Saponins from Vietnamese Ginseng, *Panax vietnamensis* HA *et* GRUSHV. Collected in Central Vietnam. I

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From rhizomes and roots of *Panax vietnamensis* HA *et* GRUSHV., Araliaceae, commonly known as Vietnamese Ginseng, two new acetylated saponins named vina-ginsenoside-R1 (13) and vina-ginsenoside-R2 (15) were isolated. On the basis of chemical and spectral data, 13 was formulated as monoacetyl 24(*S*)-pseudo-ginsenoside-F_{11} and 15 was proved to be monoacetyl majonoside-R2.

Besides the two new saponins and β-sitosteryl-3-*O*-β-D-glucopyranoside, sixteen known saponins were also isolated and identified. Dammarane saponins: ginsenoside-Rh_1 and 20(*R*)-ginsenoside-Rh_1 (1), ginsenosides-Rg_1 (2), -Re (3), -Rd (6), -Rb_3 (7), -Rb_2 (8), -Rb_1 (9), pseudo-ginsenoside-RS_1 (=monoacetyl ginsenoside-Re, 4), notoginsenosides-R1 (5) and -Fa (10). Ocotillol-type saponins: pseudo-ginsenoside-RT_4 (11), 24(*S*)-pseudo-ginsenoside-F_{11} (12), majonosides-R1 (16) and -R2 (14). Oleanolic acid saponins: ginsenoside-Ro (=chikusetsusaponin V, 17) and hemsloside-Ma3 (18), a saponin previously isolated from a cucurbitaceous plant, *Hemsleya macrosperma* C. Y. WU.

Despite having large horizontally elongated rhizomes, the underground part of this plant contains mainly dammarane saponins and a small amount of oleanolic acid saponins. In addition, the yield of ocotillol-type saponins, especially majonoside-R2, is surprisingly very high (more than 5% and *ca.* half of the total yield of saponin). This characteristic saponin composition has made Vietnamese Ginseng an interesting species among *Panax* spp.

Keywords Vietnamese Ginseng; *Panax vietnamensis*; ginsenoside; vina-ginsenoside-R1, -R2; ocotillol-type saponin; majonoside-R2

Panax ginseng C. A. MEYER (Ginseng) and its two congeners, *P. notoginseng* (BURK.) F. H. CHEN (Sanchi Ginseng), *P. quinquefolium* L. (American Ginseng) are well-known plant drugs and have been widely used in many countries of the world, especially in Asia and North America. These are now cultivated plants, differentiating them from a variety of wild *Panax* spp., which are morphologically related and distributed from Japan to the Eastern Himalayas through the South-Western Province of China. In view of the pharmacological and chemotaxonomical interest, comparative studies of the saponin composition of *P. ginseng* and other *Panax* spp. have been conducted.[1)]

Previously, South Yunnan, China and North Vietnam seemed to be the southern limit of the distribution of the *Panax* genus. However, a wild *Panax* species was discovered at Ngoc Lay, Gia Lai-Kontum, Central Vietnam in 1973.[2)] This plant was a secret medicine of the Sedang ethnic minority living in the high mountains of the South Annamitic Range in Central Vietnam and has been regarded as a life-saving plant drug used for treatment of many serious diseases and for enhancing physical strength. This new *Panax* species, which was named *Panax vietnamensis* HA *et* GRUSHV. by Vietnam and former Soviet Union botanists,[3)] appears to be an important medicinal plant of Vietnam and it has been studied by The Science-Production Centre of Vietnamese Ginseng in co-operation with other institutions. This paper, as a result of the Japan–Vietnam joint study on Vietnamese Ginseng and other medicinal plants of Vietnam, deals with the isolation and identification of saponins from rhizomes and roots of *P. vietnamensis* and discusses its chemotaxonomical characteristics in comparison with those of other related plants.

Results and Discussion

The specimen used in the present study was collected at altitudes 1500—2595 m as part of a large botanical survey in Gia Lai-Kontum Province, Central Vietnam in Autumn 1978. The underground part of the plant consists of a large horizontally elongated rhizome with many internodes and a small root. Since no significant difference in the saponin composition of the rhizome and the root was observed in a preliminary comparison using thin-layer chromatography, both parts (1.0 kg) were combined and extracted with hot methanol and then with hot 50% aqueous methanol. The combined extract was subjected to column chromatography on a highly porous polymer to give a crude saponin mixture in a yield of 19.2%. A part of the crude saponin fraction was subjected to repeated column chromatography and preparative high performance liquid chromatography (HPLC) to afford β-sitosteryl-3-*O*-β-D-glucopyranoside and sixteen known saponins as follows (yield as a % of the dried material is shown in parenthesis): ginsenoside-Rh_1 and 20 (*R*)-ginsenoside-Rh_1[4)] (**1**, 0.008%, as an epimeric mixture), ginsenoside-Rg_1[5)] (**2**, 1.37%), ginsenoside-Re[6)] (**3**, 0.17%), ginsenoside-Rd[7)] (**6**, 0.87%), ginsenoside-Rb_3 (**7**, 0.11%), ginsenoside-Rb_2[7)] (**8**, 0.012%), ginsenoside-Rb_1[7)] (**9**, 2.0%), notoginsenoside-R1[9)] (**5**, 0.36%), notoginsenoside-Fa[10)] (**10**, 0.072%), pseudo-ginsenoside-RS_1[11)] (=monoacetyl ginsenoside-Re, **4**, 0.013%), pseudo-ginsenoside-RT_4[12)] (**11**, 0.065%), 24(*S*)-pseudo-ginsenoside-F_{11}[13)] (**12**, 0.005%), majonoside-R1[14)] (**16**, 0.14%), majonoside-R2[14)] (**14**, 5.29%), ginsenoside-Ro[7)] (=chikusetsusaponin V, **17**, 0.038%) and hemsloside-Ma3[15)] (**18**, 0.052%). Each of the

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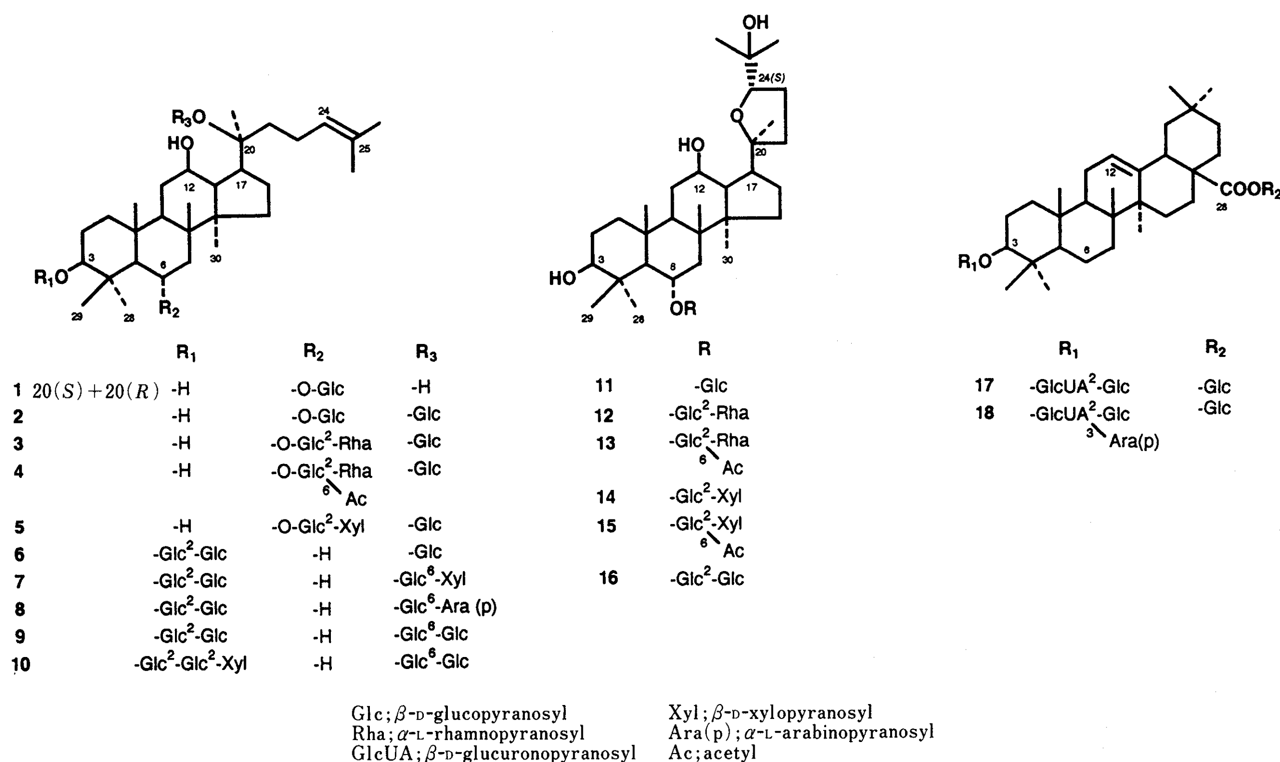

Chart 1

known saponins was unambiguously identified by comparison of optical rotation, thin-layer chromatographic (TLC) behavior, ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra, as well as mass spectrum (MS, as the trimethylsilyl ether) with those of a corresponding authentic sample. All the known saponins have been isolated from other *Panax* spp., except for **18**, which was an oleanolic acid saponin previously isolated from *Hemsleya macrosperma* C. Y. Wu, Cucurbitaceae.[15] It should be noted that this is the first identification of hemsloside-Ma3 in a *Panax* plant.

Besides the known saponins, two new acetylated saponins named vina-ginsenoside-R1 (**13**) and vina-ginsenoside-R2 (**15**) were also isolated in yields of 0.033% and 0.014%, respectively. On hydrolysis with mineral acid, **13** yielded glucose and rhamnose. The presence of an acetoxyl group in **13** was shown by ^{13}C-NMR signals at δ 20.9 and 170.7 and a ^{1}H-NMR signal at δ 2.11 (3H, *s*). On alkaline hydrolysis with methanolic KOH, **13** afforded 24(*S*)-pseudo-ginsenoside F_{11} (**12**), which was identified by ^{1}H- and ^{13}C-NMR spectra as well as other physico-chemical evidence. In the ^{13}C-NMR spectrum of **13**, carbon signals due to the aglycone moiety were almost superimposable on those of **12** except for displacement of the C-6 signal (Table I). The electron-impact mass spectrum (EI-MS) of trimethylsilylated (TMSi) **13** exhibited ions at *m*/*z* 711 [(Glc–Rha)Ac TMSi$_5$], 621 (711 − TMSiOH), 363 [(terminal Rha)TMSi$_3$] and 273 (363 − TMSiOH), indicating that the acetoxyl group of **13** is located on the inner glucosyl unit of the 6-*O*-rhamnosyl-glucosyl moiety of **12**. In the ^{13}C-NMR spectra, on going from **12** to **13**, the carbon signal due to C-6 of the glucose moiety was deshielded and the C-5 signal was displaced upfield while the other signals due to the sugar moieties remained almost unchanged (Table I). These data confirm that **13** is a monoacetate of **12**, in which the acetyl group is located at the 6-hydroxyl group of the inner β-glucopyranosyl of the 6-*O*-glycosyl moiety.

In the acid hydrolysate of **15**, glucose and xylose were identified. ^{13}C-NMR signals at δ 21.0 and 170.8, as well as a ^{1}H-NMR signal at δ 2.1 (3H, s) indicated the presence of an acetoxyl group in **15**. On alkaline hydrolysis, **15** gave majonoside-R2 (**14**), which was identified by physico-chemical and spectral data. In the ^{13}C-NMR spectrum of **15**, the signals due to the aglycone moiety were almost the same as those of **14** (Table I). The EI-MS spectrum of **15** showed fragment peaks at *m*/*z* 697 [(Glc–Xyl)AcTMSi$_5$], 607 (697 − TMSiOH), 349 [(terminal Xyl)TMSi$_3$], 259 (349 − TMSiOH), indicating that the acetoxyl group of **15** is located at the inner glucosyl unit of the 6-*O*-xylosyl-glucosyl moiety of **14**. Among the carbon resonances due to the β-glucosyl unit, on going from **14** to **15**, the C-6 signal was deshielded and the C-5 signal was shielded, while the other carbon signals due to the sugar moieties were almost unchanged (Table I). Based on these findings, **15** can be characterized as a monoacetate of **14**, in which the acetyl group is attached to the 6-hydroxyl group of the inner β-glucopyranosyl unit of the 6-*O*-glycosyl moiety.

From a taxonomical point of view, *Panax* spp. have been morphologically divided into two groups, tentatively designated as group I and II, according to the shape of the underground part. Group I consists of *P. ginseng* C. A. Meyer (Ginseng),[1] *P. quinquefolium* L. (American Ginseng)[16] and *P. notoginseng* (Burk.) F. H. Chen (Sanchi Ginseng)[9,17] which have a carrot-like root with a small rhizome and contain a number of dammarane saponins with either a small amount of the oleanolic acid saponin, **17**, or none (Sanchi Ginseng). Group II includes a variety of wild *Panax* spp. having a large rhizome, which are morphologically related to each other and distributed from the

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TABLE I. ^{13}C-NMR Chemical Shift (in C_5D_5N)

Aglycone moieties	12	13	14	15
C-1	39.3	39.5	39.5	39.5
C-2	27.6	27.7	27.7	27.8
C-3	78.4	78.2	78.0	78.7
C-4	39.8	39.8	40.1	40.1
C-5	60.8	60.7	61.4	61.3
C-6	74.0	73.4	79.4	79.3
C-7	45.8	46.0	44.8	45.3
C-8	40.9	41.1	41.0	41.1
C-9	49.7	49.8	50.2	50.2
C-10	39.4	39.6	39.5	39.6
C-11	32.0	32.1	32.2	32.2
C-12	70.7	70.8	70.8	70.8
C-13	48.9	49.1	49.0	49.2
C-14	52.1	52.2	52.2	52.3
C-15	32.4	32.1	32.4	32.6
C-16	25.6	25.7	25.8	25.8
C-17	49.2	49.4	49.4	49.5
C-18	17.7[a]	17.7[a]	17.7[a]	17.9[a]
C-19	17.4[a]	17.5[a]	17.1[a]	17.0[a]
C-20	86.9	87.0	87.0	87.0
C-21	26.8[b]	26.9[b]	26.9[b]	27.0[b]
C-22	32.4	32.5	32.5	32.6
C-23	28.5	28.6	28.6	28.6
C-24	88.2	88.3	88.3	88.4
C-25	69.9	70.0	70.0	70.0
C-26	26.4[b]	26.4[b]	26.5[b]	26.6[b]
C-27	28.8[b]	28.9[b]	28.9[b]	28.9[b]
C-28	31.9	31.9	31.6	31.7
C-29	16.8[a]	16.8[a]	16.6[a]	16.9[a]
C-30	17.8[a]	17.9[a]	17.8[a]	17.9[a]

Sugar moieties	12	13	14	15
6-Glc				
1	101.7	102.0	103.4	103.5
2	79.2[a]	79.0[a]	79.8	80.2
3	78.2[a]	78.3[a]	78.7	78.7
4	72.2	72.2	71.2[a]	71.2[a]
5	78.2[a]	75.4	80.2	75.0
6	62.9	64.9	62.8	65.0
Rha				
1	101.6	101.2	—	—
2	72.1	72.2	—	—
3	72.4	72.3	—	—
4	74.2	74.0	—	—
5	69.3	69.3	—	—
6	18.6	18.6	—	—
Xyl				
1	—	—	104.8	105.0
2	—	—	75.7	75.7
3	—	—	78.6	78.7
4	—	—	71.6[a]	71.2[a]
5	—	—	67.1	67.3
CH_3CO	—	20.9	—	21.0
CH_3CO	—	170.7	—	170.8

a, *b*) Assignments in any vertical column may be interchanged. Glc: β-D-glucopyranosyl, Rha: α-L-rhamnopyranosyl, Xyl: β-D-xylopyranosyl.

Himalayas to Japan through the South West Province of China, such as *P. japonicus* C. A. MEYER (Japan and China),[7,18–20] *P. japonicus* C. A. MEYER var. *major* (BURK.) C. Y. WU *et* K. M. FENG (China),[14] *P. zingiberensis* C. Y. WU *et* K. M. FENG (China),[21] *P. japonicus* C. A. MEYER var. *angustifolius* (BURK.) CHENG *et* CHU (China),[22] *P. pseudo-ginseng* WALL. subsp. *himalaicus* HARA and its varieties[23] (Bhutan[12,24] and Nepal[13]), *etc.* It has been revealed that the saponin composition of most of these Japanese, Chinese and Bhutanese specimens includes a large amount of oleanolic acid saponins, such as **17**, together with a smaller amount of dammarane saponins, except for *P. stipuleanatus* H. T. TSAI *et* K. M. FENG,[26] growing wild in South Yunnan, China and North Vietnam. From the rhizome of this plant, the characteristic oleanolic acid saponins, stipuleanosides R_1 and R_2, were identified but no dammarane saponins have been obtained.

However, it was found that in contrast to these specimens, rhizomes of plants (tentatively named specimens C and G)[13] collected near Annapurna, Nepal, and the rhizome of a specimen collected along a trail leading from Dhunche to Singkuba, Central Nepal, (tentatively assigned as *P. pseudo-ginseng* WALL. var. *elegantior* (BURK.) HOO *et* TSEUNG)[11] contain a number of dammarane saponins with either a relatively smaller amount of oleanolic acid saponins (the latter) or none (the two former).

Though the study of minor saponins from rhizomes and roots of *P. vietnamensis* is now in progress, the main saponin composition, as shown in the present paper, has been established. Despite having a large horizontally elongated rhizome, the underground part of this plant contains a large amount of dammarane saponins and a small quantity of oleanolic acid saponins. This saponin composition differs from that of specimens C and G with respect to containing oleanolic acid saponins and from that of the specimen collected along the trail leading from Dhunche to Singkuba, Central Nepal, because of the greater amount of dammarane saponins compared with oleanolic acid saponins. Regardless of the morphological difference in the underground part, the saponin composition of Vietnamese Ginseng is very similar to that of group I plants and a number of biologically active dammarane saponins such as **2**, **3**, **5**, **6**, **7**, **9**, in relatively high yields, strongly supports its medical use as a valuable ginseng-like plant drug. In addition, the surprisingly high yield of dammarane saponins having an ocotillol side-chain, especially majonoside-R2 (more than 5% and *ca.* half the total yield of saponin), has made Vietnamese Ginseng an insteresting member of *Panax* spp. This characteristic saponin composition seems to be significant as far as the search for further taxonomical correlation of this plant to other *Panax* spp. is concerned. Moreover, the high content of ocotillol-type saponins has also stimulated the study of this plant with a view to discovering new pharmacological actions and medicinal uses.

It should be noted that Vietnamese Ginseng has already been subjected to preliminarily pharmacological and clinical study and has been widely used in Vietnam since its discovery. Besides ginseng-like pharmacological actions, it also exhibits markedly antibacterial effects on *Streptococci*

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and is apparently effective in the treatment of sore throat, cough *etc.*[2)]

Experimental

General Procedures Melting points were measured on a Yanaco micro hot-stage and are uncorrected. Optical rotations were measured using a Union PM-101 automatic digital polarimeter. NMR spectra were recorded on JEOL JNM GX270, JEOL JNM GX400 and JEOL JNM GX500 spectrometers in C_5D_5N using tetramethylsilane (TMS) as an internal standard. MS were obtained on a JEOL JMS-SX102 spectrometer by the direct inlet method at an ionizing voltage of 70 eV. For gas-liquid chromatography (GLC), a Shimadzu GC-8A instrument was used. HPLC was carried out using a D-ODS-5 column (20.0 mm i.d. × 25 cm) with a Toyo Soda HLC 803D pump and a Toyo Soda RI-8 differential refractometer as detector. Flow rate of the mobile phase: 6 ml/min, injection volume: 0.8—1.0 ml.

For column chromatography, Kieselgel 60 (70—230 mesh, Merck, unless otherwise stated), LiChroprep RP-8 (40—63 μm, Merck) and Diaion HP-20 (Mitsubishi Chem. Ind. Co., Ltd.) were used.

Identification of the Known Saponins Each known saponin was identified by TLC on Silica gel 60 precoated plates, F-254 (Merck), with the solvent systems: $CHCl_3$–MeOH–H_2O (65:35:10, lower phase), $CHCl_3$–MeOH–H_2O (60:40:10, homogeneous), $CHCl_3$–1-BuOH–MeOH–H_2O (20:40:15:20, lower phase) and by HPTLC using RP-8 and/or RP-18 precoated plates, F-254s (Merck) with solvents 60—80% MeOH (detection: 10% H_2SO_4), as well as by comparison of optical rotation, ^{1}H- and ^{13}C-NMR spectra and mass spectrum (as trimethylsilyl ether) with those of a corresponding authentic sample.

Trimethylsilylation for EI-MS, acid hydrolysis and identification of resulting monosaccharides after hydrolysis were carried out as described in a previous paper.[13)] GLC conditions: column SE-52 bonded; 25 m × 0.25 mm; detector, flame-ionization (FID); injection temperature, 200 °C; column temperature, 180 °C; carrier gas, He, 2 kg/cm^2.

Plant Material The material in this study was collected at altitudes of 1500—2559 m as part of a special botanical survey on *P. vietnamensis* organized in Gia-Lai-Kontum Province, Central Vietnam in August 1978. The samples have been deposited at the Science-Production Centre of Vietnamese Ginseng, Ho Chi Minh City University of Medicine and Pharmacy, Ho Chi Minh City, Vietnam and at the Department of Medicinal Chemistry of Natural Products, Institute of Pharmaceutical Sciences, Hiroshima University, School of Medicine, Hiroshima, Japan.

Extraction and Separation of Saponins The dried rhizomes and roots (1.0 kg) were extracted with hot MeOH (3.0 l × 3) and then with 50% hot aqueous MeOH (3.0 l × 2) to give a MeOH extract in a yield of 47% after concentration. An aqueous suspension of 200 g of the MeOH extract was subjected to column chromatography on reversed-phase highly porous polymer, Diaion HP-20, with H_2O (20 l), MeOH (10 l) and finally $CHCl_3$ (5 l) as eluting solvents, affording an H_2O fraction (95 g), a MeOH fraction (crude saponin fraction, 81.5 g) and a $CHCl_3$ fraction (2.8 g). A part of the MeOH fraction (60 g) was chromatographed over silica gel [gradient elution with $CHCl_3$–MeOH–H_2O (30:20:1; 30:20:2; 30:20:5; all homogeneous)] to provide 8 fractions, frs. I—VIII, in increasing order of polarity.

Fraction I was separated into four fractions, frs. Ia—d, by column chromatography on silica gel [solvent, $CHCl_3$–MeOH–H_2O (300:70:7, homogeneous)]. From fr. Ia, β-sitosteryl-3-*O*-β-D-glucopyranoside (daucosterin), was obtained as colorless needles (from MeOH–H_2O) and was identified by comparison of mp (285—288 °C) and ^{13}C-NMR spectrum with reported data.[26)] Fraction Ic was chromatographed on LiChroprep RP-8 with 60% MeOH to give **11** (0.065% yield) and **1** (0.008%, a white powder), **11**, colorless needles (from MeOH–H_2O), mp 249—252 °C, $[\alpha]_D^{18}$ +8.4° (c=1.07, MeOH). Fraction Id was separated by LiChroprep RP-8 column chromatography using 55% MeOH to afford **15** (0.014% yield) and **13** (0.033% yield).

Compound **13** (vina-ginsenoside-R1), a white powder, $[\alpha]_D^{25}$ −23.1° (c=1.08, MeOH). *Anal.* Calcd for $C_{44}H_{74}O_{15}\cdot 3/2\ H_2O$: C, 60.74%; H, 8.91%. Found: C, 60.85%; H, 8.63%. Negative ion FAB-MS m/z: 841 $[M-H]^-$, 695 $[M-Rha-H]^-$, 491 $[M-(Rha–Glc–Ac)-H]^-$, EI-MS (TMSi deriv.) m/z: 711 [(Glc–Rha)AcTMSi$_5$], 621 (711−TMSiOH), 363 [(terminal Rha)TMSi$_3$], 273 (363−TMSiOH). ^{1}H-NMR δ: 1.01, 1.09, 1.31, 1.32, 1.34, 1.34 (overlapped), 1.46, 2.10 (3H, each s, CH_3 × 8), 2.11 (3H, s, CH_3CO), 1.80 (3H, d, J=6.2 Hz, CH_3 of Rha), 5.26 (1H, d, J=6.7 Hz, H-1 of Glc), 6.49 (1H, br s, H-1 of Rha). ^{13}C-NMR (see Table I).

Compound **15** (vina-ginsenoside-R2), colorless needles from MeOH–H_2O, mp 186—189 °C, $[\alpha]_D^{25}$ −17.4° (c=0.69, MeOH). *Anal.* Calcd for $C_{43}H_{72}O_{15}\cdot 5/2H_2O$: C, 59.08%; H, 8.87%. Found: C, 58.96%, H, 8.54%. Negative ion FAM-MS m/z: 827 $[M-H]^-$, 695 $[M-Xyl-H]^-$, 491 $[M-(Xyl–Glc–Ac)-H]^-$. EI-MS (TMSi deriv.) m/z: 697 [(Glc–Xyl)AcTMSi$_5$], 607 (697−TMSiOH), 349 [(terminal Xyl)TMSi$_3$], 259 (349−TMSiOH). ^{1}H-NMR δ: 0.89, 1.05, 1.28, 1.32, 1.33, 1.42, 1.47, 2.06 (3H, each s, CH_3 × 8), 2.10 (3H, s, CH_3CO), *ca.* 5.00 (1H, overlapped, H-1 of Xyl), 5.75 (1H, d, J=6.4 Hz, H-1 of Glc). ^{13}C-NMR (see Table I).

Fraction II was subjected to LiChroprep RP-8 column chromatography (solvent 60% MeOH) to give a mixture of **2** and **14** and crude **12**. Purification of crude **12** by preparative HPLC with 53% MeOH gave **12** (0.005% yield) as a white powder (MeOH–EtOAc), $[\alpha]_D^{18}$ −22.9° (c=1.53, MeOH). A part of the mixture of **2** and **14** was separated by HPLC using 55% MeOH, affording **2** (1.37% yield) and **14** (5.29% yield). **2**, a white powder (MeOH–EtOAc), $[\alpha]_D^{18}$ +29.4° (c=1.09, MeOH). **14**, a white powder (MeOH–EtOAc), $[\alpha]_D^{18}$ −3.8° (c=1.05, MeOH).

Fraction III was repeatedly chromatographed on silica gel [solvent: $CHCl_3$–MeOH–H_2O (70:30:10, lower phase)] and then on silylated Silica gel RP-8 (solvent: 55%–70% MeOH) to give **5**, **16**, **3**, **6** and crude **4**. **5** (0.36% yield), colorless needles from H_2O, mp 214—216 °C, $[\alpha]_D^{22}$ +16.1° (c=0.99, MeOH). **16** (0.14% yield), a white powder (MeOH–EtOAc), $[\alpha]_D^{18}$ +7.5° (c=1.07, MeOH). **3** (0.17% yield), colorless needles from MeOH–H_2O, mp 199—201 °C, $[\alpha]_D^{18}$ −4.6° (c=1.09, MeOH). **6** (0.87% yield), a white powder, $[\alpha]_D^{18}$ +10.6° (c=1.13, MeOH). Crude **4** was further purified by preparative HPLC using 58% MeOH and **4** was obtained as a white powder (0.013% yield), $[\alpha]_D^{25}$ −8.6° (c=0.7, MeOH).

Fraction V was subjected to column chromatography on silica gel with solvent system $CHCl_3$–MeOH–H_2O (70:30:10, lower phase) to give **7** (0.11% yield) as a white powder (MeOH–EtOAc), $[\alpha]_D^{18}$ +6.8° (c=1.03, MeOH).

Fraction VI was separated by column chromatography on silica gel [solvent: $CHCl_3$–MeOH–H_2O (65:35:10, lower phase)] into three fractions, frs. VIa—VIc. Fraction VIa was repeatedly chromatographed on Silica gel 60 (230—400 mesh, Merck) [solvent: 1-BuOH–EtOAc–H_2O (4:1:1, homogeneous)] to afford **8** (0.012% yield) as a white powder (MeOH–EtOAc), $[\alpha]_D^{20}$ +11.7° (c=1.53, MeOH). Fraction VIb was repeatedly precipitated in MeOH–EtOAc and **9** was obtained as a white powder (2.0% yield), $[\alpha]_D^{18}$ +10.0° (c=1.20, MeOH). Fraction VIc was subjected to column chromatofraphy on LiChroprep RP-8 (solvent: 55%—70% MeOH) to give **10** (0.07% yield), colorless needles from MeOH, mp 230—235 °C (dec.), $[\alpha]_D^{20}$ −13.6° (c=1.53, H_2O).

Fraction VII was chromatographed on LiChroprep RP-8 using 55% MeOH to give **17** and **18** after deionization with Amberlite MB-3. **17** (0.038% yield), a white powder (MeOH–EtOAc), $[\alpha]_D^{18}$ +5.0° (c=2.0, MeOH). **18** (0.052% yield), a white powder (MeOH–EtOAc), $[\alpha]_D^{22}$ +9.0° (c=1.0, MeOH).

Saponification of 13, 15 Each saponin (**13**, 30 mg; **15**, 12 mg) was refluxed in 2% methanolic KOH (10 ml) at 80 °C for 2 h. The reaction mixture was neutralized with Amberlite MB-3 and then evaporated to dryness to give the corresponding deacetylated compound; **12** (23 mg) from **13**, **14** (10 mg) from **15**. **12** and **14** were identified by comparing optical rotation, TLC behavior, ^{1}H- and ^{13}C-NMR spectra with samples of authentic **12** and **14**.

Acknowledgements We are grateful to Emeritus Professor Shoji Shibata, Tokyo University, for his encouragement. Thanks are also due to Fujisawa Foundation, Osaka, and Itto Institute of Life-Science Research, Tokyo, for the fellowship for one of the authors, N. M. Duc's study in Hiroshima University.

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