Saponins from Flower-Buds of *Panax ginseng* Cultivated at Jilin, China

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From flower-buds of *Panax ginseng* C. A. MEYER cultivated in Jilin, China, ginsenosides-Ro (=chikusetsusaponin V, 9), -Rb_1(1), -Rb_2(2), -Rb_3(10), -Rc(3), -Rd(4) and -Re(5), 20-gluco-ginsenoside-Rf(11) and ginsenosides-Rf(12), -Rg_1(6) and -Rg_2(13) were isolated and identified. All of these saponins have previously been isolated from ginseng roots, but the saponins 9—13 have not been isolated from flower-buds cultivated at Daikon-jima, Japan. The isolation of these pharmacologically active saponins in relatively high yields is significant in relation to the utility of the flower-buds produced at Jilin as a medicinal resource.

Keywords *Panax ginseng*; Araliaceae; flower-bud; saponin; ginsenoside; Chinese ginseng; Jilin

In earlier studies on the chemical constituents of *Panax ginseng* C. A. MEYER and the congeners, we have isolated dammarane saponins, ginsenosides-Rb_1(**1**), -Rb_2(**2**), -Rc(**3**), -Rd(**4**), -Re(**5**), -Rg_1(**6**), -F_3(**7**) and -M_{7cd}(**8**) from flower-buds of ginseng cultivated at Daikon-jima, Shimane-ken, Japan.[1,2] Jilin province of China is well-known for the cultivation of ginseng and more than 200 t/year of the flower-buds are collected. We have conducted the chemical evaluation of the flower-buds collected in this province. The present paper compares the saponin composition with that of the Japanese specimen, reporting the isolation and identification of eleven saponins.

The flower-buds were extracted with hot methanol. A suspension of the extract in water was washed with ether and then extracted with 1-butanol saturated with water. The butanolic extract was subjected to chromatography on highly porous polymer and the resulting saponin fractions were further chromatographed on silica gel to give ginsenoside-Ro (=chikusetsusaponin V, **9**),[3,4] **1**, **2**, ginsenoside-Rb_3(**10**),[5] **3**, **4**, 20-gluco-ginsenoside-Rf(**11**),[5] **5**, ginsenoside-Rf(**12**),[6] **6** and ginseoside-Rg_2(**13**)[6] in yields of 0.2, 0.3, 0.2, 0.1, 0.5, 1.1, 0.1, 2.1, 0.2, 0.3 and 0.2%, respectively. The identification of each saponin was established by comparison with a authentic sample [thin layer chromatographic (TLC) behavior, ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra, optical rotation and mass spectrum (MS, as the peracetate)]. All of these saponins have already been isolated from ginseng roots.

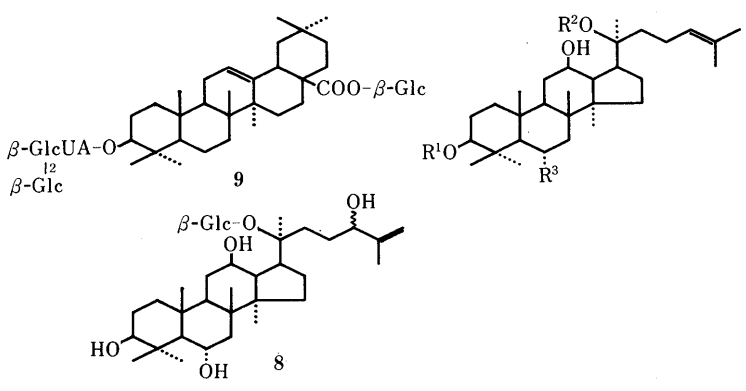
It is noteworthy that the saponins **9**—**13** have not been identified in the flower-buds produced in Japan (Daikon-jima) and this is the first example of the isolation of an oleanane saponin (**9**) from aerial parts of *Panax* spp., while **7** and **8** which are characteristic of the Japanese flower-buds, have not been isolated from ginseng root or from the Chinese specimen (Jilin) in the present study. It follows that the saponin composition of the Chinese flower-buds is more similar to that of the ginseng root than that of the Japanese specimen. This suggests that the flower-buds cultivated in Jilin may be a better medicinal resource than the Japanese specimen.

Experimental

General Procedures Optical rotations were measured on a WZZ automatic digital polarimeter. Melting points were determined on a Kofler micro hot stage and uncorrected. NMR spectra were recorded on a JEOL FX-100 spectrometer in pyridine-d_5 using tetramethylsilane as an internal standard. MS were taken on a JMS-D 300. TLC: on silica gel (Qingdao-haiyang Chemical Ind., China), solvent systems: $CHCl_3$–MeOH–H_2O (65:35:10, lower layer), $CHCl_3$–MeOH–AcOEt–H_2O (6:6:7:3, lower layer) or 1-BuOH–AcOEt–H_2O (4:1:1, homogeneous), detection: H_2SO_4.

Extraction and Separation The dried flower-buds (1.1 kg) collected in Jilin were extracted with hot MeOH. A suspension of the extract in H_2O was washed with Et_2O and then extracted with 1-BuOH saturated with H_2O. The BuOH layer was concentrated to dryness and the residue (150 g) was subjected to chromatography on highly porous polymer resin, X_5 (Nankai University Chemical Ind., China) by elution with H_2O, 35% MeOH and 95% MeOH, successively.

The 35% MeOH eluate (68 g) was separated into four fractions, fr. 1—4 by chromatography on silica gel with $CHCl_3$–MeOH–H_2O (65:35:10, lower layer). Fraction 1 (4.4 g) and 2 (5.8 g) were each further chromatographed on silica gel with the same solvent as above, affording **9** from fr. 1 and **1** from fr. 2; **9**: a white powder, $[\alpha]_D^{20}$ +14.8° (c=0.66, MeOH), yield: 0.2%. **1**: a white powder, $[\alpha]_D^{20}$ +13.2° (c=0.50, MeOH), yield: 0.3%.



	R^1	R^2	R^3
1	-β-Glc^{2}–β-Glc	-β-Glc^{6}–β-Glc	-H
2	-β-Glc^{2}–β-Glc	-β-Glc^{6}–α-Ara(*p*)	-H
3	-β-Glc^{2}–β-Glc	-β-Glc^{6}–α-Ara(*f*)	-H
4	-β-Glc^{2}–β-Glc	-β-Glc	-H
5	-H	-β-Glc	-β-Glc^{2}–α-Rha
6	-H	-β-Glc	-β-Glc
7	-H	-β-Glc^{6}–α-Ara(*p*)	-OH
10	-β-Glc^{2}–β-Glc	-β-Glc^{6}–β-Xyl	-H
11	-H	-β-Glc	-β-Glc^{2}–β-Glc
12	-H	-H	-β-Glc^{2}–β-Glc
13	-H	-H	-β-Glc^{2}–α-Rha

Chart 1

Fraction 3 (13.4 g) was chromatographed on silica gel with 1-BuOH–AcOEt–H_2O (4 : 1 : 1, homogeneous) to give three saponins, **2**, **10** and **3** in yields of 0.2, 0.1 and 0.5%, respectively; **2**: a white powder, $[\alpha]_D^{20}$ +18.7° (c=0.24, MeOH), **10**: a white powder, $[\alpha]_D^{20}$ +17.6° (c=0.45, MeOH) and **3**: a white powder, $[\alpha]_D^{20}$ +1.9° (c=0.66, MeOH). Fraction 4 (18.6 g) was chromatographed on silica gel with 1-BuOH–AcOEt–H_2O (4 : 1 : 1, homogeneous) to give **4** and **11** in yields of 1.1 and 0.1%, respectively; **4**: a white powder, $[\alpha]_D^{20}$ +20.6° (c=1.08, MeOH) and **11**: a white powder, $[\alpha]_D^{20}$ +11.6° (c=0.30, MeOH).

The 95% MeOH eluate (73 g) was separated into two fractions, fr. 5 (43.5 g) and 6 (15.4 g), by chromatography on silica gel with $CHCl_3$–MeOH–AcOEt–H_2O (2 : 2 : 4 : 1, lower layer). Fraction 5 was rechromatographed on silica gel with the same solvent system to give **5** in a yield of 2.1%; **5**: colorless needles from MeOH–H_2O, mp 199—201 °C, $[\alpha]_D^{20}$ −1.5° (c=0.52, MeOH). Fraction 6 was separated into three fractions, fr. 6a (4.0 g), fr. 6b (6.2 g) and fr. 6c (4.2 g) by chromatography on silica gel with the same solvent system and each fraction was further purified by rechromatography on silica gel with the same solvent system. From fr. 6a, **12** was obtained as a white powder, $[\alpha]_D^{20}$ +7.4° (c=0.54, MeOH) in a yield of 0.2%. Fraction 6b afforded **6**, a white powder, $[\alpha]_D^{20}$ +26.7° (c=0.82, MeOH) in a yield of 0.3% and fr. 6c gave **13** as colorless needles, mp 183—184 °C from MeOH–AcOEt, $[\alpha]_D^{20}$ +6.5° (c=0.47, MeOH).

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References

1) S. Yahara, K. Matsuura, R. Kasai and O. Tanaka, *Chem. Pharm. Bull.*, **24**, 3212 (1976).
2) S. Yahara, K. Kaji and O. Tanaka, *Chem. Pharm. Bull.*, **27**, 88 (1979).
3) N. Kondo, Y. Marumoto and J. Shoji, *Chem. Pharm. Bull.*, **19**, 1103 (1971).
4) S. Sanada, N. Kondo, J. Shoji, O. Tanaka and S. Shibata, *Chem. Pharm. Bull.*, **22**, 421 (1974).
5) S. Sanada and J. Shoji, *Chem. Pharm. Bull.*, **26**, 1694 (1978).
6) S. Sanada, N. Kondo, J. Shoji, O. Tanaka and S. Shibata, *Chem. Pharm. Bull.*, **22**, 2407 (1974).