Bioactive Saponins and Glycosides. IX.[1] Notoginseng (2): Structures of Five New Dammarane-Type Triterpene Oligoglycosides, Notoginsenosides-E, -G, -H, -I, and -J, and a Novel Acetylenic Fatty Acid Glycoside, Notoginsenic Acid β-Sophoroside, from the Dried Root of *Panax notoginseng* (BURK.) F. H. CHEN

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Following the characterization of notoginsenosides-A, -B, -C, and -D, new dammarane-type triterpene oligoglycosides, notoginsenosides-E, -G, -H, -I, and -J, and a novel acetylenic fatty acid glycoside, notoginsenic acid β-sophoroside, were isolated from the glycoside fraction with hepatoprotecting activity obtained from the dried roots of *Panax notoginseng* (BURK.) F. H. CHEN. Their chemical structures were elucidated on the basis of chemical and physicochemical evidence as follows: notoginsenoside E; 3-*O*-[β-D-glucopyranosyl(1→2)-β-D-glucopyranosyl]-20-*O*-(β-D-glucopyranosyl)-3β,12β,20(*S*)-trihydroxy-25-hydroperoxydammar-23-ene, G; 3-*O*-[β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl]-20-*O*-(β-D-glucopyranosyl)-3β,7β,20(*S*)-trihydroxydammar-5,24-diene, H; 6-*O*-[β-D-xylopyranosyl(1→2)-β-D-glucopyranosyl]-20-*O*-(β-D-glucopyranosyl)-3β,6α,12β,20(*S*), 25-pentahydroxydammar-23-ene, I; 3-*O*-[β-D-glucopyranosyl(1→2)-β-D-glucopyranosyl]-20-*O*-[β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl]-3β,20(*S*)-dihydroxydammar-24-ene, J; 6-*O*-(β-D-glucopyranosyl)-20-*O*-(β-D-glucopyranosyl)-3β,6α,12β,-20(*S*),24ξ,25-hexahydroxydammarane, and notoginsenic acid β-sophoroside; 10-hydroxydeca-4,6-diynoic acid 10-*O*-β-D-glucopyranosyl (1→2)-β-D-glucopyranoside, respectively.

Key words notoginsenoside; notoginsenic acid β-sophoroside; *Panax notoginseng*; notoginseng; dammarane-type triterpene oligoglycoside; acetylenic fatty acid glycoside

During the course of our studies in search of bioactive saponins and glycosides from natural medicines[2] and medicinal foodstuffs,[3] we have found that the glycosidic fraction from the dried roots of *Panax notoginseng* (BURK.) F. H. CHEN showed potent protective effect on liver injury induced by D-galactosamine and lipopolysaccharide. Thus far we have isolated nine new dammarane-type triterpene oligoglycosides called notoginsenosides-A (**1**), -B (**3**), -C (**4**), -D (**5**), -E (**6**), -G (**7**), -H (**8**), -I (**9**), and -J (**10**) and a novel acetylenic fatty acid glycoside called notoginsenic acid β-sophoroside (**11**) from the active glycosidic fraction together with fourteen known saponins such as notoginsenoside-K (**2**). In the preceding paper,[1] we reported the hepatoprotecting activity of the glycosidic fraction from the dried roots of *P. notoginseng* and the structures of notoginsenosides-A (**1**), -B (**3**), -C (**4**), and -D (**5**). As a continuing study, we describe here the structure elucidation of the remaining five new dammarane-type triterpene oligoglycosides, notoginsenosides-E (**6**), -G (**7**), -H (**8**), -I (**9**), and J (**10**), and an acetylenic fatty acid glycoside, notoginsenic acid β-sophoroside (**11**).[4]

Notoginsenoside-E (6) Notoginsenoside-E (**6**) was isolated as colorless fine crystals of mp 202—204 °C from aqueous methanol. The IR spectrum of **6** showed strong absorption bands at 3432 and 1078 cm^{-1} suggestive of the glycosidic structure, and **6** was shown to possess a hydroperoxyl group by its positive response to the *N*,*N*-dimethyl-*p*-phenylenediammonium dichloride reagent and the ferrous thiocyanate reagent.[5] The molecular formula $C_{48}H_{82}O_{20}$ was determined from the quasimolecular ion peaks observed in the positive and negative-mode FAB-MS and by high-resolution MS measurement. Namely, a quasimolecular ion peak was determined at *m/z* 1001 $(M+Na)^+$ in the positive-mode FAB-MS, while the negative-mode FAB-MS showed a quasimolecular ion peak at *m/z* 977 $(M-H)^-$. Methanolysis of **6** with 9% hydrogen chloride in dry methanol liberated a methyl glucoside. The ^{1}H-NMR (pyridine-d_5) spectrum[6] of **6** showed signals assignable to a β-sophorosyl moiety [δ 4.95 (d, J=7.0 Hz, 1′-H) and 5.39 (d, J=6.7 Hz, 1″-H)], a β-D-glucopyranosyl moiety [δ 5.22 (d, J=7.6 Hz, 1‴-H)], and a disubstituted olefin [δ 6.16 (m, 23-H) and 6.07 (d, J=15.0 Hz, 24-H)]. The carbon signals of the saccharide moieties in the ^{13}C-NMR (Table 1) spectrum[6] of **6** were almost superimposable on those of ginsenoside-Rd (**12**),[7] whereas the carbon signals of the sapogenol moiety were very similar to those (Table 1) of notoginsenoside-K (**2**).[1] The glycoside structure of **6** was characterized by means of a heteronuclear multiple bond correlation (HMBC) experiment. Thus, long-range correlations were observed between the 1″-proton and 2′-carbon, between the 1′-proton and the 3-carbon, and between the 1‴-proton and the 20-carbon. Furthermore, the side chain structure of the sapogenol moiety was also identified by the HMBC experiment, which showed long-range correlations between the following protons and carbons: 23-H and 22-C; 24-H and 25-C; 26, 27-H_3 and 24, 25-C. Finally, **6** was synthesized from **12** using photosensitized oxygenation in

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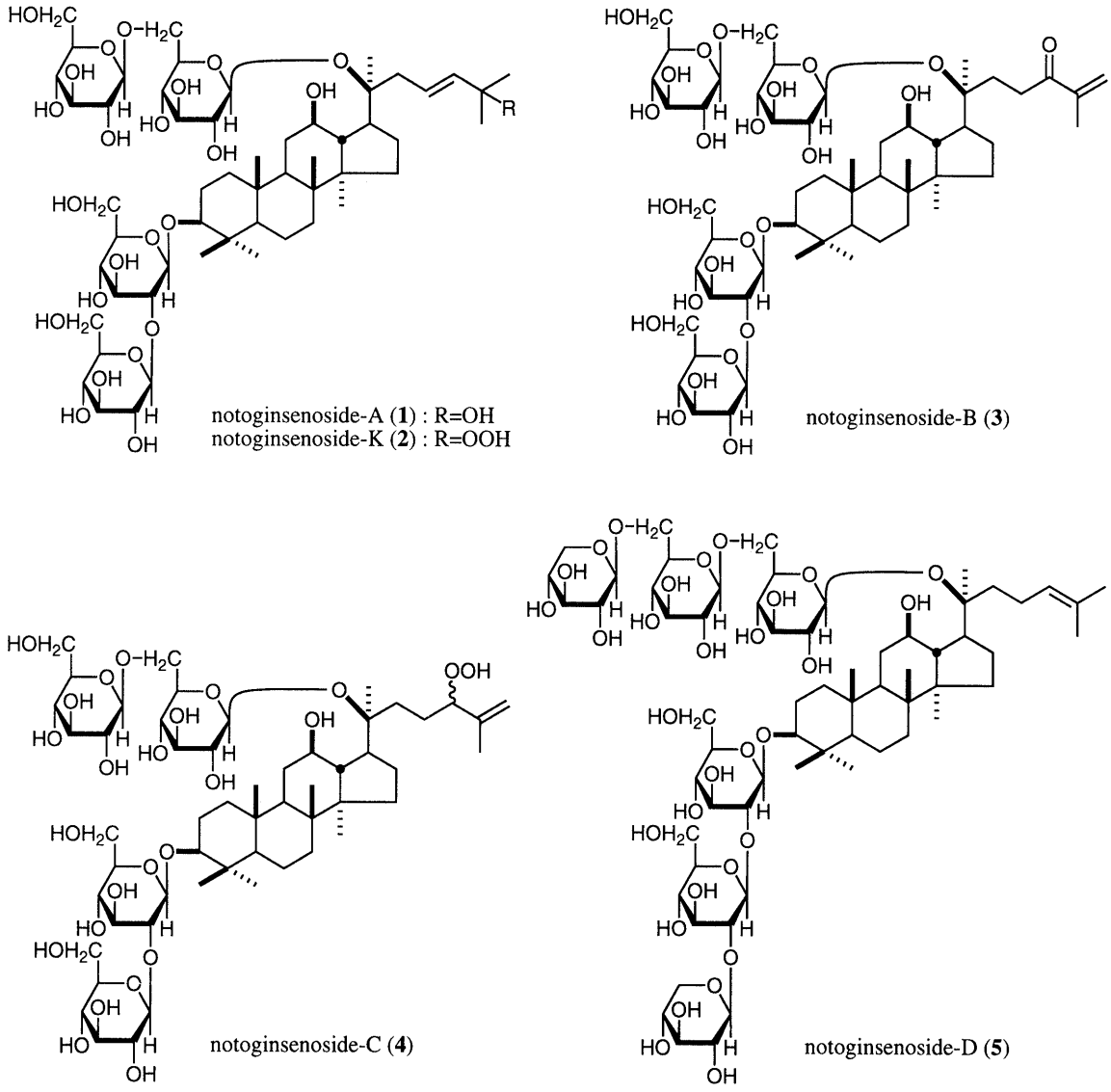

Chart 1

the presence of Rose Bengal together with **13**, whose structure was characterized by comparison of the ^{1}H-NMR and ^{13}C-NMR (Table 1) data for **13** with those for notoginsenoside-C (**4**). On the basis of this evidence, the structure of notoginsenoside-E (**6**) was determined as shown.

Notoginsenoside-G (7) Notoginsenoside-G (**7**) was also obtained as colorless fine crystals of mp 204—206 °C and its IR spectrum showed absorption bands due to hydroxyl and olefin groups at 3410, 1637, and 1078 cm^{-1}. In the negative and positive-mode FAB-MS of **7**, quasimolecular ion peaks were observed at *m/z* 959 $(M-H)^-$, *m/z* 983 $(M+Na)^+$, and *m/z* 1005 $(M+2Na-H)^+$ and high-resolution MS analysis revealed the molecular formula of **7** to be $C_{48}H_{80}O_{19}$. Furthermore, a fragment ion peak at *m/z* 797 $(M-C_6H_{11}O_5)^-$ was observed in the negative-mode FAB-MS. The methanolysis of **7** liberated a methyl glucoside. The ^{1}H-NMR (pyridine-d_5) spectrum[6] of **7** showed signals due to a β-sophorosyl moiety [δ 4.88 (d, J=7.6 Hz, 1′-H) and 5.34 (d, J=7.6 Hz, 1″-H)], a β-D-glucopyranosyl moiety [δ 5.22 (d, J=7.6 Hz, 1‴-H)], two trisubstituted olefin parts [δ 5.83 (d, J=2.1 Hz, 6-H) and 5.27 (dd-like, 24-H)], and three methine protons bearing an oxygen function [δ 3.33 (dd, J=4.6, 11.9 Hz, 3-H), 4.70 (d, J=2.1 Hz, 7-H), and 4.09 (m, 12-H)]. The carbon signals in the ^{13}C-NMR (Table 1) spectrum[6] of **7** were very similar to those of ginsenoside-Rd (**12**), except for the signals due to the B-ring part of the sapogenol moiety. The plane structure of this part in **7** was characterized by the HMBC experiment, which showed long-range correlations between the protons and carbons (Fig. 1). In the difference rotating frame nuclear Overhauser effect spectroscopy (difference ROESY) of **7**, ROE correlations were observed between the 7-proton and the 9-proton [δ 1.77 (m)] and the 7-proton and the 30-H$_3$ [δ 1.13 (s)]. Consequently, the structure of notoginsenoside-G (**7**) was determined as shown.

Notoginsenoside-H (8) Notoginsenoside-H (**8**), obtained as colorless fine crystals of mp 201—203 °C, showed absorption bands due to hydroxyl and olefin groups (3410, 1647, and 1078 cm^{-1}) in the IR spectrum. The molecular formula $C_{47}H_{80}O_{19}$ was determined from the quasimolecular ion peaks [*m/z* 947 $(M-H)^-$ and *m/z* 971 $(M+Na)^+$] in the negative and positive-mode FAB-MS

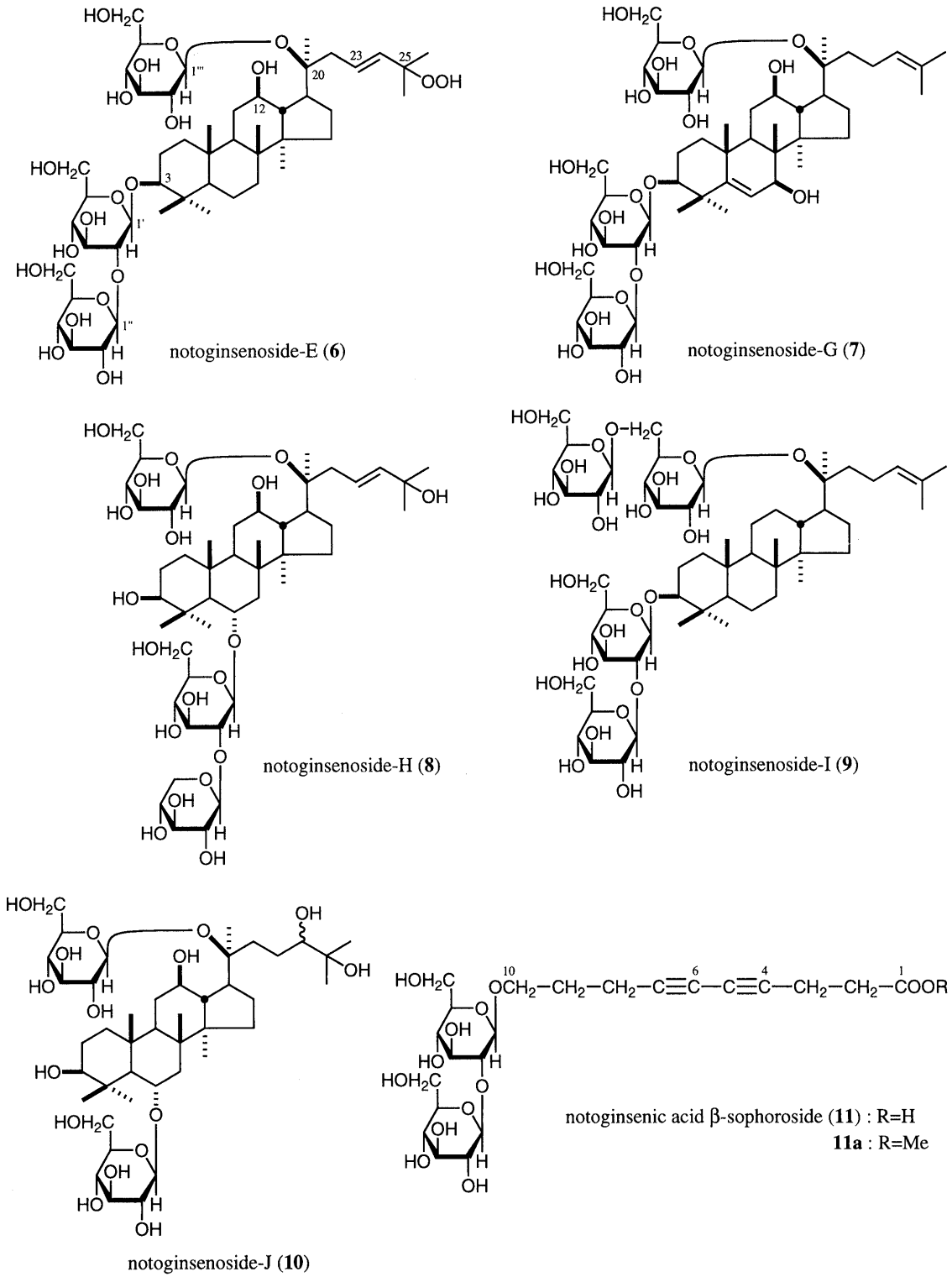

Chart 2

and by high-resolution MS measurement. The methanolysis of **8** liberated methyl glucoside and methyl xyloside in a 2:1 ratio. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **8** showed signals assignable to two β-D-glucopyranosyl parts [δ 4.93 (d, J=7.3 Hz, 1′-H) and 5.19 (d, J=7.3 Hz, 1‴-H)], a β-D-xylopyranosyl parts [δ 5.77 (d, J=7.9 Hz, 1″-H)], a disubstituted olefin [δ 6.30 (ddd-like, 23-H) and 6.04 (d, J=15.6 Hz, 24-H)], and three methine protons bearing an oxygen function [δ 3.50 (dd, J=3.7, 10.4 Hz, 3-H), 4.35 (m, 6-H), and 5.76 (br s, 12-H)]. The carbon signals in the ^{13}C-NMR spectrum of **8** were shown to be very similar to those of notoginsenoside-R1,[8] except for some signals due to the side chain part (C-22—27) of the sapogenol moiety, whereas the carbon signals of the side chain part closely resembled those observed for notoginsenoside-A (**1**). Furthermore, the HMBC experiment of **8** showed long-range correlations between the following protons and carbons [1″-H and 2′-C, 1′-H and 6-C, 1‴-H and 20-C, 23-H and 25-C, 24-H and 23, 25, 26, 27-C] (Fig. 1). Consequently, the structure of

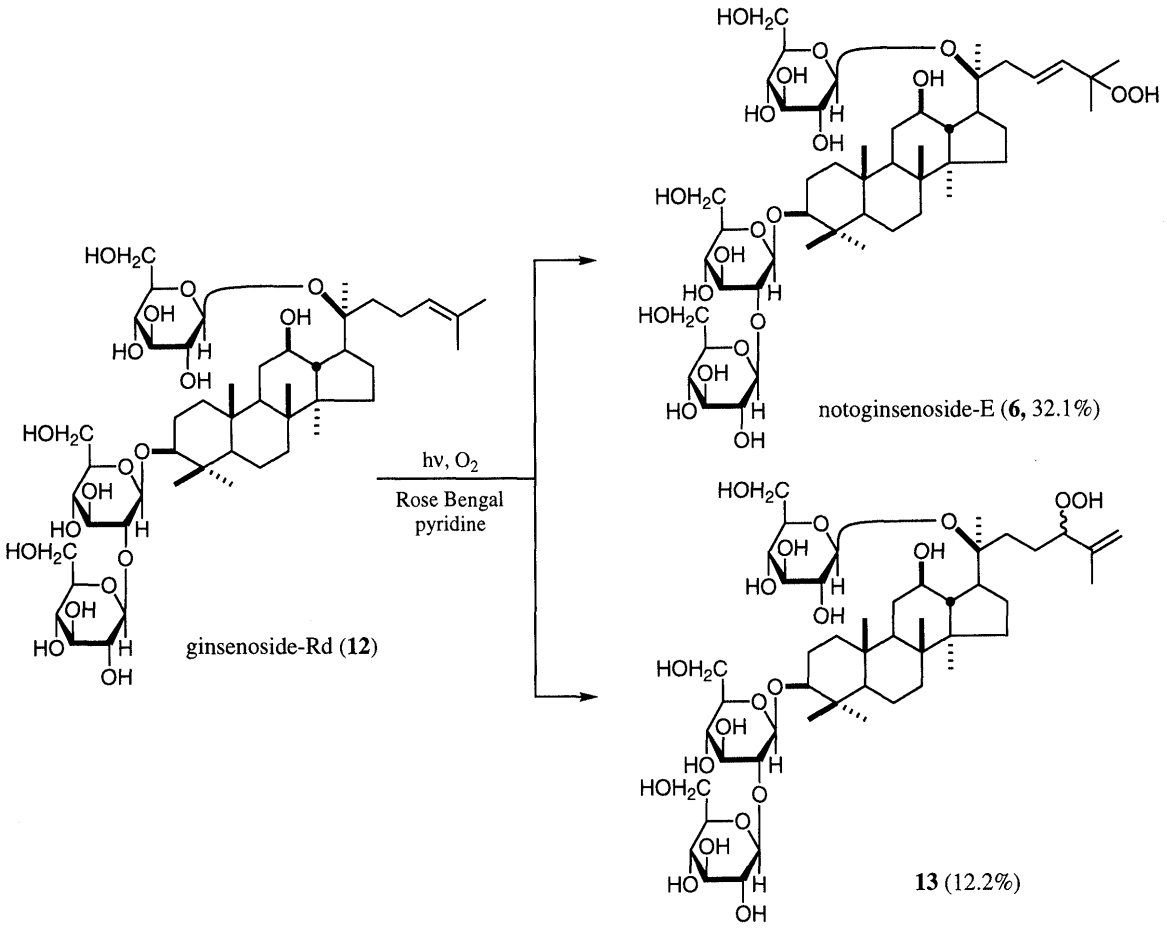

Chart 3

Table 1. ^{13}C-NMR Data of Notoginsenosides-E (**6**), -G (**7**), -H (**8**), -I (**9**), -J (**10**), and -K (**2**) and **13** (125 MHz, Pyridine-d_5)

	6	**7**	**8**	**9**	**10**	**2**	**13**		**6**	**7**	**8**	**9**	**10**	**2**	**13**
C-1	39.0	39.5	39.4	39.3	39.5	39.2	39.8	Glc-1′	105.0	104.9	103.4	105.0	106.0	105.1	105.1
C-2	26.5	27.1	27.8	26.8	28.0	26.8	26.8	2′	83.0	83.5	80.1	83.2	75.5	83.2	83.0
C-3	88.9	88.0	78.8	89.0	78.8	89.0	89.1	3′	78.1	78.2	79.8	78.2	78.8	78.1	78.2
C-4	39.6	42.7	40.2	39.7	40.4	39.7	39.8	4′	71.5	71.6	71.7	71.7	72.0	71.7	71.8
C-5	56.3	147.1	61.3	56.3	61.5	56.4	56.5	5′	78.1	78.3	78.0	78.0	78.0	78.0	78.2
C-6	18.3	127.5	79.5	18.4	80.1	18.5	18.5	6′	62.8	62.8	62.8	62.8	63.2	62.8	63.0
C-7	35.0	71.2	44.8	35.6	45.2	35.1	35.2	Glc (Xyl)-1″	105.8	106.1	104.8	105.9	98.3	106.0	106.0
C-8	39.9	42.3	41.1	40.6	41.2	40.0	40.1	2″	77.0	77.1	75.9	77.0	75.4	77.1	77.1
C-9	50.0	47.4	49.8	51.0	50.0	50.1	50.2	3″	77.8	77.9	78.7	77.9	78.8	78.0	78.0
C-10	36.8	38.1	39.6	36.9	39.8	36.9	37.0	4″	71.6	71.6	71.3	71.6	71.8	71.6	71.9
C-11	30.8	33.2	30.9	21.9	30.9	30.8	31.1	5″	78.2	78.4	67.2	78.3	78.8	78.2	78.4
C-12	70.4	69.8	70.6	25.5	70.5	70.5	70.3	6″	62.6	62.7		62.6	63.4	62.7	62.9
C-13	49.3	50.4	49.1	42.5	49.0	49.6	49.6	Glc-1‴	98.2	98.4	98.2	98.6		98.2	98.3
C-14	51.4	51.0	51.5	50.6	51.5	51.5	51.5	2‴	75.2	75.2	75.3	75.4		75.2	75.2
C-15	30.5	34.5	30.6	31.5	31.2	30.5	30.9	3‴	78.6	79.1	78.8	78.8		78.8	79.1
C-16	26.3	27.0	26.4	28.0	26.8	26.3	26.7	4‴	71.4	71.5	71.5	71.6		71.6	71.7
C-17	52.2	51.2	52.4	48.4	52.8	52.0	51.9	5‴	78.0	78.1	78.3	76.7		77.0	78.0
C-18	15.8	10.7	17.5	15.7	17.5	16.0	16.0	6‴	62.8	62.8	62.8	70.4		69.9	63.0
C-19	16.1	18.2[a]	17.6	16.4	17.6	16.3	16.3	Glc-1⁗				105.4		105.0	
C-20	83.3	82.5	83.2	82.4	83.5	83.4	83.5	2⁗				75.1		75.0	
C-21	23.2	22.6	23.1	21.3	22.8	23.4	22.6	3⁗				78.3		78.3	
C-22	39.5	36.4	39.1	40.4	33.9	39.7	32.6	4⁗				71.7		71.8	
C-23	126.3	23.3	122.7	23.2	27.1	126.6	26.4	5⁗				78.3		78.4	
C-24	138.0	125.9	142.1	126.1	79.8	138.1	89.9	6⁗				62.8		62.8	
C-25	81.2	131.0	70.0	130.6	72.9	81.3	145.8								
C-26	25.0[a]	25.8	30.6[a]	25.8	26.0[a]	25.1[a]	113.5								
C-27	25.3[a]	17.8	30.9[a]	18.0	26.5[a]	25.5[a]	17.6								
C-28	28.0	28.3	31.7	28.0	31.8	28.1	28.2								
C-29	16.4	23.9	16.7	16.6	16.4	16.6	16.6								
C-30	17.0	20.4[a]	16.9	16.8	17.1	17.2	17.4								

a) May be interchangeable.

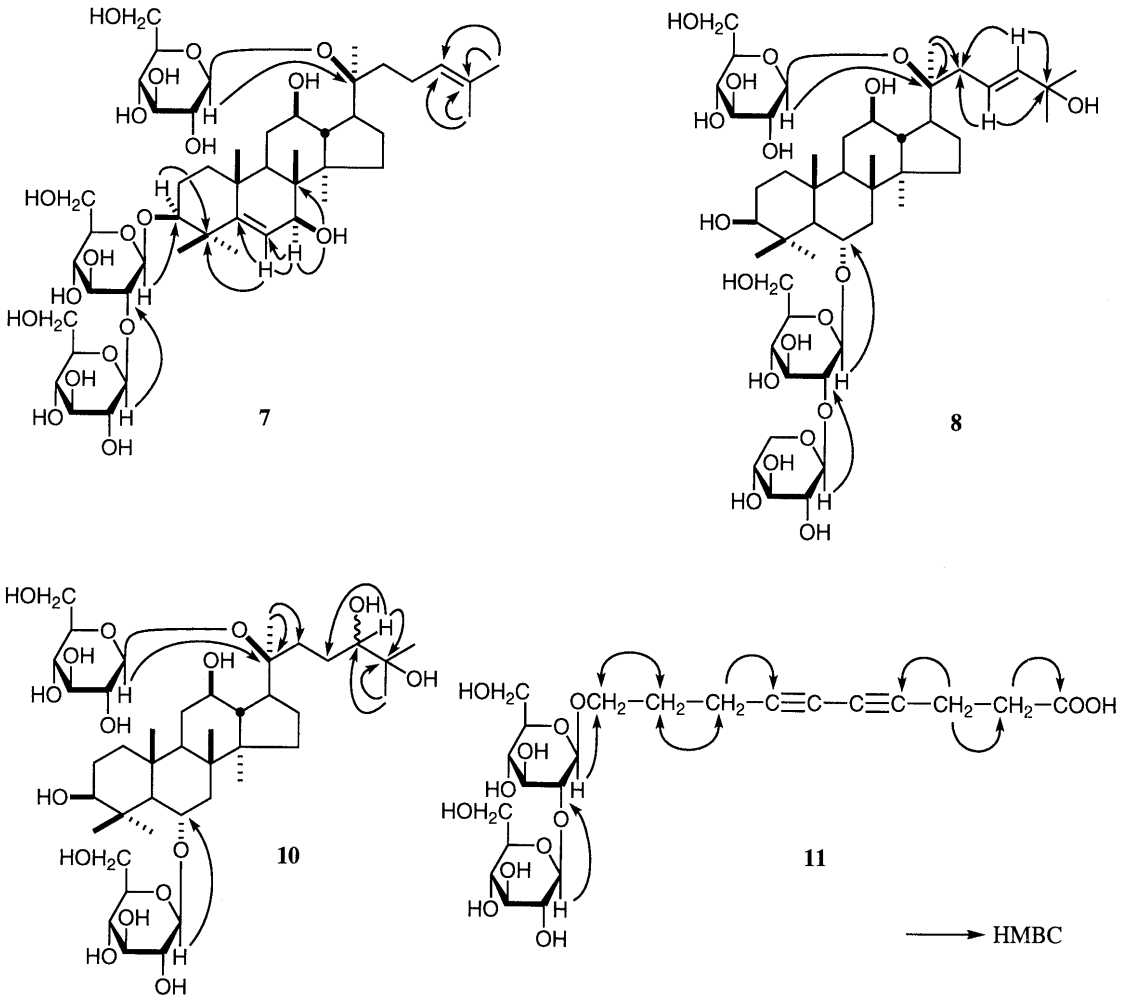

Fig. 1. Long-Range Correlations in the HMBC Spectrum of **7**, **8**, **10**, and **11**

notoginsenoside-H (**8**) was determined as shown.

Notoginsenoside-I (9) Notoginsenoside-I (**9**) was isolated as colorless fine crystals of mp 209—211 °C and showed absorption bands due to hydroxyl and olefin group in its IR spectrum. Here again, the molecular formula $C_{54}H_{92}O_{22}$ of **9** was clarified from its negative and positive-mode FAB-MS and by high-resolution MS measurement. Thus, in the positive-mode FAB-MS of **9**, the quasimolecular ion peak was observed at *m/z* 1115 $(M+Na)^+$, while the negative-mode FAB-MS of **9** showed the quasimolecular ion peak at *m/z* 1091 $(M-H)^-$ in addition to fragment ion peaks at *m/z* 929 $(M-C_6H_{11}O_5)^-$ and *m/z* 767 $(M-C_{12}H_{21}O_{10})^-$. The methanolysis of **9** liberated methyl glucoside. The ^{1}H-NMR (pyridine-d_5) spectrum[6] of **9** showed signals due to a dammarenediol II moiety [δ 3.29 (dd, J=4.0, 11.3 Hz, 3-H)], a β-sophorosyl moiety [δ 4.93 (d, J=7.6 Hz, 1′-H) and 5.37 (d, J=7.6 Hz, 1″-H)], and a β-gentiobiosyl moiety [δ 5.05 (d, J=7.6 Hz, 1‴-H) and 5.09 (d, J=7.6 Hz, 1⁗-H)]. The carbon signals of the sapogenol moiety in the ^{13}C-NMR (Table 1) spectrum[6] of **9** were superimposable on those of dammarenediol II glycosides,[9] whereas the carbon signals of the glycosidic moieties were very similar to those of notoginsenosides-A (**1**), -B (**3**), -C (**4**), and -K (**2**). Furthermore, in the HMBC experiment of **9**, long-range correlations were observed between the following protons and carbons [1″-H and 2′-C, 1′-H and 3-C, 1⁗-H and 6‴-C. 1‴-H and 20-C]. Based on this evidence, the structure of notoginsenoside-I (**9**) was characterized as shown.

Notoginsenoside-J (10) Notoginsenoside-J (**10**), obtained as colorless fine crystals of mp 205—207 °C, liberated methyl glucoside by the methanolysis and the IR spectrum of **10** showed absorption bands assignable to hydroxyl group. In the positive-mode FAB-MS of **10**, the quasimolecular ion peak was observed at *m/z* 857 $(M+Na)^+$, while the negative-mode FAB-MS showed the quasimolecular ion peak at *m/z* 833 $(M-H)^-$ and fragment ion peaks at *m/z* 671 $(M-C_6H_{11}O_5)^-$ and *m/z* 509 $(M-C_{12}H_{21}O_{10})^-$. The ^{1}H-NMR (pyridine-d_5) spectrum[6] of **10** showed signals due to two β-D-glucopyranosyl moieties [δ 4.98 (d, J=7.6 Hz, 1′-H) and 5.19 (d, J=7.6 Hz, 1″-H)] and three methine protons bearing an oxygen function [δ 3.49 (dd, J=3.4, 11.6 Hz, 3-H), 4.47 (ddd-like, 6-H), and 3.74 (dd-like, 24-H)]. The ^{13}C-NMR (Table 1) spectrum of **10** was very similar to those of ginsenoside-Rg_1,[10] except for signals due to the side chain part of the sapogenol moiety. The HMBC experiment showed long-range correlations between the following protons and carbons: 1′-H and 6-C; 1″-H and 20-C; 21-H_3 [δ 1.58 (s)] and 20, 22-C; 24-H and 25-C; 26, 27-H_3 [δ 1.53, 1.54 (both s)] and 24, 25-C (Fig. 1). Consequently, the structure of

Table 2. ^{13}C-NMR Data of Notoginsenic Acid β-Sophoroside (**11**) and Its Methyl Ester (**11a**) (125 MHz, DMSO-d_6)

	11	**11a**		**11**	**11a**
C-1	175.0	171.6	Glc-1′	101.3	101.1
C-2	36.0	32.0	2′	82.5	82.3
C-3	15.9[a)]	14.3[a)]	3′	76.0	75.9
C-4	77.7[b)]	76.3[b)]	4′	69.8	69.6
C-5	79.0[b)]	78.4[b)]	5′	76.7	76.5
C-6	64.9[b)]	64.9[b)]	6′	60.8	60.7
C-7	65.5[b)]	65.5[b)]	Glc-1″	104.5	104.3
C-8	15.2[a)]	15.0[b)]	2″	75.0	74.9
C-9	28.3	28.1	3″	75.9	75.9
C-10	67.2	67.0	4″	69.8	69.7
OMe		51.5	5″	77.1	77.0
			6″	60.9	60.8

a, b) May be interchangeable.

notoginsenoside-J (**10**) was determined as shown except for its C-24 configuration.

Notoginsenic Acid β-Sophoroside (11) Notoginsenic acid β-sophoroside (**11**) was also isolated as colorless fine crystals of mp 165—168 °C from aqueous methanol. The IR spectrum of **11** showed absorption bands at 3410, 2257, 1734, and 1076 cm^{-1} assignable to hydroxyl, acetylene, and carboxyl groups. The positive-mode FAB-MS of **11** showed the quasimolecular ion peaks at *m/z* 527 $(M+Na)^+$ and *m/z* 549 $(M+2Na-H)^+$, while the negative-mode FAB-MS showed the quasimolecular ion peak at *m/z* 503 $(M-H)^-$. Furthermore, a fragment ion peak was observed at *m/z* 341 $(M-C_6H_{11}O_5)^-$. The molecular formula of **11** was determined to be $C_{22}H_{32}O_6$ by high-resolution MS analysis of the quasimolecular ion peak $(M+Na)^+$. The methanolysis of **11** liberated methyl glucoside. The ^{1}H-NMR (DMSO-d_6) and ^{13}C-NMR (Table 2) spectra[6)] of **11** showed signals due to a β-sophorosyl moiety [δ 4.27 (d, *J*=7.9 Hz, 1′-H) and 4.36 (d, *J*=7.6 Hz, 1″-H)], four methylenes [δ 1.70 (m, 9-H_2), 2.13 (m, 2-H_2), and 2.39 (m, 3, 8-H_2)], and an oxymethylene [δ 3.50, 3.81 (both m, 10-H_2)]. The HMBC experiment of **11** showed long-range correlations between the following protons and carbons: 1″-H and 2′-C, 1′-H and 10-C, 10-H_2 and 9-C, 9-H_2 and 8, 10-C, 2-H_2 and 1, 3-C (Fig. 1). Methylation of **11** with diazomethane in methanol furnished the monomethyl ester (**11a**), whose ^{1}H-NMR (DMSO-d_6) and ^{13}C-NMR (Table 2) spectra[6)] showed signals due to a monomethyl ester [δ 3.35 (s)]. Comparison of the ^{1}H-NMR and ^{13}C-NMR data for **11** with those for **11a** led us to formulate the structure of notoginsenic acid β-sophoroside as shown.

We are currently engaged in examination of the hepatoprotecting effect of various ginsenosides and notoginsenosides obtained from glycosidic fraction, which will be reported in our forthcoming paper.

Experimental

The following instruments were used to obtain physical data: melting points, Yanagimoto micro-melting point apparatus MP-500D (values are uncorrected); specific rotations, Horiba SEPA-300 digital polarimeter (*l*=5 cm); UV spectra, Shimadzu UV-1200 spectrometer; IR spectra, Shimadzu FTIR-8100 spectrometer; FAB-MS and high-resolution MS, JEOL JMS-SX 102A mass spectrometer; ^{1}H-NMR spectra, JEOL EX-270 (270 MHz) spectrometer and LNM-LA500 (500 MHz) spectrometer; ^{13}C-NMR spectra, JEOL EX-270 (68 MHz) spectrometer and LNM-LA500 (125 MHz) spectrometer with tetramethylsilane as an internal standard.

The following experimental conditions were used for chromatography: ordinary-phase silica gel column chromatography, Silica gel BW-200 (Fuji Silysia Chemical, Ltd., 150—350 mesh); reversed-phase silica gel column chromatography, Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100—200 mesh); TLC, pre-coated TLC plate with Silica gel 60F_{254} (Merck, 0.25 mm) (ordinary phase) and Silica gel RP-18 60F_{254} (Merck, 0.25 mm) (reversed phase); reversed-phase HPTLC, pre-coated TLC plate with Silica gel RP-18 60WF_{254S} (Merck, 0.25 mm); detection was done by spraying 1% $Ce(SO_4)_2$–10% aqueous H_2SO_4 and heating.

Isolation of Notoginsenosides-E (6), -G (7), -H (8), -I (9), and -J (10) and Notoginsenic Acid β-Sophoroside (11) from the Dried Roots of *Panax notoginseng* (Burk.) F. H. Chen Notoginsenosides-E (**6**), -G (**7**), -H (**8**), -I (**9**), and -J (**10**) and notoginsenic acid β-sophoroside (**11**) were isolated as described earlier.[1)]

Notoginsenoside-E (**6**): Colorless fine crystals from aqueous MeOH, mp 202—204 °C, $[\alpha]_D^{24}$ +19.2° (*c*=0.1, MeOH). High-resolution positive-mode FAB-MS (*m/z*): Calcd for $C_{48}H_{82}O_{20}Na$ $(M+Na)^+$: 1001.5297. Found: 1001.5312. IR (KBr): 3432, 1638, 1078 cm^{-1}. ^{1}H-NMR (pyridine-d_5, δ): 0.83, 0.89, 1.00, 1.12, 1.30, 1.58, 1.59, 1.61 (3H each, all s, 19, 30, 18, 29, 28, 26, 27, 21-H_3), 3.26 (1H, dd-like, 3-H), 4.01 (1H, m, 12-H), 4.95 (1H, d, *J*=7.0 Hz, 1′-H), 5.22 (1H, d, *J*=7.6 Hz, 1‴-H), 5.39 (1H, d, *J*=6.7 Hz, 1″-H), 6.07 (1H, d, *J*=15.0 Hz, 24-H), 6.16 (1H, m, 23-H). ^{13}C-NMR: given in Table 1. Negative-mode FAB-MS (*m/z*): 977 $(M-H)^-$. Positive-mode FAB-MS (*m/z*): 1001 $(M+Na)^+$.

Notoginsenoside-G (**7**): Colorless fine crystals from aqueous MeOH, mp 204—206 °C, $[\alpha]_D^{21}$ +39.2° (*c*=0.1, MeOH). High-resolution positive-mode FAB-MS (*m/z*): Calcd for $C_{48}H_{80}O_{19}Na$ $(M+Na)^+$: 983.5191. Found: 983.5195. IR (KBr): 3410, 1637, 1078 cm^{-1}. ^{1}H-NMR (pyridine-d_5, δ): 1.13 (6H, s, 19, 30-H_3), 1.26, 1.42, 1.49, 1.59, 1.60, 1.65 (3H each, all s, 18, 29, 28, 26, 27, 21-H_3), 1.77 (1H, m, 9-H), 3.33 (1H, dd, *J*=4.6, 11.9 Hz, 3-H), 4.09 (1H, m, 12-H), 4.70 (1H, d, *J*=2.1 Hz, 7-H), 4.88 (1H, d, *J*=7.6 Hz, 1′-H), 5.22 (1H, d, *J*=7.6 Hz, 1‴-H), 5.27 (1H, dd-like, 24-H), 5.34 (1H, d, *J*=7.6 Hz, 1″-H), 5.83 (1H, d, *J*=2.1 Hz, 6-H). ^{13}C-NMR: given in Table 1. Negative-mode FAB-MS (*m/z*): 959 $(M-H)^-$, 797 $(M-C_6H_{11}O_5)^-$. Positive-mode FAB-MS (*m/z*): 983 $(M+Na)^+$, 1005 $(M+2Na-H)^+$.

Notoginsenoside-H (**8**): Colorless fine crystals from aqueous MeOH, mp 201—203 °C, $[\alpha]_D^{25}$ +14.9° (*c*=0.1, MeOH). High-resolution positive-mode FAB-MS (*m/z*): Calcd for $C_{47}H_{80}O_{19}Na$ $(M+Na)^+$: 971.5192. Found: 971.5197. IR (KBr): 3410, 1647, 1078 cm^{-1}. ^{1}H-NMR (pyridine-d_5, δ): 0.73, 0.99, 1.19, 1.48, 1.55, 2.08 (3H each, all s, 30, 19, 18, 29, 26, 28-H_3), 1.56 (6H, s, 21, 27-H_3), 3.50 (1H, dd, *J*=3.7, 10.4 Hz, 3-H), 4.35 (1H, m, 6-H), 4.93 (1H, d, *J*=7.3 Hz, 1′-H), 5.19 (1H, d, *J*=7.3 Hz, 1‴-H), 5.76 (1H, br s, 12-H), 5.77 (1H, d, *J*=7.9 Hz, 1″-H), 6.04 (1H, d, *J*=15.6 Hz, 24-H), 6.30 (1H, ddd-like, 23-H). ^{13}C-NMR: given in Table 1. Negative-mode FAB-MS (*m/z*): 947 $(M-H)^-$, 1895 $(2M-H)^-$. Positive-mode FAB-MS (*m/z*): 971 $(M+Na)^+$.

Notoginsenoside-I (**9**): Colorless fine crystals from aqueous MeOH, mp 209—211 °C, $[\alpha]_D^{24}$ +0.8° (*c*=0.1, MeOH). High-resolution positive-mode FAB-MS (*m/z*): Calcd for $C_{54}H_{92}O_{22}Na$ $(M+Na)^+$: 1115.5978. Found: 1115.5968. IR (KBr): 3432, 1637, 1076 cm^{-1}. ^{1}H-NMR (pyridine-d_5, δ): 0.81, 0.98, 0.99, 1.12, 1.28, 1.53 (3H each, all s, 19, 30, 18, 29, 28, 21-H_3), 1.72 (6H, s, 26, 27-H_3), 3.29 (1H, dd, *J*=4.0, 11.3 Hz, 3-H), 4.93 (1H, d, *J*=7.6 Hz, 1′-H), 5.05 (1H, d, *J*=7.6 Hz, 1‴-H), 5.09 (1H, d, *J*=7.6 Hz, 1⁗-H), 5.37 (1H, d, *J*=7.6 Hz, 1″-H), 5.40 (1H, br s, 24-H). ^{13}C-NMR : given in Table 1. Negative-mode FAB-MS (*m/z*): 1091 $(M-H)^-$, 929 $(M-C_6H_{11}O_5)^-$, 767 $(M-C_{12}H_{21}O_{10})^-$. Positive-mode FAB-MS (*m/z*): 1115 $(M+Na)^+$.

Notoginsenoside-J (**10**): Colorless fine crystals from aqueous MeOH, mp 205—207 °C, $[\alpha]_D^{28}$ +9.3° (*c*=0.3, MeOH). High-resolution positive-mode FAB-MS (*m/z*): Calcd for $C_{42}H_{74}O_{16}Na$ $(M+Na)^+$: 857.4875. Found: 857.4893. IR (KBr): 3403, 1078 cm^{-1}. ^{1}H-NMR (pyridine-d_5, δ): 0.77, 1.03, 1.13, 1.53, 1.54, 1.57, 1.58, 2.03 (3H each, all s, 30, 19, 18, 26, 27, 29, 21, 28-H_3), 3.49 (1H, dd, *J*=3.4, 11.6 Hz, 3-H), 3.74 (1H, dd-like, 24-H), 4.47 (1H, ddd-like, 6-H), 4.98 (1H, d, *J*=7.6 Hz, 1′-H), 5.19 (1H, d, *J*=7.6 Hz, 1″-H). ^{13}C-NMR: given in Table 1. Negative-mode FAB-MS (*m/z*): 833 $(M-H)^-$, 671 $(M-C_6H_{11}O_5)^-$, 509 $(M-C_{12}H_{21}O_{10})^-$. Positive-mode FAB-MS (*m/z*): 857 $(M+Na)^+$.

Notoginsenic acid β-sophoroside (**11**): Colorless fine crystals from

aqueous MeOH, mp 165—168 °C, $[\alpha]_D^{25}$ −9.6° (c=0.1, MeOH). High-resolution positive-mode FAB-MS (m/z): Calcd for $C_{22}H_{32}O_{13}Na$ $(M+Na)^+$: 527.1740. Found: 527.1763. IR (KBr) : 3410, 2257, 1734, 1632, 1578, 1406, 1076 cm^{-1}. ^{1}H-NMR (DMSO-d_6, δ): 1.70 (2H, m, 9-H_2), 2.13 (2H, m, 2-H_2), 2.39 (4H, m, 3, 8-H_2), 3.50 (1H, m), 3.81 (1H, m) (10-H_2), 4.27 (1H, d, J=7.9 Hz, 1′-H), 4.36 (1H, d, J=7.6 Hz, 1″-H). ^{13}C-NMR: given in Table 2. Negative-mode FAB-MS (m/z): 503 $(M-H)^-$, 341 $(M-C_6H_{11}O_5)^-$. Positive-mode FAB-MS (m/z): 527 $(M+Na)^+$, 549 $(M+2Na-H)^+$.

Methanolysis of Notoginsenosides-E (6), -G (7), -H (8), -I (9), and -J (10) and Notoginsenic Acid β-Sophoroside (11) A solution of notoginsenosides (1 mg each of **6**, **7**, **8**, **9**, and **10**) and notoginsenic acid β-sophoroside (**11**, 1 mg) in 9% HCl–dry MeOH (0.5 ml) was heated under reflux for 2 h. After cooling, the reaction mixture was neutralized with Ag_2CO_3 and the insoluble portion was removed by filtration. After removal of the solvent *in vacuo* from the filtrate, the residue was dissolved in pyridine (0.01 ml) and the solution was treated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, 0.02 ml) for 1 h. The reaction solution was then subjected to GLC analysis to identify the trimethylsilyl (TMS) derivatives of methyl glucoside (i) from **6**, **7**, **9**, **10**, and **11**; i and methyl xyloside (ii) from **8**; GLC conditions: column CBR1-M25-025 [0.25 mm (i.d.) × 25 m], injector temperature: 140 °C, detector temperature: 280 °C, column temperature: 140—240 °C, 5 °C/min, initial time: 5 min, He flow rate: 15 ml/min, t_R: i: 17.8, 18.2, 19.2 min, ii: 15.8, 16.2 min.

Photosensitized Oxygenation of Ginsenoside-Rd (12) Giving Notoginsenoside-E (6) and 13 A solution of **12** (126 mg) and Rose Bengal (13 mg) in dry pyridine (5 ml) was irradiated for 1.5 h with a 400 W Hg lamp at room temperature (25 °C) in a Pyrex tube under an O_2 atmosphere. Removal of the solvent from the filtrate under reduced pressure gave a crude product (198 mg), which was purified by HPLC [MeOH–H_2O (65 : 35, v/v)] to give **6** (41.7 mg, 32.1%) and **13** (15.9 mg, 12.2%). Thus obtained **6** was identified with an authentic notoginsenoside-E by TLC, IR, $[\alpha]_D$, and ^{1}H- and ^{13}C-NMR spectral comparisons.

13: Colorless fine crystals from aqueous MeOH, mp 201—203 °C, $[\alpha]_D^{27}$ +13.3° (c=0.1, MeOH). High-resolution positive-mode FAB-MS (m/z): Calcd for $C_{48}H_{82}O_{20}Na$ $(M+Na)^+$: 1001.5297. Found: 1001.5333. IR (KBr) 3453, 1076 cm^{-1}. ^{1}H-NMR (pyridine-d_5, δ): 0.83, 0.92, 0.98, 1.10, 1.29, 1.60, 1.92 (3H each, all s, 19, 30, 18, 29, 28, 21, 27-H_3), 3.27 (1H, dd, J=4.6, 11.3 Hz, 3-H), 4.74 (1H, dd-like, 24-H), 4.89 (1H, d, J=7.3 Hz, 1′-H), 5.06, 5.23 (1H each, all s, 26-H_2), 5.15 (1H, d, J=7.4 Hz, 1‴-H), 5.34 (1H, d, J=7.0 Hz, 1″-H), 5.51 (1H, br s, 12-H). ^{13}C-NMR: given in Table 1. Negative-mode FAB-MS (m/z): 977 $(M-H)^-$, 815 $(M-C_6H_{11}O_5)^-$. Positive-mode FAB-MS (m/z): 1001 $(M+Na)^+$.

Diazomethane Methylation of Notoginsenic Acid β-Sophoroside (11) An ice cooled solution of **11** (10 mg) in MeOH (3 ml) was treated with ethereal diazomethane (*ca.* 4 ml) until the yellow color was constant. The solution was stirred for 1 h at room temperature, then the solvent was removed under pressure to furnish a residue (11 mg). The residue was purified by HPLC [MeOH–H_2O (50 : 50, v/v)] to give **11a** (5.5 mg, 53.5%).

11a: A white powder, ^{1}H-NMR (DMSO-d_6, δ): 1.70 (2H, m, 9-H_2), 2.38 (4H, m, 3, 8-H_2), 2.54 (4H, m, 2, 3-H_2), 3.50 (1H, m), 3.80 (1H, m) (10-H_2), 4.27 (1H, d, J=7.9 Hz, 1′-H), 4.36 (1H, d, J=7.6 Hz, 1″-H). ^{13}C-NMR: given in Table 2.

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