C-NMR (500 MHz, pyridine) data: Table 1.

Table 1. ^{1}H- and ^{13}C-NMR data for compounds **1**, **8**, **10**, **11**, **12**, **19**, and **20**

No.	**1**		**8**		**10**		**11**		**12**		**19**		**20**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1	0.84, 1.56	40.1	0.74, 1.51	40.2	0.81, 1.54	40.1	0.82, 1.45	39.9	0.75, 1.50	40.2	0.78, 1.46	39.7	0.85, 1.45	39.1
2	1.71, 1.95	26.2	1.81, 2.15	27.0	1.82.2.19	27.3	1.79, 1.97	27.2	1.75, 2.03	27.2	1.78, 1.95	28.3	1.84, 2.12	28.7
3	3.25	89.5	3.52	80.27	3.54	79.8	3.49	78.8	3.48	79.7	3.41	80.1	3.24	89.9
4	-	40.4	-	39.9	-	39.9	-	40.1	-	39.9	-	39.7	-	39.1
5	0.71	56.9	1.45	61.9	1.51	61.3	1.49	61.3	1.45	61.9	1.21	61.9	0.76	56.3
6	1.47, 1.38	18.2	4.63	78.7	4.63	78.8	4.37	79.1	4.35	80.7	4.51	80.5	1.28, 1.48	18.3
7	1.23, 1.45	35.1	1.95, 2.54	45.9	1.84, 2.46	46.3	1.88, 2.45	46.4	1.78, 2.51	46.2	1.91, 2.45	45.5	1.27, 1.42	33.5
8	-	40.1	-	40.7	-	40.1	-	40.4	-	40.7	-	39.9	-	40.0
9	1.38	52.2	1.56	52.1	1.52	50.1	1.53	49.0	1.57	51.9	1.53	49.6	1.61	49.9
10	-	40.1	-	40.7	-	40.1	-	40.6		40.7	-	40.8	-	37.4
11	1.39, 1.92	31.2	1.41, 1.95	31.4	1.43, 1.87	32.6	1.50, 2.09	31.3	1.45, 1.93	31.4	1.45, 2.01	31.1	1.94, 2.13	24.1
12	4.09	70.7	3.95	70.7	4.03	70.9	3.90	70.4	4.01	70.9	4.05	70.1	5.36	123.8
13	2.04	51.9	1.99	51.9	1.95	52.0	2.06	49.5	2.02	51.9	2.08	50.4	-	144.6
14	-	52.2	-	49.7	-	50.0	-	50.0	-	50.5	-	52.7	-	52.6
15	1.02, 1.57	32.7	1.16, 1.72	31.3	1.02, 1.67	33.3	0.97, 1.52	31.5	1.15, 1.65	31.4	1.09, 1.54	31.5	1.12, 2.14	28.7
16	1.37, 1.75	26.2	1.42, 1.85	28.3	1.35, 1.85	27.2	1.32, 1.77	26.2	1.37, 1.84	26.2	1.45, 1.77	26.9	1.85	23.9
17	2.46	52.2	2.45	52.1	2.54	52.6	2.36	52.0	2.42	51.4	2.40	52.7	-	46.7
18	0.98	17.1	1.05	17.0	0.94	17.6	0.94	17.5	1.15	17.0	1.21	16.8	3.42	42.2
19	0.91	17.7	0.92	17.8	1.02	17.7	1.04	17.7	0.98	17.3	1.09	17.4	1.84	47.5
20	-	83.8	-	83.8	-	83.8	-	83.7	-	83.8	-	83.7	-	31.3
21	1.59	22.79	1.58	21.4	1.54	23.3	1.52	23.1	1.51	23.2	1.56	23.0	1.23, 1.47	34.5
22	1.83, 2.34	37.3	1.79, 2.33	36.6	2.08, 2.71	31.1	2.45, 2.75	39.9	1.78, 2.45	36.5	2.42, 2.72	40.8	1.82, 2.04	33.6
23	2.25, 2.45	22.9	2.24, 2.51	22.9	3.08, 3.45	32.3	6.31	123.7	2.22, 2.54	22.5	6.31	123.7	1.26	28.6
24	5.27	126.4	5.26	126.4	-	203.0	6.01	142.6	5.27	126.4	6.01	142.6	1.06	16.5
25	-	131.4	-	131.4	-	144.9	-	69.9	-	131.5	-	70.4	0.92	16.0
26	1.62	26.2	1.59	26.2	5.74, 6.31	124.4	1.55	31.3	1.57	26.2	1.55	31.5	1.02	17.1
27	1.57	18.0	1.55	18.0	1.86	17.6	1.52	31.3	1.60	17.8	1.52	32.2	1.31	26.6
28	1.27	28.5	2.10	31.3	2.12	31.2	2.11	31.5	2.15	31.4	2.07	32.6	-	177.0
29	1.09	18.2	1.64	18.2	1.57	18.3	1.11	18.0	1.35	18.0	1.32	18.0	0.94	33.6
30	0.93	18.0	0.87	18.2	0.91	18.1	0.94	18.1	0.82	18.3	0.94	18.1	1.01	24.2
$\underline{C}OCH_3$	-	-	-	171.4	-	-	-	-	-	-	-	-	-	-
$CO\underline{CH_3}$	-	-	2.05	21.4	-	-	-	-	-	-	-	-	-	-
$\underline{C}O$	-	-	-	-	-	203.0	-	-	-	-	-	-	-	-

Chemical shifts are reported in parts per million (δ) and coupling constants (J) are expressed in Hertz.

Table 1. Continued

No.	1		8		10		11		12		19		20	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
3-O-glc-1'	4.92 d (7.5)	105.6	-	-	-	-	-	-	-	-	-	-	4.47 d (7.5)	105.8
2'	4.15	83.8	-	-	-	-	-	-	-	-	-	-	4.05	83.8
3'	4.13	77.6	-	-	-	-	-	-	-	-	-	-	4.21	80.3
4'	4.02	72.1	-	-	-	-	-	-	-	-	-	-	4.19	78.9
5'	3.86	78.6	-	-	-	-	-	-	-	-	-	-	4.03	79.8
6'	4.33, 4.45	63.24	-	-	-	-	-	-	-	-	-	-	4.41, 4.56	63.0
2'-O-glc-1"	5.31 d (7.5)	106.5	-	-	-	-	-	-	-	-	-	-	-	-
2"	4.02	77.6	-	-	-	-	-	-	-	-	-	-	-	-
3"	4.13	78.4	-	-	-	-	-	-	-	-	-	-	-	-
4"	4.16	72.1	-	-	-	-	-	-	-	-	-	-	-	-
5"	4.15	78.8	-	-	-	-	-	-	-	-	-	-	-	-
6"	4.42, 4.51	63.24	-	-	-	-	-	-	-	-	-	-	-	-
6-O-glc-1'	-	-	5.01 d (7.5)	106.3	5.17 d(7.5)	102.4	5.18 d (7.5)	102.4	-	-	5.05 d (8.0)	106.4	-	-
2'	-	-	4.04	75.6	4.35	79.4	4.25	79.1	-	-	4.26	75.9	-	-
3'	-	-	4.25	79.7	4.24	78.8	4.21	78.8	-	-	4.22	78.8	-	-
4'	-	-	4.15	71.9	4.17	72.0	4.12	72.1	-	-	4.11	72.1	-	-
5'	-	-	3.95	75.8	3.96	79.2	3.87	78.8	-	-	3.96	78.8	-	-
6'	-	-	4.31, 4.48	65.7	4.32, 4.48	63.3	4.35, 4.42	63.4	-	-	4.36, 4.50	63.5	-	-
6-O-xyl-1'	-	-	-	-	-	-	-	-	5.17 d (8.0)	106.4	-	-	-	-
2'	-	-	-	-	-	-	-	-	4.09	75.6	-	-	-	-
3'	-	-	-	-	-	-	-	-	4.27	78.8	-	-	-	-
4'	-	-	-	-	-	-	-	-	4.25	72.3	-	-	-	-
5'	-	-	-	-	-	-	-	-	4.36	65.8	-	-	-	-
6'	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2'-O-rha-1"	-	-	-	-	6.47 brs	102.4	6.49 brs	102.4	-	-			-	-
2"	-	-	-	-	4.51	72.7	4.53	72.7	-	-			-	-
3"	-	-	-	-	4.62	72.9	4.58	72.9	-	-			-	-
4"	-	-	-	-	4.21	74.6	4.17	74.6	-	-			-	-
5"	-	-	-	-	4.87	70.0	4.79	69.9	-	-			-	-
6"	-	-	-	-	1.77	19.2	1.77	19.2	-	-			-	-

Chemical shifts are reported in parts per million (δ) and coupling constants (J) are expressed in Hertz.

Table 1. Continued

No.	1		8		10		11		12		19		20	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
20-O-glc-1'''	5.14 d (8.0)	98.7	5.17 d (7.5)	98.7	5.25 d (7.5)	98.8	5.27 d (7.5)	98.8	5.10 d (8.0)	98.8	5.19 d (8.0)	98.8	-	-
2'''	3.84	74.6	3.97	75.8	4.01	75.0	3.95	75.1	3.97	75.9	3.99	75.8	-	-
3'''	4.31	78.8	4.19	79.6	4.21	79.8	4.20	79.8	4.18	79.7	4.26	79.8	-	-
4'''	4.08	72.1	4.13	72.1	4.15	73.0	4.16	72.7	4.12	72.0	4.21	72.7	-	-
5'''	4.05	78.6	3.91	79.1	3.97	79.4	3.98	79.1	4.05	79.2	4.02	79.1	-	-
6'''	4.36, 4.75	70.7	4.43, 4.29	63.3	4.42, 4.35	63.5	4.39, 4.31	63.6	4.45, 4.28	63.3	4.50, 4.29	63.4	-	-
28-O-glc-1'''	-	-	-	-	-	-	-	-	-	-	-	-	6.31 d (7.5)	96.2
2'''	-	-	-	-	-	-	-	-	-	-	-	-	4.35	73.3
3'''	-	-	-	-	-	-	-	-	-	-	-	-	4.54	79.4
4'''	-	-	-	-	-	-	-	-	-	-	-	-	4.49	72.2
5'''	-	-	-	-	-	-	-	-	-	-	-	-	4.57	78.6
6'''	-	-	-	-	-	-	-	-	-	-	-	-	3.92, 4.12	62.7
6'''-O-rha-1	6.44 brs	102.3	-	-	-	-	-	-	-	-	-	-	-	-
2	4.75	72.2	-	-	-	-	-	-	-	-	-	-	-	-
3	4.63	72.8	-	-	-	-	-	-	-	-	-	-	-	-
4	4.31	74.6	-	-	-	-	-	-	-	-	-	-	-	-
5	4.92	69.9	-	-	-	-	-	-	-	-	-	-	-	-
6	1.36	19.2	-	-	-	-	-	-	-	-	-	-	-	-
4'-O-gal-1''	-	-	-	-	-	-	-	-	-	-	-	-	4.91 d (7.5)	106.3
2''	-	-	-	-	-	-	-	-	-	-	-	-	4.54	77.5
3''	-	-	-	-	-	-	-	-	-	-	-	-	4.64	79.8
4''	-	-	-	-	-	-	-	-	-	-	-	-	4.27	72.2
5''	-	-	-	-	-	-	-	-	-	-	-	-	4.25	78.5
6''	-	-	-	-	-	-	-	-	-	-	-	-	3.92	63.3

Chemical shifts are reported in parts per million (δ) and coupling constants (J) are expressed in Hertz.

Table 2. Semi-preparative HPLC conditions for the separation of WGBs

Fraction	Time (min)	Water (%)	ACN (%)	Detection wavelength (nm)	t_R (min)
WGB 2.5.4.7	0	80	20	204	42
	40	65	35		
	45	0	100		
	50	0	100		
	55	80	20		
	60	80	20		
WGB 4.4.9.5.2	0	80	20	204	16
	40	65	35		
	45	0	100		
	50	0	100		
	55	80	20		
	60	80	20		
WGB 5.3.3	0	80	20	204	36
	10	70	30		
	40	50	50		
	45	30	70		
	50	0	100		
	70	0	100		
	75	80	20		
	80	80	20		

Compound **12**; White amorphous powder; TLC (Rf = 0.61, $CHCl_3$:MeOH:water = 70:30:2); IR (KBr): ν_{max} 3363 and 1073 (hydroxyl groups and glycosidic linkage) cm^{-1}; FAB-MS: *m/z* 793 $[M+Na]^+$; ^1H- and ^{13}C-NMR (500 MHz, pyridine) data: Table 1.

Compound **19**; White amorphous powder; TLC (Rf = 0.46, $CHCl_3$:MeOH:water = 70:30:2); IR (KBr): ν_{max} 3362 and 1077 (hydroxyl groups and glycosidic linkage) cm^{-1}; FAB-MS: *m/z* 839 $[M+Na]^+$; ^1H- and ^{13}C-NMR (500 MHz, pyridine) data: Table 1.

Compound **20**; White amorphous powder; TLC (Rf = 0.23, $CHCl_3$:MeOH:water = 50:50:2); IR (KBr): ν_{max} 3378 and 1073 (hydroxyl groups and glycosidic linkage) cm^{-1}; FAB-MS: *m/z* 965 $[M+Na]^+$; ^1H- and ^{13}C-NMR (500 MHz, pyridine) data: Table 1.

Acid hydrolysis of compounds 1, 8, 10, 11, 12, 19, and 20 – Compounds **1**, **8**, **10**, **11**, **12**, **19**, and **20** (each 10 mg) were refluxed with 5% HCl in 60% aqueous dioxane (10 mL) for 2 h. The reaction solution was evaporated under reduced pressure, and the hydrolysate was extracted with ether. The ether extract was evaporated to yield aglycone hederagenin, which was identified by direct comparison with an authentic sample. The water layer was neutralized with Ag_2CO_3 and filtered, and the filtrate was concentrated under reduced pressure. The residue was compared with standard sugars by cellulose TLC [pyridine-EtOAc-HOAc-water (36:36:7:21)], which showed the sugars to be xylopyranoside, rhamnopyranoside, glucopyranoside, and galactopyranoside.

Determination of the absolute configuration of sugars of compounds 1, 8, 10, 11, 12, 19, and 20 – Compounds **1**, **8**, **10**, **11**, **12**, **19**, and **20** (each 10 mg) were treated as above, the dried sugar mixture was dissolved in pyridine (0.1 mL), and then the solution was added to a pyridine solution (0.1 mL) of L-cysteine methyl ester hydrochloride (2 mg) and warmed at 60 °C for 1 h. The solvent was evaporated under a N2 stream and dried in vacuo. The residue was trimethylsilylated with TMS-HT (0.1 mL) at 60 °C for 30 min. After the addition of *n*-hexane and water, the *n*-hexane layer was removed and checked by GC. The retention times (t_R) of the peaks were 6.18 (L-rhamnopyranoside), 8.85 (D-xylopyranoside), 22.03 (D-glucopyranoside), and 22.21 min (D-galactopyranoside).

Results and discussion

A chromatographic separation of the EtOH extract of *P.*

ginseng root led to the isolation of compounds **1** - **21**. These compounds were identified as ginsenosides by comparing their mass spectrometry (MS) and nuclear magnetic resonance (NMR) spectroscopic data in literature. Known compounds **1** - **21** can be divided into several groups. PPD, PPT, and oleanene are the three main groups of ginsenosides. Ginsenosides-Rb1 (**2**), -Rb2 (**3**), -Rb3 (**4**), -Rc (**5**), and -Rd (**6**) are PPD types. 20(*S*)-Notoginsenoside-R2 (**7**), 20(*S*)-*O*-glucoginsenoside-Rf (**9**), ginsenosides-Re (**13**), -Re5 (**14**), -Rf (**15**), -Rg1 (**16**), -Rg2 (**17**), and -Rh1 (**18**) are PPT types. Ginsenoside-Ro (**21**) is an oleanene type.[17,20-24]

Compound **1** was obtained as a white amorphous powder. Its molecular formula was determined to be $C_{54}H_{92}O_{22}$ based on the fast atom bombardment (FAB)-MS ($[M+Na]^+$, *m/z* 1,115) and NMR. The ^{1}H-NMR spectrum showed one olefinic (δ 5.27), four anomeric (δ 4.92, 5.14, 5.31, and 6.44), and an L-rhamnopyranosyl-methyl (δ 1.78) proton signal. In the ^{13}C-NMR spectrum, the chemical shifts of four anomeric carbons were noted at δ 98.7, 105.6, 106.5, and 102.3 (Table 1). Acid hydrolysis of **1** yielded D-glucopyranoside and L-rhamnopyranoside. Therefore, the anomeric carbon signals indicated three β-D-glucopyranosyl and one α-L-rhamnopyranosyl moieties. The significant downfield shift of C-2' (δ 83.8) in the inner β-D-glucopyranosyl moiety at C-3 of aglycone in the ^{13}C-NMR spectrum of C-2' (δ 83.8) showed that the terminal β-D-glucopyranosyl moiety is linked to the inner β-D-glucopyranosyl moiety at C-3. Additionally, C-6''' (δ 70.7) was significantly downfield in the inner β-D-glucopyranosyl moiety at C-20 of aglycone in the ^{13}C-NMR spectrum of C-6''' (δ 70.7), which showed that the terminal α-L-rhamnopyranosyl moiety is linked to the inner β-D-glucopyranosyl moiety at C-20. As a result, the structure of **1** was elucidated as gypenoside-V by spectral data analysis with an authentic sample in the literature.[25-28] Compound **1** has been isolated from *Gynostemma pentaphyllum*.[28]

Compound **8** has a molecular formula of $C_{44}H_{74}O_{15}$ based on the FAB-MS ($[M+Na]^+$, *m/z* 865) and NMR. The ^{1}H-NMR spectrum showed one olefinic (δ 5.26), two anomeric (δ 5.01 and 5.17), and a methyl proton signals of acetyl group (δ 2.05). In the ^{13}C-NMR spectrum, the chemical shifts of two anomeric carbons were noted at δ 98.7 and 106.3 (Table 1). Acid hydrolysis of **8** yielded D-glucopyranoside. Therefore, the anomeric carbons signals indicated two β-D-glucopyranosyl moieties. In addition, these NMR features indicated two additional signals at δ 171.4 and 21.4, owing to the acetyl group. A difference in the chemical-shift value of C-6' (δ 65.7) allowed the acetyl group to be placed at C-6' of the β-D-glucopyranosyl moiety. As a result, the structure of **8** was elucidated as notoginsenoside-Rt (= yesanchinoside D) by spectral data analysis with an authentic sample in the literature.[29-30] Compound **8** has been isolated from *P. japonicus* root.[30]

Compound **10** was obtained as a white amorphous powder. Its molecular formula was determined to be $C_{48}H_{80}O_{19}$ based on the FAB-MS ($[M+Na]^+$, *m/z* 983) and NMR. The ^{1}H-NMR spectrum showed one exomethylene (δ 5.74 and 6.31), three anomeric (δ 5.17, 5.25, and 6.47), and a L-rhamnopyranosyl-methyl (δ 1.77) proton signal. In the ^{13}C-NMR spectrum, the chemical shifts of three anomeric carbons were noted at δ 98.8, 102.4, and 102.4 (Table 1). Acid hydrolysis of **10** yielded D-glucopyranoside and L-rhamnopyranoside. Therefore, the anomeric carbon signals indicated two β-D-glucopyranosyl and an α-L-rhamnopyranosyl moieties. The significant downfield shift of C-2' (δ 79.4) in the inner β-D-glucopyranosyl moiety at C-6 of aglycone in the ^{13}C-NMR spectrum of C-2' (δ 79.4) showed that the terminal α-L-rhamnopyranosyl moiety is linked to the inner β-D-glucopyranosyl moiety at C-6. As shown in Table 1, the ^{13}C-NMR spectrum of **10** was quite similar to that of majoroside-F_6 (**11**) except for the side chain. Additionally, C-1''' (δ 98.8) was shown in the β-D-glucopyranosyl moiety at C-20 of aglycone in the ^{13}C-NMR spectrum. As a result, the structure of **10** was elucidated as 6-*O*-[α-L-rhamnopyranosyl(1 → 2)-β-D-glucopyranosyl]-20-*O*-β-D-glucopyranosyl-3β,12β,20(*S*)-dihydroxy-dammar-25-en-24-one by spectral data analysis with an authentic sample in the literature[31]. Compound **10** has been isolated from *P. ginseng* flower buds.[31]

Compound **11** was isolated as a white amorphous powder with a formula of $C_{48}H_{82}O_{19}$ based on the FAB-MS ($[M+Na]^+$, *m/z* 985) and NMR. The ^{1}H-NMR spectrum showed two olefinic (δ 6.01 and 6.31), three anomeric (δ 5.18, 5.27, and 6.49), and an L-rhamnopyranosyl-methyl (δ 1.77) proton signals. In the ^{13}C-NMR spectrum, the chemical shifts of three anomeric carbons were noted at δ 98.8 and 102.4 (Table 1). Acid hydrolysis of **11** yielded D-glucopyranoside and L-rhamnopyranoside. Therefore, the anomeric carbon signals indicated two β-D-glucopyranosyl and an α-L-rhamnopyranosyl moieties. The significant downfield shift of C-2' (δ 79.1) in the inner β-D-glucopyranosyl moiety at C-6 of aglycone in the ^{13}C-NMR spectrum of C-2' (δ 79.1) showed that the terminal α-L-rhamnopyranosyl moiety is linked to the inner β-D-glucopyranosyl moiety at C-6. Furthermore, the olefinic carbon signals (δ 123.7 and 142.6) and an oxygenated carbon signal (δ 69.9) were observed, in

which a double bond at C-23 and -24 and a hydroxyl group at C-25 of the chain. As results, the structure of **11** was elucidated as majoroside-F6 by spectral data analysis with an authentic sample in the literature.[27] Compound **11** has been isolated from *P. japonicus* root.[32]

Compound **12** has a molecular formula of $C_{42}H_{70}O_{13}$ based on the FAB-MS ([M+Na]$^+$, *m/z* 793) and NMR. The ^{1}H-NMR spectrum showed one olefinic (δ 5.27) and two anomeric (δ 5.10 and 5.17) proton signals. In the ^{13}C-NMR spectrum, the chemical shifts of two anomeric carbons were noted at δ 98.8 and 106.4 (Table 1). Acid hydrolysis of **12** yielded D-glucopyranoside and D-xylopyranoside. Therefore, the anomeric carbon signals indicated a *β*-D-glucopyranosyl and *β*-D-xylopyranosyl moieties. The C-1' of *β*-D-xylopyranosyl moiety was attached to C-6 (δ 80.7) of the skeleton. As a result, the structure of **12** was elucidated as pseudoginsenoside-Rt3 by spectral data analysis with an authentic sample in the literature.[33] Compound **12** has been isolated from *P. pseudo-ginseng* root. [33]

Compound **19** was obtained as colorless crystals. Its molecular formula was determined to be $C_{42}H_{72}O_{15}$ based on the FAB-MS ([M+Na]$^+$, *m/z* 839) and NMR. The ^{1}H-NMR spectrum showed two olefinic (δ 6.01 and 6.31) and two anomeric (δ 5.05 and 5.19) proton signals. In the ^{13}C-NMR spectrum, the chemical shifts of two anomeric carbons were noted at δ 98.7 and 106.4 (Table 1). Acid hydrolysis of **19** yielded D-glucopyranoside. Therefore, the anomeric carbon signals indicated two *β*-D-glucopyranosyl moieties. As shown in Table 1, the ^{13}C-NMR spectrum of **19** was quite similar to that of majoroside F_6 (**11**), except for the *α*-L-rhamnopyranosyl moiety. Furthermore, the olefinic carbon signals (δ 123.7 and 142.6) and an oxygenated carbon signal (δ 70.4) were observed, in which a double bond at C-23 and -24 and a hydroxyl group at C-25 of the chain. As a result, the structure of **19** was elucidated as vinaginsenoside-R15 by spectral data analysis with an authentic sample in the literature.[34] Compound **19** has been isolated from *P. vietnamensis* root. [35]

Compound **20** is a white amorphous powder. Its molecular formula was determined to be $C_{48}H_{78}O_{18}$ based on the FAB-MS ([M+Na]$^+$, *m/z* 965) and NMR. The ^{1}H-NMR spectrum showed one olefinic (δ 5.36) and three anomeric (δ 4.47, 4.91, and 6.31) proton signals. In the ^{13}C-NMR spectrum, the chemical shifts of three anomeric carbons were noted at δ 96.2, 105.8, and 106.3. The aglycone was recognized to be an oleanolic acid on ^{1}H- and ^{13}C-NMR analysis, with the typical olefinic carbons at δ 123.8 and 144.6. Moreover, the peak at δ 177.0 was indicated to be an ester carbon (Table 1). Acid hydrolysis of **20** yielded D-glucopyranoside and D-glactopyranoside. Therefore, the anomeric carbon signals indicated two *β*-D-glucopyranosyl and *β*-D-glactopyranosyl moieties. Additionally, C-1''' (δ 96.2) was shown in the *β*-D-glucopyranosyl moiety at C-28 of aglycone in the ^{13}C-NMR spectrum. As a result, the structure of **20** was elucidated as calenduloside-B by spectral data analysis with an authentic sample in the literature [36]. Compound **20** has been isolated from *Calendula officinalis* root.[36]

Dammarane-type triterpenoid saponins were isolated and identified as protopanaxadiol ginsenosides [gypenoside-V (**1**), ginsenosides-Rb1 (**2**), -Rb2 (**3**), -Rb3 (**4**), -Rc (**5**), and -Rd (**6**)], protopanaxatriol ginsenosides [20(*S*)-notoginsenoside-R2 (**7**), notoginsenoside-Rt (**8**), 20(*S*)-*O*-glucoginsenoside-Rf (**9**), 6-*O*-[α-L-rhamnopyranosyl(1 → 2)-β-D-glucopyranosyl]-20-*O*-β-D-glucopyranosyl-3β,12β, 20(*S*)-dihydroxy-dammar-25-en-24-one (**10**), majoroside-F6 (**11**), pseudoginsenoside-Rt3 (**12**), ginsenosides-Re (**13**), -Re5 (**14**), -Rf (**15**), -Rg1 (**16**), -Rg2 (**17**), and -Rh1 (**18**), and vinaginsenoside-R15 (**19**)], and oleanene ginsenosides [calenduloside-B (**20**) and ginsenoside-Ro (**21**)] from *P. ginseng* root. To the best of our knowledge, this is the first report on the isolation of compounds **1**, **8**, **10**, **11**, **12**, **19**, and **20** from *P. ginseng* root.

P. ginseng is a popular herbal medicine used worldwide for a broad range of indications. Many clinical trials and systematic reviews are now available. Their conclusions are diverse, but for some indications, they are encouraging. So, *P. ginseng* root should be a various active experiments and more saponins isolation. Thus, these results will be useful information in the application of these ginsenosides from ginseng in the nutraceutical, pharmaceutical, and cosmeceutical areas.

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