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Saponin and Sapogenol. XXXVII.[1] Chemical Constituents of Astragali Radix, the Root of *Astragalus membranaceus* BUNGE. (4). Astragalosides VII and VIII

ISAO KITAGAWA,* HUI KANG WANG, and MASAYUKI YOSHIKAWA

Faculty of Pharmaceutical Sciences, Osaka University
1-6, Yamada-oka, Suita, Osaka 565, Japan

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By means of enzymatic degradation and by application of a selective cleavage method for the glucuronide linkage, as well as by the carbon-13 nuclear magnetic resonance (^{13}C-NMR) analysis, the structures of two astragalosides, which were isolated as two of eleven astragalosidesfrom Astragali Radix (the root of Korean *Astragalus membranaceus*, Leguminosae), were elucidated: astragaloside VII is 3-*O*-β-D-xylopyranosyl-6-*O*-β-D-glucopyranosyl-25-*O*-β-D-glucopyranosyl-cycloastragenol (**4**) and astragaloside VIII is 3-*O*-[α-L-rhamnopyranosyl(1→2)-β-D-xylopyranosyl(1→2)-β-D-glucuronopyranosyl]soyasapogenl B (**8**). Astragaloside VII (**4**) is an unprecedented example of a triterpene-tridesmoside.

Keywords——*Astragalus membranaceus*; Leguminosae; 9,19-cyclolanostane-oligoglycoside; oleanene-oligoglycoside; triterpene-tridesmoside; glucuronide-saponin; astragaloside; cycloastragenol; soyasapogenol B; selective cleavage of glucuronide linkage

In previous papers, we reported the isolation of eleven astragalosides and soyasaponin I (**9**) from Astragali Radix, the root of Korean *Astragalus membranaceus* BUNGE (Leguminosae),and elucidated the structures of nine astragalosides: acetylastragaloside I, isoastragalosides I and II, and astragalosides I, II, III, IV (**3**), V, and VI.[1,2] This paper describes the structural elucidation of the remaining two astragalosides: astragaloside VII (**4**), which is a tridesmoside of cycloastragenol (**1**), and astragaloside VIII (**8**), which is a new glucuronide-saponin of soyasapogenol B (**5**).[3]

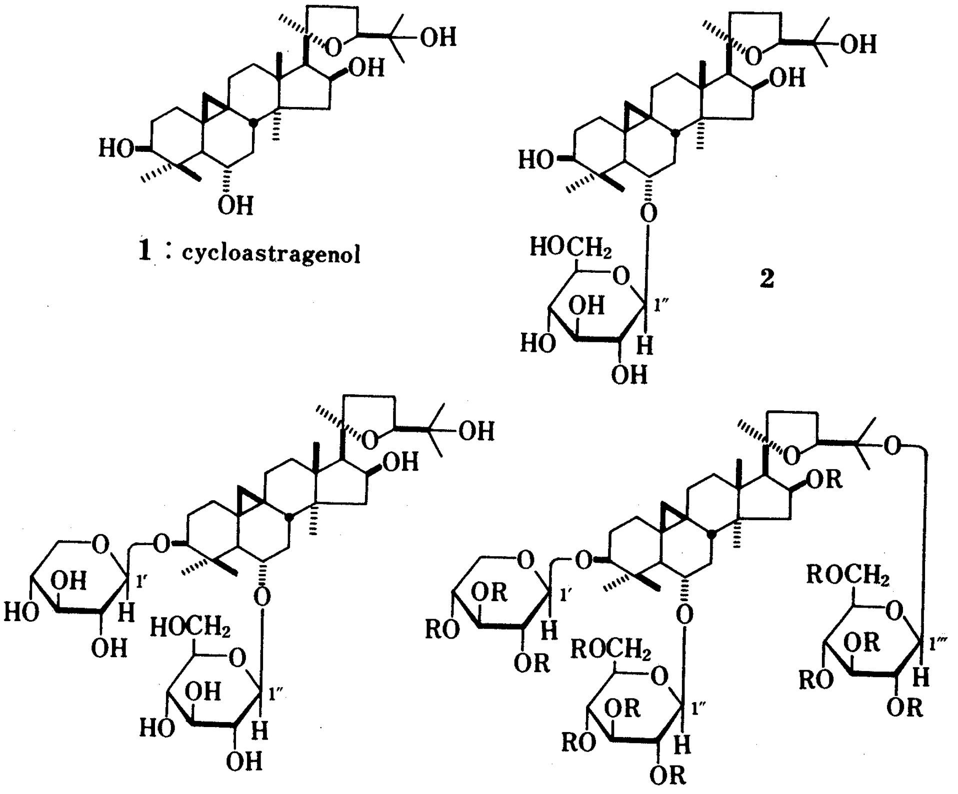
Astragaloside VII (4)

The infrared (IR) spectrum of astragaloside VII (**4**) exhibited strong hydroxyl absorption bands characteristic of glycosidic nature. Methanolysis of **4** with 9% hydrogen chloride in dry methanol disclosed the carbohydrate composition in **4** to be glucose and xylose in 2:1 ratio. Enzymatic hydrolysis of **4** with crude hesperidinase[1,2,4] yielded 6-*O*-glucopyranosyl-cycloastragenol (**2**)[2b] and astragaloside IV (**3**).[2b]

The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of astragaloside VII (**4**) indicated the occurrence of significant glycosidation shifts[5] of the 3-C, 6-C and 25-C signals. It also showed two β-anomeric carbon signals at δc 104.8 and 107.3 and a signal at δc 98.8 which was assignable to a β-anomeric carbon of a glucopyranosyl residue attached to the tertiary 25-OH function.[1,5] Consequently, astragaloside VII (**4**) was suggested to be a tridesmoside which possessed an additional glucopyranosyl residue attached to the 25-OH function of astragaloside IV (**3**).

Complete methylation of astragaloside VII (**4**) with methyl iodide and dimsyl carbanion[7] afforded the dodeca-*O*-methyl derivative (**4a**). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **4a** showed three β-anomeric proton signals. Methanolysis of **4a** provided methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**a**) and methyl 2,3,4-tri-*O*-methyl xylopyranoside (**b**) in 2:1 ratio,which further supported the tridesmoside structure of **4**.

Based on the above-mentioned evidence, the structure of astragaloside VII was deter-



1 : cycloastragenol

2

3 : astragaloside IV

4 : R=H (astragaloside VII)
4a : R=Me

Chart 1

mined to be 3-*O*-β-D-xylopyranosyl-6-*O*-β-D-glucopyranosyl-25-*O*-β-D-glucopyranosyl-cycloastragenol (**4**). Astragaloside VII (**4**) is the first example of a triterpene-tridesmoside.

Astragaloside VIII (8)

The IR spectrum of astragaloside VIII (**8**) showed a carboxyl absorption band together with strong hydroxyl bands. Diazomethane methylation of **8** furnished the monomethyl ester (**8a**), while methanolysis of **8** disclosed the carbohydrate composition in **8** to be glucuronic acid, xylose and rhamnose in 1 : 1 : 1 ratio.

Since astragaloside VIII (**8**) was shown to contain a glucuronide linkage, a photochemical degradation[8] which is one of four selective cleavage methods for the glucuronide linkage[9] was applied to **8**. External irradiation of a methanolic solution of astragaloside VIII monomethyl ester (**8a**) in a Vycor tube with a 500 W high pressure mercury lamp for 2 h liberated soyasapogenol B (**5**) in high yield. Therefore, it became evident that astragaloside VIII (**8**) was a soyasapogenol B glucuronide possessing a xylose residue and a rhamnose residue attached to the glucuronide moiety.

Complete methylation of astragaloside VIII (**8**) provided the deca-*O*-methyl derivative (**8b**). The ^{1}H-NMR spectrum of **8b** showed three anomeric proton signals, among which two doublets ($J=7$ Hz) at δ 4.44 and 4.89 were attributable to β-anomeric protons in the glucuronopyranosyl and xylopyranosyl moieties.

Lithium aluminum hydride reduction of **8b** and subsequent methanolysis provided 22,24-di-*O*-methylsoyasapogenol B (**5a**)[10] from the aglycone part and methyl 3,4-di-*O*-methylglucopyranoside (**c**), methyl 3,4-di-*O*-methylxylopyranoside (**d**) and methyl 2,3,4-tri-

TABLE I. ^{13}C-NMR Data for Cycloastragenol (**1**), **2**, Astragaloside IV (**3**) and Astragaloside VII (**4**) (25.05 MHz, in d_5-pyridine, δc)[a]

		1	2	3	4
Aglycone moiety	C-3	78.4	78.6	$\underline{88.7}$	$\underline{88.6}$ (d)
	C-5	54.0	52.7	54.2	52.4 (d)
	C-6	68.5	$\underline{79.9}$	$\underline{79.2}$	$\underline{79.1}$ (d)
	C-16	73.6	73.7	73.5	73.5 (d)
	C-17	58.5	58.7	58.7	58.1 (d)
	C-20	87.4	87.5	87.3	87.2 (s)
	C-24	81.8	82.2	82.0	82.2 (d)
	C-25	71.4	71.6	71.5	$\underline{78.6}$ (s)
3-*O*-β-D-Xylopyranosyl moiety	C-1′			107.1	107.3 (d)
	C-2′			75.2	75.3 (d)[b]
	C-3′			77.7	77.8 (d)
	C-4′			71.3	71.4 (d)[c]
	C-5′			66.6	66.8 (t)
6-*O*-β-D-Glucopyranosyl moiety	C-1″		105.0	105.0	104.8 (d)
	C-2″		75.7	75.6	75.5 (d)[b]
	C-3″		79.1	79.0	78.7 (d)
	C-4″		72.3	72.2	72.0 (d)[c]
	C-5″		77.8	77.9	77.8 (d)
	C-6″		63.5	63.4	62.8 (t)
25-*O*-β-D-Glucopyranosyl moiety	C-1‴				98.8 (d)
	C-2‴				75.1 (d)[b]
	C-3‴				78.4 (d)
	C-4‴				71.5 (d)[c]
	C-5‴				77.8 (d)
	C-6‴				62.8 (t)

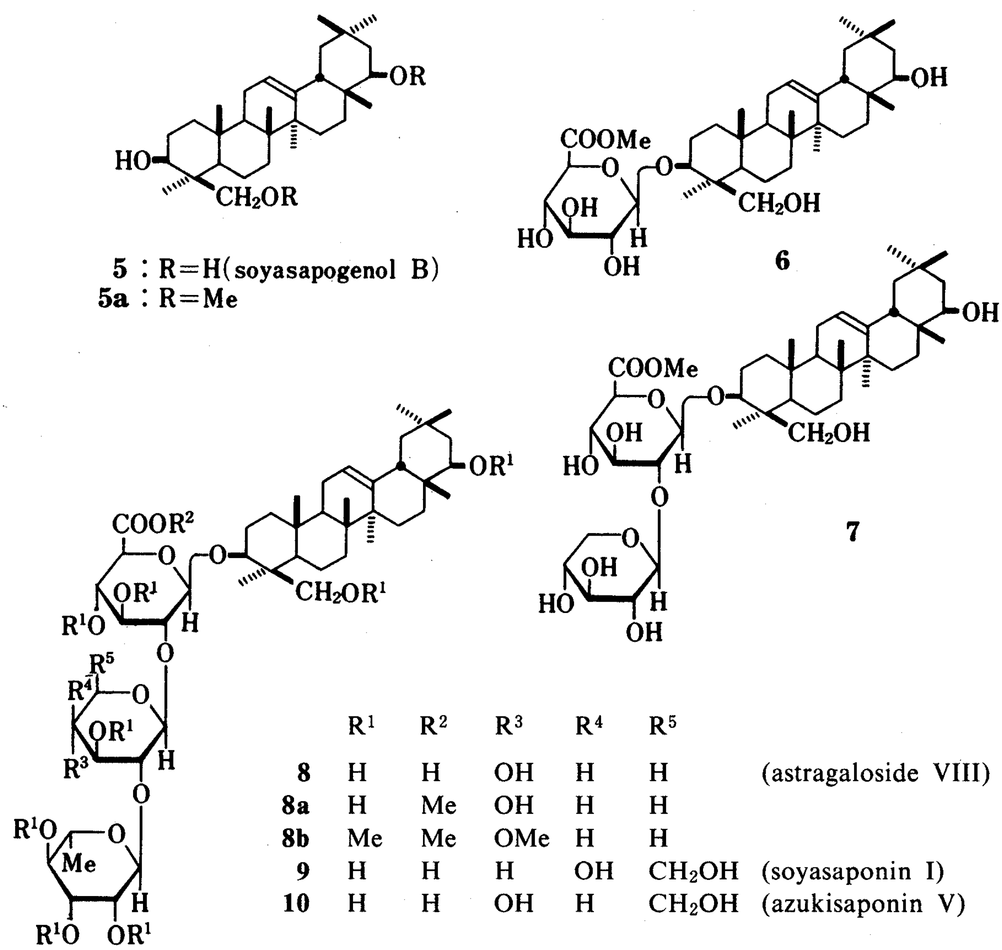
a) The off-resonance patterns of the signals are given in parentheses with abbereviations: d=doublet, s=singlet and t=triplet. The carbon signals affected by glycosidation shifts are underlined.
b, *c*) Assignments may be interchangeable within the same column.

O-methylrhamnopyranoside (**e**) from the carbohydrate portion. Consequently, the carbohydrate sequence in astragaloside VIII (**8**) was substantiated.

Next, astragaloside VIII monomethyl ester (**8a**) was subjected to partial hydrolysis with 20% oxalic acid in methanol to furnish 3-*O*-β-D-glucuronopyranosyl-soyasapogenol B monomethyl ester (**6**)[10] and a new diglycoside of soyasapogenol B (**7**). Methanolysis of the diglycoside (**7**) provided soyasapogenol B (**5**) together with methyl glucuronide and methyl xyloside in 1 : 1 ratio. Thus, the structure of **7** was elucidated. Application of Klyne's rule[11] to **7** and astragaloside VIII (**8**) finally indicated the α-linkage of the terminal rhamnopyranosyl residue in **8**.

Based on the above-mentioned results, the structure of astragaloside VIII was determined to be 3-*O*-[α-L-rhamnopyranosyl(1→2)-β-D-xylopyranosyl(1→2)-β-D-glucuronopyranosyl] soyasapogenol B (**8**).

Astragaloside VIII (**8**) seems to be the fifth example of naturally occurring glucuronide-saponins of soyasapogenol B (**5**). Recently, we demonstrated the wide occurrence of two glucuronide-saponins of soyasapogenol B in several leguminous plants: soyasaponin I (**9**) from the seeds of *Glycine max* MERRILL,[10] the root of *Sophora flavescens* AITON[12] and the root of *Hedysarum fruticosum* PALLAS var. *mongholicum* TURCZ.[12]; azukisaponin V (**10**) from the seeds of *Vigna angularis* (WILLD.) OHWI *et* OHASHI.[13] Since total soyasaponin, which includes soyasaponin I (**9**) as the major constituent, exhibits various biological activities,[14] astragaloside VIII (**8**) and azukisaponin V (**10**) might have interesting biological activities.



5 : R=H(soyasapogenol B)
5a : R=Me

6

7

	R^1	R^2	R^3	R^4	R^5	
8	H	H	OH	H	H	(astragaloside VIII)
8a	H	Me	OH	H	H	
8b	Me	Me	OMe	H	H	
9	H	H	H	OH	CH_2OH	(soyasaponin I)
10	H	H	OH	H	CH_2OH	(azukisaponin V)

Chart 2

Experimental[15]

Astragaloside VII (4)———Astragaloside VII (**4**, 0.1 g) was obtained from Korean Astragali Radix (8 kg) as described previously.[2b] **4**, mp 292—293°C (colorless needles from MeOH), $[\alpha]_D^{18}+10.3°$ (c=0.6, MeOH). *Anal.* Calcd for $C_{47}H_{78}O_{19}\cdot 2H_2O$: C, 57.42; H, 8.41. Found: C, 57.42; H, 8.50. IR ν_{max}^{KBr} cm^{-1}: 3400, 1070, 1040. ^{13}C-NMR: as given in Table I.

Methanolysis of 4———A solution of **4** (2 mg) in 9% HCl-dry MeOH (0.5 ml) was heated under reflux for 1 h. After neutralization with Ag_2CO_3 powder, the reaction mixture was filtered to remove the inorganic material. The solvent was evaporated off from the filtrate under reduced pressure and the dried residue was dissolved in pyridine (0.1 ml). The solution was treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (0.2 ml) and allowed to stand at room temp. for 10 min. The reaction mixture was subjected to gas liquid chromatography (GLC) analysis and was shown to contain TMS derivatives of methyl glucoside and methyl xyloside in 2:1 ratio as judged from the peak area. GLC: 1) 5% silicone SE-52 on Chromosorb WAW DMCS (80—100 mesh); 2 m×3 mm glass column; column temp., 190°C; N_2 flow rate, 33 ml/min. t_R: TMS-methyl glucoside 7′30″ (major), 7′59″; TMS-methyl xyloside 3′21″ (major), 3′33″.

Enzymatic Hydrolysis of 4 with Crude Hesperidinase———A solution of **4** (70 mg) in water-acetone (9:1, 10 ml) was treated with crude hesperidinase (700 mg) and the whole mixture was incubated with stirring at 36°C for 12 h. The reaction mixture was extracted with $CHCl_3$-MeOH (5:1). The extract was washed with water and dried over $MgSO_4$ powder. Removal of the solvent under reduced pressure gave the product,which was purified by column chromatography (SiO_2 5 g; $CHCl_3$-MeOH=10:1→5:1) to furnish 6-*O*-glucopyranosylcycloastragenol (**2**, 8 mg) and astragaloside IV (**3**, 20 mg). **2** and **3** were shown to be identical with the respective authentic samples by mixed mp determination and thin-layer chromatography (TLC) ($CHCl_3$-MeOH-H_2O=10:3:1, lower phase; n-BuOH-AcOEt=4:1; $CHCl_3$-MeOH-AcOEt-H_2O=15:9:23:3) and IR (KBr) comparisons.

Complete Methylation of 4——A solution of **4** (100 mg) in dimethyl sulfoxide (DMSO) (5 ml) was treated with dimsyl carbanion (10 ml)[7] and the whole mixture was stirred under an N_2 atmosphere for 2 h. The reaction mixture was then treated with CH_3I (15 ml). The whole mixture was stirred in the dark for 6 h, poured into ice-water and extracted with AcOEt. The AcOEt extract was washed successively with aq. $Na_2S_2O_3$ and water, and dried over $MgSO_4$ powder. The product, obtained by evaporation of the solvent under reducerd pressure, was purified by column chromatography (SiO_2 5 g; benzene–acetone=5:1) to furnish the dodeca-O-methyl derivative (**4a**, 60 mg). **4a**, white powder,[16] $[\alpha]_D^{16}$ +19.8° (c=1.0, $CHCl_3$). *Anal.* Calcd for $C_{59}H_{102}O_{19}$: C, 63.53; H, 9.22. Found: C, 63.66; H, 9.41. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1095. ^{1}H-NMR ($CDCl_3$–d_6-acetone=1:1, δ): 0.24, 0.55 (1H each, both d, J=4 Hz, 19-H_2), 0.99 (6H), 1.16 (3H), 1.25 (12H) (all s, *tert*-$CH_3 \times 7$), 2.31 (1H, d, J=8 Hz, 17-H), 3.13, 3.33, 3.36, 3.42, 3.47, 3.49 (3H each), 3.52 (6H), 3.56 (12H) (all s, $OCH_3 \times 12$), 4.26, 4.30, 4.52 (1H each, all d, J=8 Hz, anomeric H×3). MS m/z (%): 219 (9), 187 (100).

Methanolysis of 8——A solution of **8** (10 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 2 h. After neutralization of the reaction mixture as described for the methanolysis of **4**, the reaction material. Removal of the solvent from the filtrate under reduced pressure provided the product, from which methyl 2,3,4,6-tetra-*O*-methylglucopranoside (**a**) and methyl 2,3,4-tri-*O*-methylxylopyranoside (**b**) were identified by TLC (benzene–acetone=4:1; n-hexane–AcOEt=1:1) and GLC comparisons. GLC: 2) 15% ethylene glycol succinate polyester on Uniport B (80—100 mesh); 1 m×3 mm glass column; column temp., 160°C; N_2 flow rate, 30 ml/min. t_R: **a** 6′48″ (major), 10′06″; **b** 3′19″, 4′16″ (major). 3) 15% polyneopentylglycol succinate on Chromosorb WAW (80—100 mesh); 2 m×3 mm glass column; column temp., 170°C; N_2 flow rate, 35 ml/min. t_R: **a** 7′22″ (major), 10′17″; **b** 3′33″, 4′24″ (major).

Astragaloside VIII (8)——Astragaloside VIII (**8**, 0.6 g) was obtained from Korean Astragali Radix (8 kg) as described previously.[2b)] **8**, mp 223—224°C (colorless fine crystals from MeOH), $[\alpha]_D^{18}$ −12.1° (c=1.0, MeOH). *Anal.* Calcd for $C_{47}H_{76}O_{17} \cdot H_2O$: C, 60.83; H, 8.44. Found: C, 60.81; H, 8.60. IR ν_{max}^{KBr} cm^{-1}: 3400, 1725, 1040.

Methanolysis of 8——A solution of **8** (10 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 2 h. After neutralization of the reaction mixture as described for the methanolysis of **4**, the reaction product was subjected to TLC analysis ($CHCl_3$–MeOH=20:1; benzene–acetone=4:1; n-hexane–AcOEt=1:1) and the product was shown to be identical with authentic soyasapogenol B (**5**). Removal of the solvent from the reaction mixture under reduced pressure yielded the residue, which was treated with *N,O*-bis (trimethylsilyl) trifluoroacetamide–pyridine (2:1, 0.6 ml). The mixture was allowed to stand at room temp. for 10 min. The products were shown to be identical with TMS derivatives of methyl glucuronide, methyl xyloside and methyl rhamnoside by GLC analysis: GLC: 4) 3% silicone SE-30 on Chromosorb WAW DMCS (80—100 mesh); 1 m×3 mm glass column; column temp., 140°C; N_2 flow rate,39 ml/min. t_R: TMS-methyl glucuronide 4′15″, 9′50″ (major); TMS-methyl xyloside 2′50″ (major), 3′10″; TMS-methyl rhamnoside 2′03″. 5) 5% silicone SE-52 on Chromosorb WAW DMCS (80—100 mesh); 2 m×3 mm glass column; column temp., 190°C; N_2 flow rate,35 ml/min. t_R: TMS-methyl glucuronide 6′40″, 13′42″ (major); TMS-methyl xyloside 4′15″ (major), 4′32″. TMS-methyl rhamnoside 3′22″.

Diazomethane Methylation of 8——A solution of **8** (100 mg) in MeOH (10 ml) was treated with excess ethereal diazomethane and the whole solution was allowed to stand for 12 h. Removal of the solvent under reduced pressure provided the monomethyl ester (**8a**, 100 mg). **8a**, mp 278—280°C (colorless fine crystals from MeOH), $[\alpha]_D^{18}$ −12.9° (c=1.0, MeOH). *Anal.* Calcd for $C_{48}H_{78}O_{17} \cdot 2H_2O$: C, 59.86; H, 8.58. Found: C, 60.12; H, 8.60. IR ν_{max}^{KBr} cm^{-1}: 3400, 1740, 1040.

Photolysis of 8a——A solution of **8a** (50 mg) in MeOH (50 ml) in a Vycor tube was irradiated externally with a 500 W high pressure mercury lamp (PIH-500, Eikosha) for 2 h. The reaction mixture was neutralized with aq. 5% K_2CO_3 and the solvent was evaporated off under reduced pressure. Purification of the product by column chromatography (SiO_2 2 g; $CHCl_3$–MeOH=20:1) furnished soyasapogenol B (**5**, 15 mg) which was shown to be identical with an authentic sample by mixed mp determination and TLC (as described above) and IR (KBr) comparisons.

Complete Methylation of 8——A solution of **8** (200 mg) in DMSO (5 ml) was treated with dimsyl carbanion (10 ml) and the whole solution was stirred under an N_2 atmosphere for 2 h. After addition of CH_3I (5 ml), the reaction mixture was stirred in the dark for 1 h and worked up as described in the case of **4a**. Purification of the product by column chromatography (SiO_2 15 g; benzene–acetone=5:1) provided the deca-*O*-methyl derivative (**8b**, 90 mg). **8b**, mp 203—204°C (colorless needles from MeOH), $[\alpha]_D^{14}$ −3.6° (c=1.0, $CHCl_3$). *Anal.* Calcd for $C_{57}H_{96}O_{17}$: C,65.77; H, 8.98. Found: C, 65.69; H, 9.02. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1750, 1075. ^{1}H-NMR (d_6-benzene, δ): 0.96, 1.03 (3H each), 1.13 (6H), 1.16, 1.18, 1.28 (3H each) (all s, *tert*-$CH_3 \times 7$), 3.10, 3.14, 3.22 (3H each), 3.37 (12H), 3.47 (6H), 3.77 (3H) (all s, $OCH_3 \times 10$), 4.44, 4.89 (1H each, both d, J=7 Hz, anomeric H×2), 5.26 (1H, br s, 12-H), 5.54 (1H, s, anomeric H of rhamnoside).

$LiAlH_4$ Reduction followed by Methanolysis of 8b——A solution of **8b** (45 mg) in ether (5 ml) was treated with a suspension of $LiAlH_4$ (90 mg) in ether (5 ml) and the whole mixture was stirred at 21°C for 1 h. The reaction mixture was treated with wet ether to decompose excess $LiAlH_4$ and acidified with aq. 5% HCl. The whole mixture was then extracted with AcOEt and the AcOEt extract was washed with aq. sat. $NaHCO_3$ and water, and dried over $MgSO_4$ powder. Evaporation of the solvent from the filtrate under reduced pressure gave the reduction product (42 mg), IR $\nu_{\text{max}}^{\text{CCl}_4}$cm^{-1}: 3600, 1100, no $COOCH_3$. The product (15 mg) was dissolved in 9% HCl–dry MeOH (0.5 ml) and the solution was heated under reflux for 1 h. After neutralization of the reaction mixture as described for the methanolysis of **4a**, the solution was concentrated under reduced pressure then allowed to stand at room temp. The separated crystals were collected by filtration and purified by recrystallization from MeOH to furnish 22,24-di-*O*-methylsoyasapogenol B (**5a**, 5 mg) as colorless needles. **5a** was shown to be identical with an authentic sample by mixed mp determination and TLC (benzene–acetone=15:1; benzene–MeOH=30:1; *n*-hexane–AcOEt=4:1) and IR (KBr) comparisons.

From the filtrate after removal of **5a**, methyl 3,4-di-*O*-methylglucopyranoside (**c**), methyl 3,4-di-*O*-methylxylopyranoside (**d**) and methyl 2,3,4-tri-*O*-methylrhamnopyranoside (**e**) were identified by TLC (benzene–acetone=1:1; benzene–AcOEt=1:3) and GLC comparisons. GLC: 6) column temp., 185°C; N_2 flow rate, 25 ml/min; other conditions were the same as described for 3). t_R: **d** 7′38″ (major), 8′50″; **e** 3′30″. 7) column temp., 205°C; other conditions were as described for 6). t_R: **c** 27′05″, 30′45″. 8) 15% butane-1,4-diol succinate on Uniport B (80—100 mesh); 2 m×3 mm glass column; column temp., 180°C; N_2 flow rate, 33 ml/min. t_R: **d** 4′50″ (major), 5′50″; **e** 2′02″. 9) column temp., 200°C; other conditions were the same as described for 8). t_R: **c** 13′40″ (major), 16′08″.

Partial Hydrolysis of 8a———A solution of **8a** (250 mg) in 20% oxalic acid–MeOH (5 ml) was heated under reflux for 72 h. The solution was neutralized with 5% aq. K_2CO_3, and the solvent was evaporated off under reduced pressure. Purification of the product by column chromatography (SiO_2 30 g; $CHCl_3$–MeOH–H_2O=10:3:1, lower phase) furnished **6** (26 mg) and **7** (30 mg). **6** was shown to be identical with an authentic sample by mixed mp determination and TLC ($CHCl_3$–MeOH–H_2O=10:3:1, lower phase; *n*-hexane–AcOEt=4:1; $CHCl_3$–MeOH–AcOEt–H_2O=15:9:23:3) and IR (KBr) comparisons. **7**, mp 243—245°C (colorless fine crystals from MeOH), $[\alpha]_D^{18}$ +12.0° (*c*=1.0, MeOH). *Anal.* Calcd for $C_{42}H_{68}O_{13}\cdot H_2O$: C, 63.14; H, 8.83. Found: C, 62.99; H, 9.00. IR $\nu_{\text{max}}^{\text{KBr}}$cm^{-1}: 3400, 1740, 1040.

Methanolysis of 7———A solution of **7** (6 mg) in 9% HCl–dry MeOH (0.5 ml) was heated under reflux for 2 h. The reaction mixture was worked up as described for the methanolysis of **4** and soyasapogenol B (**5**) was identified from the products by TLC comparison as described above. After trimethylsilylation as described above, the TMS derivatives of methyl xyloside and methyl glucuronide were identified in 1:1 ratio by GLC analysis as described above.

Application of Klyne's Rule———$[M]_D$ of astragaloside VIII methyl ester (**8a**)$-[M]_D$ of **7**$=-213.0°$; $[M]_D$ of methyl α-L-rhamnopyranoside$=-109°$; $[M]_D$ of methyl β-L-rhamnopyranoside$=+169°$ [10a]

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15) The instruments used to obtain the physical data and the experimental conditions for chromatography were the same as those described in the preceding paper.[2a)]

16) All attempts at crystallization were unsuccessful. These compounds are therefore described as they appeared in noncrystalline form.