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Dammarane-Saponins of Sanchi-Ginseng, Roots of *Panax notoginseng* (Burk.) F.H. Chen (Araliaceae): Structures of New Saponins, Notoginsenosides-R1 and -R2, and Identification of Ginsenosides-Rg_2 and -Rh_1

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From Sanchi-Ginseng, roots of *Panax notoginseng* cultivated in Yunnan, China, two new dammarane-saponins named notoginsenosides-R1 (**5**) and -R2 (**7S**) were isolated by means of reverse phase high performance liquid chromatography. The structures of these saponins were established as 20(*S*)-protopanaxatriol 6-[O-β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyl]-20-O-β-D-glucopyranoside (**5**) and 20(*S*)-protopanaxatriol 6-O-β-D-xylopyranosyl(1→2)-β-D-glucopyranoside (**7S**), respectively, mainly by ^{13}C NMR spectroscopy and mass spectrometry. In connection with this study, assignments of carbon signals of ginsenoside-*Rf* (**11**), a minor saponin of Ginseng roots, were substantiated by the application of selective deuteration of the sugar moiety as reported by Stuart *et al.*

Besides these saponins, two known saponins, ginsenosides-Rh_1 (**12**) and -Rg_2 (**13**) which have previously been isolated from Ginseng roots, were also isolated and identified.

Keywords——Sanchi-Ginseng (Tienchi-Ginseng); *Panax notoginseng*; Araliaceae; dammarane-saponin; notoginsenosides-R1, -R2; ^{13}C NMR of oligoglycosides; selective deuteration with deuterated Raney nickel; ginsenosides-Rf, -Rh_1, -Rg_2; reverse phase high performance liquid chromatography

A Chinese traditional crude drug, Sanchi-Ginseng (=Tienchi-Ginseng), roots of *Panax notoginseng* (Burk.) F.H. Chen (Araliaceae, cultivated in Yunnan, China) has been used as a tonic and a hemostatic. Recently, this crude drug has attracted much attention because of its action in preventing and curing coronary disease.[1] With regard to the saponin constituents of this drug, Shoji *et al.*[2] in 1978 isolated four known dammarane-saponins, ginsenosides-Rb_1 (**1**),[3a] -Rd(**2**),[3a] -Re(**3**),[3b] and -Rg_1(**4**),[4] as the root-saponins of *P. ginseng* C. A. Meyer, a well-known oriental crude drug. Later, Wu also reported the identification of these saponins.[5] In 1980, Wei *et al.* described six saponins named sanchinosides C_1, C_3, D_1, D_3, E_1, and E_2, among which C_1 and E_1 were identified as **4** and **1**, respectively, while others were left unidentified.[6] The present paper deals with a further study on saponins of this drug, reporting the isolation and structure determination of two new dammarane-saponins. The isolation and identification of two minor saponins are also described.

An aqueous solution of a crude saponin fraction of the methanolic extract of the drug was dialyzed. The non-dialyzed fraction mainly consisted of **1** and **2**. The dialyzed fraction was separated by chromatography on silica gel, affording two major saponins, one of which was found to be identical with **4**[2] by comparison of the ^{13}C nuclear magnetic resonance (NMR) spectra, while the other major saponin of this fraction was proved to be still a mixture of two saponins by ^{13}C NMR spectroscopy, though its thin layer chromatogram (TLC) on silica gel showed a single spot which seemed to be identical with that of **3**. Reverse phase TLC on octadecylsilylated silica gel(ODS-silica gel) of this saponin-mixture (tentatively named Re-fraction) exhibited two spots, one of which had the same *Rf* value as **3**, while the other showed a higher *Rf* value. Preparative high performance liquid chromatography (HLC) of Re-fraction

on an ODS-silica gel column (Fig. 1) resulted in complete separation, affording two saponins, **3** and a new saponin (**5**), colorless needles, mp 215—217°C, $C_{47}H_{81}O_{20}\cdot H_2O$ named notoginsenoside-R1 (yield 0.16%). Identification of **3** was performed by comparison of its ^{13}C NMR spectrum with that of an authentic sample.[7]

A number of studies on ^{13}C NMR spectroscopy for carbohydrates have been published. We have reported the carbon resonance displacements of both sugar and aglycone moieties upon glycosylation (glycosylation shifts) for a variety of glucosides,[8] mannosides, rhamnosides[9] and arabinosides,[10] demonstrating a close relationship between the glycosilation shifts and absolute configurations of both sugar and aglycone structure. Assignments of carbon signals of dammarane-triterpenes[11] and their glycosides[7,8,12] have also been elaborated and this technique is now the most substantial tool for identification as well as structure determination of saponins of this type including the stereochemistry at C-20 of the aglycon. Upon comparison of the ^{13}C NMR spectrum of **5** with that of **3**,[7] the carbon signals due to the aglycone moiety of both saponins were found to be almost superimposable indicating that **5** must be a glycoside of 20(*S*)-protopanaxatriol(**6**) having O-glycosyl linkages at its C-6 and -20 positions (Table I). Inspection of the molecular formulae and carbon signals due to the sugar moiety, especially anomeric carbon signals, indicated the presence of three monosaccharide units in **5** (Table II).

On hydrolysis with mineral acid, **5** yielded glucose and xylose. As shown in Chart 2, the mass spectra of the acetate and trimethylsilyl (TMSi) ether of **5** revealed the presence of terminal glucosyl and xylosyl units as well as a glucose-xylose moiety (see Chart 2). It has been observed that the glycosyl linkage at C-20 hydroxyl group of dammarane-saponins is readily hydrolyzed even under mild acidic conditions, yielding a C-20-epimeric mixture of the corresponding prosapogenin or sapogenin.[13] In the mass spectra of their acetates or TMSi ethers, M^+ or fragment ions having an intact O-glycosyl group at the C-20 position could not be observed.[14] On mild hydrolysis with aqueous acetic acid, **5** afforded a prosapogenin (**7**). The mass spectrum of the TMSi ether of **7** exhibited ions due to terminal xylose $(TMSi)_3$ and glucose$(TMSi)_3$–xylose $(TMSi)_3$ but showed no ion due to a terminal glucosyl unit, indicating that the -O-glucose-xylose moiety must be located at C-6 (not at C-20) (see Chart 2). This was further supported by the fragment ions at *m/z* 1088 (**8**) and 1089 (**9**) (Chart 2) in the spectrum of the acetate of **5**; these fragments were formed by loss of the C-20 glucosyl unit.[14a] The presence of a free hydroxyl group at C-20 in **7** was also revealed by a characteristic fragment ion at *m/z* 199 (**10**) (Chart 2)[14b] in the spectrum of the TMSi ether of **7** which was not observed in that of the TMSi ether of **5**. As shown in Table I, the ^{13}C NMR signals of **7**, especially duplicate signals due to C-17, -21 and -22, indicated that **7** must be a C-20 epimeric mixture (**7S** and **7R**) of 6-O-glycosylated protopanaxatriol.[8,11] It follows that **5** can be formulated as 20-O-glucosyl-6-O-xyloglucosyl-20(*S*)-protopanaxatriol.

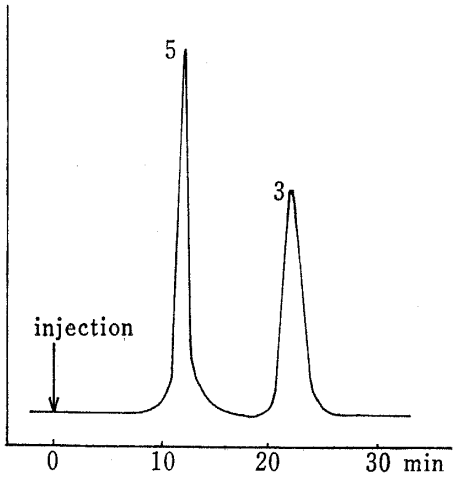
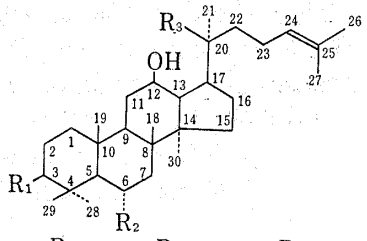


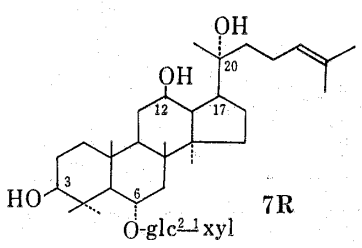
Fig. 1. Separation of Ginsenoside-Re (3) and Notoginsenoside-R1 (5) by Reverse Phase High Performance Liquid Chromatography
Conditions: see "Experimental."

The coupling constants (J=6—8 Hz) of three anomeric proton signals of **5** revealed β-anomeric configurations of all of its glucosyl and xylosyl linkages. The structure of the 6-O-β-glucose-β-xylose moiety of **5** was established mainly by ^{13}C NMR spectroscopy, by comparison with the spectrum of the related Ginseng-root saponin, ginsenoside-Rf(**11**, 6-O-β-

sophorosyl-20(*S*)-protopanaxatriol[3b]). Recently, Stuart *et al.* reported that treatment of methyl glucoside or its derivatives with deuterated Raney nickel (Ni-d_2) led to exchange of the carbinyl protium of free hydroxyl groups by deuterium, resulting in the disappearance of the corresponding carbon signals in the proton-decoupled FT ^{13}C NMR spectra.[15] Since a protium on a carbon having an O-glycosyl linkage or a protected hydroxyl group is not replaced by deuterium, this procedure is promising for the definite assignment of sugar-carbon signals of complex carbohydrates and glycosides. On going from **11** to **11**-d_{11}, which was prepared from **11** by refluxing with Ni-d_2 in deuterium oxide, the lost carbon signals in the region of δ 60—80 ppm should be due to C-3′, -4′ and -6′ of the inner glucosyl unit and C-2″ -3″ -4″ and -6″ of the terminal glucosyl unit, while signals which remained unaffected must be attributable to C-2′ and -5′ of the inner glucosyl unit, C-5″ of the terminal glucosyl unit and C-6 and -20 of the aglycone. It was found that because of the slow deuterium exchange rate of a carbinyl protium bearing an isolated (non-glycolic) hydroxyl group, the carbon signals due to C-3 and -12 of the aglycon were almost unaffected on this treatment (the double bond on the side chain was catalytically deutero-hydrogenated). This procedure was especially valuable for the differentiation of signals of C-5′ and -5″ of both glucosyl units from those of their C-3′ and -3″, as well as for the substantial characterization of C-2′ of the inner glucosyl unit, leading to complete assignments of the carbon signals of **11** in this region (Table II). It should be noted that the signal due to C-2′ of the inner glucosyl unit appears at unexpectedly higher field than that of the usual β-sophoroside such as **1** or **2**. This can be explained in terms of the steric interaction between the gem-dimethyl group at C-4 of the aglycone and this sophorosyl group in **11**. By reference to these assignments and the reported data on carbon signals of β-D-xylopyranosides,[16] the carbon resonances of the sugar moiety of **7** were found to be con-



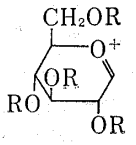
	R_1	R_2	R_3
1 :	O-glc$^{2\text{-}1}$glc	H	O-glc$^{6\text{-}1}$glc
2 :	O-glc$^{2\text{-}1}$glc	H	O-glc
3 :	OH	O-glc$^{2\text{-}1}$rha	O-glc
4 :	OH	O-glc	O-glc
5 :	OH	O-glc$^{2\text{-}1}$xyl	O-glc
6 :	OH	OH	OH
7S :	OH	O-glc$^{2\text{-}1}$xyl	OH
11 :	OH	O-glc$^{2\text{-}1}$glc	OH
12 :	OH	O-glc	OH
13 :	OH	O-glc$^{2\text{-}1}$rha	OH



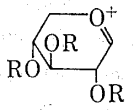
7R

glc : β-D-glucopyranosyl
rha : α-L-rhamnopyranosyl
xyl : β-D-xylopyranosyl

Chart 1

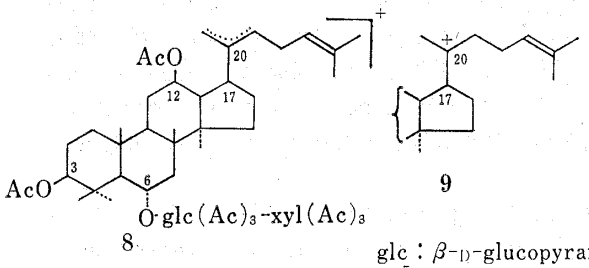


terminal glucosyl
R=Ac *m/z* 331
R=TMSi *m/z* 451



terminal xylosyl
R=Ac *m/z* 259
R=TMSi *m/z* 349

glc(R)$_3$-xyl(R)$_3^+$ R=Ac *m/z* 547
R=TMSi *m/z* 727



8

9

glc : β-D-glucopyranosyl
xyl : β-D-xylopyranosyl

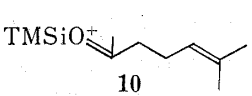


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Chart 2. Mass Fragment Ions

Table I. ^{13}C NMR Chemical Shifts: Aglycone Moiety

	6	12	11	7S	7R	5
C-1	39.2	39.4	39.6	39.6		39.5
C-2	28.0	27.9	27.5	27.6		27.6
C-3	78.3	78.0	77.9	77.8		78.0
C-4	40.2	40.3	40.0	40.1		40.1
C-5	61.7	61.4	61.0	61.2		61.2
C-6	67.6	78.6	79.5	79.4		79.4
C-7	47.4	45.2	45.0	44.9		44.8
C-8	41.1	41.1	41.1	41.0		41.0
C-9	50.1	50.2	50.0	50.1		49.9
C-10	39.3	39.6	39.6	39.6		39.5
C-11	31.9	32.0	31.1	31.6		30.7
C-12	70.9	71.0	70.4	71.1		70.3
C-13	48.1	48.2	48.1	48.1		48.9
C-14	51.6	51.6	51.6	51.6		51.3
C-15	31.3	31.1	31.9	31.6		30.7
C-16	26.8	27.2	26.8	26.6		26.6
C-17	54.6	54.7	54.5	54.6	(50.4)	51.7
C-18	17.5[a]	17.4[a]	17.6[a]	17.5[a]		17.7[a]
C-19	17.4[a]	17.6[a]	17.5[a]	17.3[a]		17.0[a]
C-20	72.9	73.0	72.4	72.9		83.3
C-21	26.9	26.8	26.8	27.0	(22.7)	22.4
C-22	35.7	35.8	35.7	35.7	(44.9)	35.9
C-23	22.9	23.0	22.9	22.9		23.2
C-24	126.2	126.3	125.7	126.2		125.8
C-25	130.6	130.6	130.1	130.9		130.9
C-26	25.8	25.8	25.8	25.8		25.7
C-27	17.7[a]	17.6[a]	17.5[a]	17.5[a]		17.4[a]
C-28	31.9	31.7	31.9	32.0		31.5
C-29	16.4[a]	16.4[a]	17.6[a]	17.9[a]		17.4[a]
C-30	17.0[a]	16.8[a]	16.7[a]	16.6[a]		16.6[a]

δ ppm from internal TMS in C_5D_5N.
a) Values in any column may be reversed, though those given here are preferred.

sistent with the formulation as -O-β-D-glucopyranose$\overset{}{\underset{2}{\underset{1}{}}}$-$\beta$-D-xylopyranose, excluding all other formulations (Table II).

Comparison of the ^{13}C NMR spectrum of **5** with those of deuterated **5** (**5**-d_{14}), **4** and ginsenoside-Rh_1 (**12**, 6-O-β-D-glucopyranosyl-20(*S*)-protopanaxatriol, a minor saponin of Ginseng roots[17]) led to establishment of the structure of **5** as 20(*S*)-protopanaxatriol 6-[O-β-D-xylopyranosyl(1→2)-β-D-glucopyranosyl]-20-O-β-D-glucopyranoside.

A comparison of ^{13}C NMR spectra and the HLC behavior of a sample of sanchinoside-Dl[6] which was sent to us by Mr. Zhenxion Chen and Mr. Baiping Yin, Shanghai Institute of Materia Medica, Academia Sinica, proved the complete identity of this saponin with our Re-fraction, a mixture of **3** and **5**.

In continuing our chemical studies on saponins of Sanchi-Ginseng, several minor saponins have also been isolated. The crude saponin fraction of the methanolic extract was subjected to repeated chromatography on silica gel, affording a minor saponin (yield 0.06%) which was proved to be identical with ginsenoside-Rh_1 (**12**) (*loc. cit.*)[17] A fraction of minor saponins which showed intermediate *Rf* values between **4** and **12** on silica gel TLC was further purified by chromatography on silica gel followed by acetylation and repeated chromatography of the resulting acetates mixture on silica gel followed by HLC on ODS-silica gel, furnishing two minor saponins after alkaline saponification. The absence of acetyl groups in the original saponins of this fraction was confirmed by TLC (on a silica gel plate; solvent: $CHCl_3$–MeOH–H_2O (13: 7: 2, lower phase)) before and after purification *via* acetylation. One of the saponins

Table II. ^{13}C NMR Chemical Shifts: Sugar Moiety

		12	11	7S	5
6-glc (inner)	1′		103.2	103.3	103.4
	2′		79.5	79.6	79.4
	3′		78.7[a]	78.6	78.9[a]
	4′		71.7	71.6	71.4
	5′		79.8	79.9	79.9
	6′		62.9	62.7	62.6
6-glc (terminal)	1″	105.9	103.2		
	2″	75.4	75.9		
	3″	80.0[a]	78.4[a]		
	4″	71.8	72.3		
	5″	79.5[a]	79.8		
	6″	63.1	63.3		
6-xyl	1			104.6	104.5
	2			75.6	75.6
	3			78.6	78.9[a]
	4			71.6	71.4
	5			67.1	67.0
20-glc	1				98.1
	2				75.0
	3				78.5[a]
	4				71.1
	5				79.9
	6				62.6

glc: β-D-glucopyranosyl.
xyl: β-D-xylopyranosyl.
δ ppm from internal TMS in C_5D_5N.
a) Values in any column may be reversed, though those given here are preferred.

(yield 0.03%) was proved to be identical with ginsenoside-Rg_2 (**13**), one of the minor saponins of Ginseng roots.[3b]

Another compound, a new saponin named notoginsenoside-R2, white powder, $C_{41}H_{70}O_{13}\cdot 2H_2O$ (yield 0.04%), afforded glucose and xylose on acid hydrolysis and the mass spectrum of its TMSi ether exhibited fragment ions due to terminal xylose $(TMSi)_3$ and glucose $(TMSi)_3$–xylose $(TMSi)_3$ (Chart 2). Upon comparison of the ^{13}C NMR spectrum of this saponin with that of **7**, signals due to the sugar moiety of both compounds appeared at almost the same positions (Table II). With regard to the aglycone moiety, the signals of this saponin were consistent with those of 6-O-glycosylated 20(*S*)-protopanaxatriol (Table I). This was further supported by the presence of the strong fragment ion (**10**) in the mass spectrum of the TMSi ether (Chart 2), which is characteristic of dammarane-triterpenes having a free hydroxyl group at C-20.[14b] It follows that this saponin can be represented as 20(*S*)-protopanaxatriol 6-O-β-D-xylopyranosyl(1→2)-β-D-glucopyranoside (**7S**), one of the components of the prosapogenin (**7**).

Isolation and structure determination of other minor saponins of this crude drug are in progress.

Experimental

General Procedures——NMR spectra were taken on a JEOL PFT-100 spectrometer in C_5D_5N using TMS as an internal standard (^1H NMR at 100 MHz and ^{13}C NMR at 25.15 MHz). FT NMR conditions: spectral width, 4 and 6.25 KHz; acquisition time, 0.5 and 0.3 sec; recycle time, 1 s; number of data points, 4096 or 8192; pulse flipping angle, 90°; concentration, 40—150 mg/ml; temperature, 25°C.

MS were taken at 75 eV on a JEOL 01-SG-2 spectrometer by the direct inlet method; ionization current, 200 μA; accelerating voltage, 8 kV. Trimethylsilylation for MS: A saponin (1—2 mg) was heated with N-trimethylsilylimidazole (10 drops) in a sealed micro-tube at 80°C for 2—3 h. The reaction mixture was diluted with H_2O and then extracted with *n*-C_6H_{14}. The C_6H_{14} layer was washed with H_2O and concentrated

by blowing N_2 gas over it at room temperature. The residue was subjected to MS. Acetylation for MS: A saponin (1—2 mg) was heated with $(CH_3CO)_2O$ (2—3 drops) and C_5H_5N (5—6 drops) in a sealed micro-tube at 80°C for 2—3 h. The reaction mixture was concentrated by blowing N_2 gas over it at room temperature and the residue was subjected to MS.

Melting points were taken on a micro hot-stage and are uncorrected.

Hydrolysis of a Saponin and Identification of the Resulting Monosaccharides——A saponin (a few mg) was heated with 10% HCl in H_2O–dioxane (1: 1) in a sealed tube at 90°C for 2 h. The reaction mixture was concentrated to dryness by blowing N_2 gas over it at room temperature. The residue was subjected to TLC analysis. For GLC analysis, the residue was trimethylsilylated by the same procedure as that used for MS (*vide supra*). TLC: on Kieselgel 60 F_{254} (Merck); solvent, $CHCl_3$–MeOH–H_2O (60: 40: 10, homogeneous); detection, H_2SO_4. GLC: on a Shimadzu GC-4A gas chromatograph; column, 1.5% SE-30 on Chromosorb W, glass column 4 mm×2 m; detector, FID; injection temperature, 200°C; column temperature, 180°C; carrier gas, N_2, 1.0 kg/cm^2.

Separation of Notoginsenoside-R1 (5)——The crude drug (500 g) was extracted with hot MeOH (500 ml× 3). The extract was concentrated to dryness. A suspension of the residue in H_2O (300 ml) was washed with Et_2O and then extracted with 1-BuOH (saturated with H_2O, 300 ml×4). The combined BuOH layer was concentrated to dryness *in vacuo* to give a crude saponin fraction (42 g). A solution of this fraction (42 g) in H_2O (100 ml) was dialyzed through cellulose film (MW 8000, Visking) against H_2O (500 ml/d for 7 days) at 4°C to give the dialyzed fraction (19.5 g), the non-dialyzed fraction (9.7 g) and the precipitate from the non-dialyzed fraction (9.3 g). The dialyzed fraction was subjected to repeated column chromatography on silica gel (solvent, $CHCl_3$–MeOH–H_2O (13: 7: 2, lower layer) to give Re-fraction (0.9 g from 7.0 g of the dialyzed fraction), which showed two spots (3 and 5) on reverse phase TLC (on an ODS plate: RP-18 F_{254} Merck Art. 13724; solvent, MeOH–H_2O (55: 45); detection, H_2SO_4). The Re-fraction was further purified by preparative HLC on a Toyo Soda HLC 802UR liquid chromatograph; column, TSK-gel LS-410 (7.5 mm× 30 cm); temperature, room temperature; mobile phase, MeOH–H_2O (55: 45); flow rate, 2.0 ml/min; monitored with a differential refractometer; injection, 20 mg/ml (1 ml).

Notoginsenoside-R1 (5) was obtained as colorless needles mp 215—217°C (from H_2O) in a yield of 0.16%; $[\alpha]_D^{25}$ +15.0° (c=1.0, MeOH). *Anal.* Calcd for $C_{47}H_{81}O_{20}\cdot H_2O$: C, 57.36; H, 8.50. Found: C, 57.12; H, 8.40. ^{1}H NMR (in C_5D_5N): 5.07 (1H, d, J=8 Hz), 5.05 (1H, d, J=8 Hz), 4.85 (1H, d, J=6 Hz) anomeric protons.

A solution of **5** (80 mg) in CH_3COOH–H_2O (1: 1) (15 ml) was heated at 70°C for 5 h. The reaction mixture, after dilution with H_2O, was extracted with 1-BuOH (saturated with H_2O). The aqueous layer was concentrated to dryness to give glucose. The BuOH layer was concentrated to dryness and the residue (60 mg) was purified by column chromatography on silica gel (solvent: $CHCl_3$–MeOH–H_2O (60: 40: 10, homogeneous)), affording prosapogenin (**7**=**7S**+**7R**) as a white powder (20 mg).

C-Deuteration of Saponins——A saponin (**5** or **11**) (60 mg) was suspended in D_2O (3 ml); the suspension was allowed to stand at room temperature for 1 h and then evaporated to dryness. R–Ni-d_2[18] (W-7) (0.5 ml in D_2O) was added to a solution of the residue in D_2O–CD_3OD (3 ml: 0.4 ml) and the mixture was heated at 85°C for 12—15 h. The mixture was filtered to remove R–Ni and the filtrate was concentrated to dryness to give **5**-d_{14} or **11**-d_{11} (OD→OH on washing with H_2O).

Separation of Minor Saponins——The crude saponin fraction prepared from the crude drug (500 g) as described above was chromatographed on silica gel (solvent, $CHCl_3$–MeOH–H_2O (50: 10: 1, homogeneous) and finally with MeOH) to yield three fractions, A, B and C (eluted with MeOH) in order of increasing polarity. Fraction B was further subjected to chromatography on silica gel (solvent, AcOEt–$CHCl_3$–MeOH–H_2O (4: 2: 2: 1, lower layer)), providing three fractions, I—III (in order of increasing polarity). Fraction I was re-chromatographed on silica gel (solvent, $CHCl_3$–MeOH–H_2O (50: 10: 1, homogeneous)), affording ginsenoside-Rh_1 (**12**) as a white powder in a yield of 0.06%. This product was identified by comparison of its ^{13}C NMR spectrum with that of an authentic sample.

Fraction II (1.17 g) after chromatography on silica gel (solvent: $CHCl_3$–MeOH–H_2O (50: 10: 1) homogeneous), was acetylated with Ac_2O (7.5 ml) and C_5D_5N (12 ml) at room temperature overnight. The resulting acetates mixture was further separated by repeated chromatography on silica gel (solvent: n-C_6H_{14}–$CHCl_3$–EtOAc (1: 1: 1)) followed by HLC, furnishing two saponins, **7S** and **13**. A Waters' radial compression separative system was used; column: Radial Pak A (ODS, 8 mm×10 cm); room temperature; mobile phase, 90% MeOH; flow rate, 2 ml/min; monitored with a differential refractometer (Waters R-401). The acetates were each saponified by refluxing with 2.5% KOH/MeOH (10 ml) for 1.5 h, yielding **7S** (yield 0.04% from the drug) and **13** (yield 0.03% from the drug), respectively. The identity of **13**, colorless needles, mp 187—189°C (from EtOH) was confirmed by comparison of its ^{13}C NMR spectrum with that of an authentic sample.

Notoginsenoside-R2 (**7S**) was obtained as a white powder (reprecipitated from EtOH–EtOAc), $[\alpha]_D^{15}$ +10.3° (c=1.0, MeOH). *Anal.* Calcd for $C_{41}H_{70}O_{13}\cdot 2H_2O$: C, 61.17; H, 9.01. Found: C, 61.25; H, 9.01.

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