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Saponin and Sapogenol. XXXV.[1] Chemical Constituents of Astragali Radix, the Root of *Astragalus membranaceus* BUNGE. (2). Astragalosides I, II and IV, Acetylastragaloside I and Isoastragalosides I and II

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Twelve triterpene-oligoglycosides were isolated from the glycosidic constituents of Astragali Radix, the root of Korean *Astragalus membranaceus* BUNGE. (Leguminosae). They were acetylastragaloside I (**3**), isoastragalosides I (**5**) and II (**7**), astragalosides I (**4**, major), II (**6**), III, IV (**8**), V, VI and VII, which contain a 9,19-cyclolanostane cycloastragenol (**1**) as the aglycone, and astragaloside VIII and soyasaponin I (**9**),which possess an oleanene-type aglycone, soyasapogenol B. By means of chemical degradations, which included a selective cleavage method for the glucuronide linkage, and ^{13}C-NMR examinations, the structure of astragaloside IV was elucidated as 3-*O*-*β*-D-xylopyranosyl-6-*O*-*β*-D-glucopyranosylcycloastragenol (**8**). In addition, the structures of five acetyl derivatives of **8**: acetylastragaloside I, astragaloside I, isoastragaloside I, astragaloside II and isoastragaloside II, were elucidated as 3-*O*-*β*-(2′,3′,4′-tri-*O*-acetyl)-D-xylopyranosyl- (**3**), 3-*O*-*β*-(2′,3′-di-*O*-acetyl)-D-xylopyranosyl- (**4**), 3-*O*-*β*-(2′,4′-di-*O*-acetyl)-D-xylopyranosyl- (**5**), 3-*O*-*β*-(2′-*O*-acetyl)-D-xylopyranosyl- (**6**) and 3-*O*-*β*-(3′-*O*-acetyl)-D-xylopyranosyl-6-*O*-*β*-D-glucopyranosylcycloastragenol (**7**), respectively.

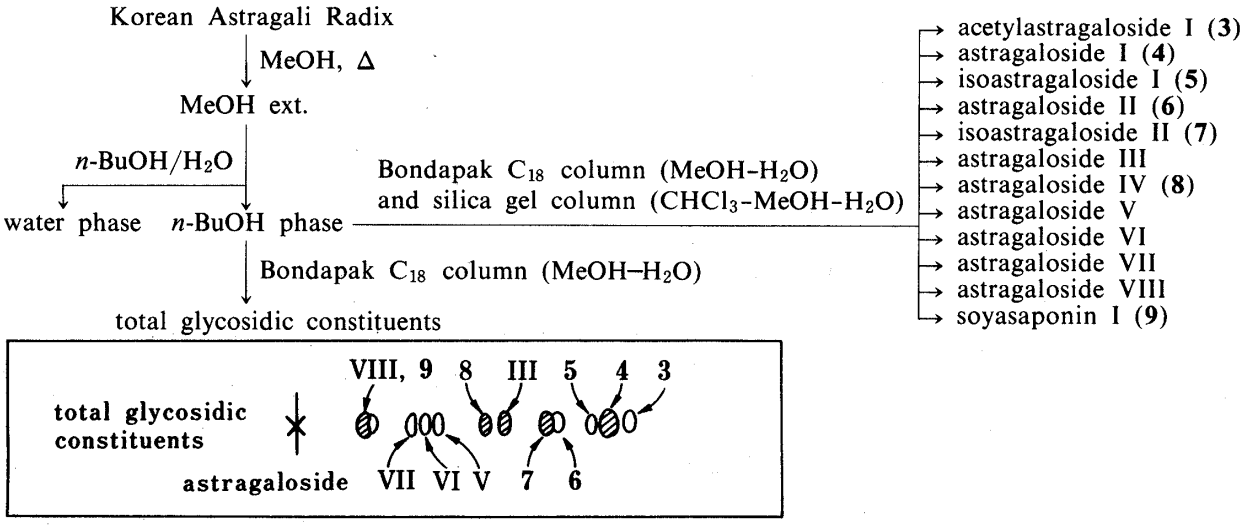
Keywords——*Astragalus membranaceus*; Leguminosae; 9,19-cyclolanostane-oligoglycoside; astragaloside; acetylastragaloside; isoastragaloside; selective cleavage of glucuronide linkage; reversed-phase column chromatography; ^{13}C-NMR; FD-MS

In the preceding paper,[1] we reported the isolation of the triterpene-oligoglycosidic constituents of Astragali Radix, the root of Korean *Astragalus membranaceus* BUNGE (Leguminosae). By means of various degradation methods applied to the total glycosidic mixture, we identified two genuine aglycones: cycloastragenol (**1**, major) and soyasapogenol B (minor),[2] and one artifact aglycone,astragenol (**2**), which was secondarily formed from **1** during acidic hydrolysis. In a continuing study on the oligoglycosidic constituents, we separated twelve triterpene-oligoglycosides: acetylastragaloside I (**3**), isoastragalosides I (**5**) and II (**7**), astragalosides I (**4**), II (**6**), III , IV (**8**), V, VI, VII and VIII and soyasaponin I (**9**).[2] This paper describes the structural elucidation of **3**, **4**, **5**, **6**, **7** and **8**.[3]

The methanol extract of Astragali Radix was partitioned into an *n*-butanol–water solvent system. Reversed-phase column chromatography with Bondapak C_{18} of the *n*-butanol-soluble portion provided the total glycosidic constituents,[1] while purification by a combination of ordinary silica gel and reversed-phase column chromatography furnished the above-mentioned eleven astragalosides and soyasaponin I as shown in Chart 1. Since alkaline treatment of acetylastragaloside I (**3**),isoastragalosides I (**5**) and II (**7**), and astragalosides I (**4**) and II (**6**) afforded astragaloside IV (**8**), we initiated the structural elucidation of **8**.

Astragaloside IV (8)

The infrared (IR) spectrum of astragaloside IV (**8**) exhibited strong hydroxyl absorption bands characteristic of glycosidic nature. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **8** showed signals ascribable to seven tertiary methyl groups and one cyclopropane methylene group, so **8** was suggested to be a glycoside of cycloastragenol (**1**). Methanolysis of



TLC diagram of total glycosidic constituents
adsorbent: pre-coated silica gel 60 F-254
solvent: $CHCl_3$:MeOH:H_2O=65:35:10 (lower phase)

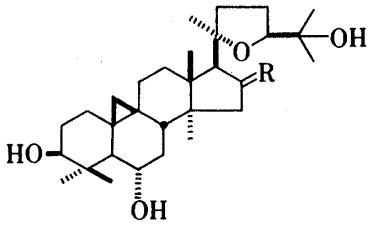
Chart 1

8 with methanolic hydrogen chloride provided methyl glucoside and methyl xyloside in 1:1 ratio, although attempts to isolate the aglycone were without success due to the formation of a complex mixture. However, acidic hydrolysis of **8** with aqueous methanolic sulfuric acid furnished the artifact aglycone astragenol (**2**), while the isolation of the genuine aglycone cycloastragenol (**1**) was effected by heterogeneous acidic hydrolysis of **8** with a mixture of aqueous hydrochloric acid, ethanol and benzene.[1] The field-desorption mass spectrum (FD-MS) of astragaloside IV (**8**) gave two ion peaks m/z 785 $(M+1)^+$ and m/z 807 $(M+Na)^+$. Thus, astragaloside IV (**8**) was considered to be a diglycoside of cycloastragenol possessing one glucoside moiety and one xyloside moiety. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **8**, in comparison with the spectra of cycloastragenol (**1**), methyl glucopyranoside and methyl xylopyranoside, exhibited significant glycosidation shifts[4] on the C-3 and C-6 signals of the aglycone of **8**. It also gave two anomeric carbon signals at δc 105.0 and 107.1, which suggested β-orientation of the glucopyranoside and the xylopyranoside residues in **8** (Table I).

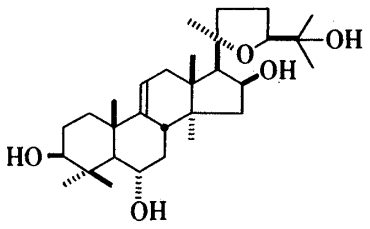
Complete methylation of astragaloside IV (**8**) with methyl iodide and dimsyl carbanion[5] provided the nona-*O*-methyl derivative (**8a**). The ^{1}H-NMR spectrum of **8a** showed two anomeric proton signals at δ 4.28 and 4.30 (both d, J=7 Hz) which further confirmed the β-orientation of two glycosidic linkages in **8**. Methanolysis of **8a** liberated methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**a**) and methyl 2,3,4-tri-*O*-methylxylopyranoside (**b**). It thus became clear that astragaloside IV (**8**) was a 3,6-di-*O*-glycoside of cycloastragenol (**1**) having a glucopyranoside moiety and a xylopyranoside moiety.

Enzymatic hydrolysis of astragaloside IV (**8**) with crude hesperidinase[1] provided cycloastragenol (**1**) together with the 6-*O*-glucoside (**10**). The ^{13}C-NMR spectrum of **10** showed a glycosidation shift of the C-6 signal and a β-anomeric carbon signal at δc 105.0. Methylation of **10** with methyl iodide and dimsyl carbanion yielded the hepta-*O*-methyl derivative (**10a**). The anomeric proton signal, observed at δ4.27 (d, J=7 Hz) in the ^{1}H-NMR spectrum of **10a**, and methanolysis of **10a**, giving methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**a**),substantiated the structure **10**.

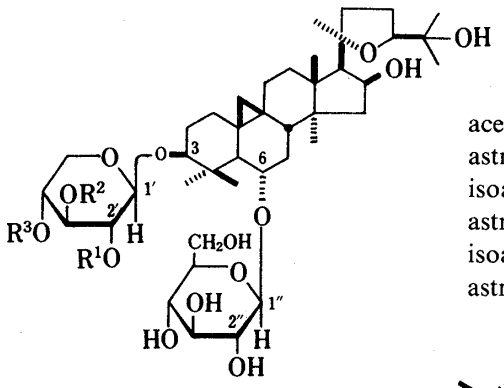
Consequently, it became evident that astragaloside IV (**8**) had a 3-*O*-β-D-xylopyranoside moiety and a 6-*O*-β-D-glucopyranoside moiety. In order to ascertain the location of the two glycosidic linkages, the following examinations were carried out.



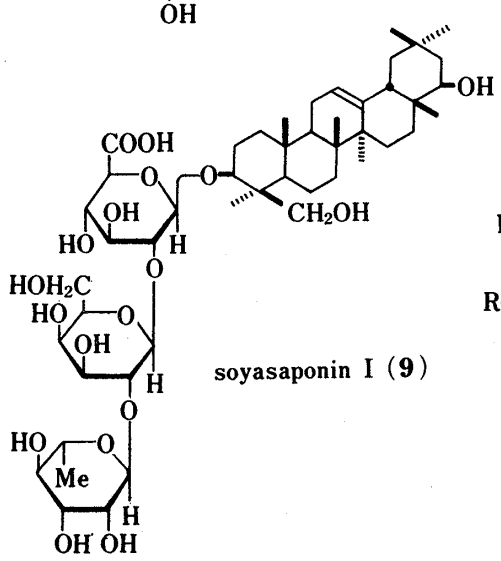
1 : R=β-OH, α-H (cycloastragenol)
1a : R=O



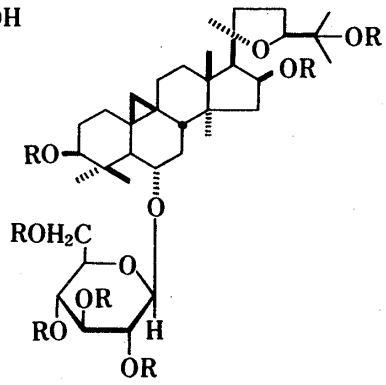
2 : (astragenol)



		R^1	R^2	R^3
acetylastragaloside I	(**3**) :	Ac	Ac	Ac
astragaloside I	(**4**) :	Ac	Ac	H
isoastragaloside I	(**5**) :	Ac	H	Ac
astragaloside II	(**6**) :	Ac	H	H
isoastragaloside II	(**7**) :	H	Ac	H
astragaloside IV	(**8**) :	H	H	H



soyasaponin I (**9**)



10 : R=H
10a : R=Me

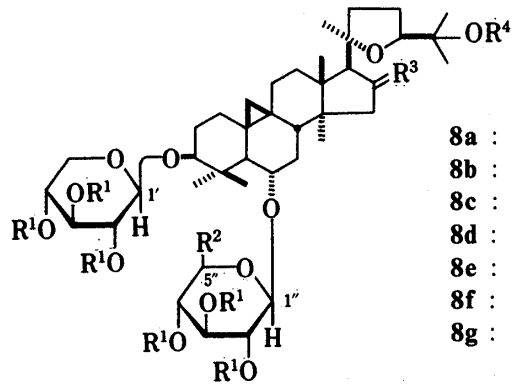
Chart 2

Acetylaton of **8** furnished the hepta-*O*-acetate **8b** (major) and the octa-*O*-acetate **8c**. Pyridinium chlorochromate (PCC) oxidation[6] of **8b** yielded the 16-keto-hepta-*O*-acetate **8d**. The circular dichroism (CD) spectrum of the 16-ketone (**8d**) exhibited a negative maximum of $[\theta]_{310}$ −17000 which was characteristic of the 16-keto-cyclolanostane derivative.[1] On the other hand, the mass spectrum (MS) of **8d** gave fragment ion peaks **i** and **ii** which suggested retention of the 25-OH function in **8**. The presence of the 25-OH function in **8** was further supported by the MS of the nona-*O*-methyl derivative (**8a**), which gave fragment ion peaks **ii** and **iii**.[1,7] Alkaline treatment followed by mild acidic hydrolysis of **8d** provided 16-keto-cycloastragenol (**1a**)[1] and the enone (**11**),[1] and thus 16-OH and 25-OH were excluded as possible locations for the carbohydrate residue in **8**.

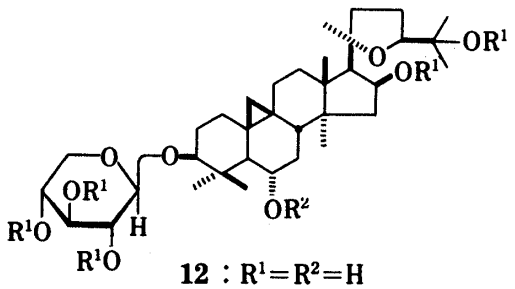
Next, in order to chemically verify the location of the glucopyranoside moiety in **8**, we converted the glucopyranoside group in **8** to a glucuronopyranoside function and applied a

selective cleavage method for the glucuronide linkage[8] to the resulting glucuronide derivative (**8f**).

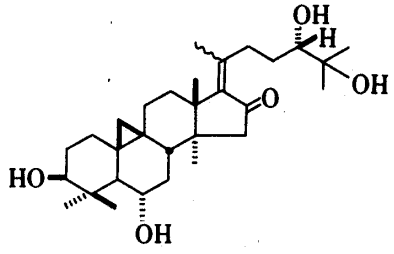
Tritylation followed by methylation with methyl iodide and dimsyl carbanion of **8** gave the octa-*O*-methyl tritylate (**8e**). The IR spectrum of **8e** showed no hydroxyl group peak, but



	R^1	R^2	R^3	R^4
8a :	Me	CH_2OMe	β-OMe, α-H	Me
8b :	Ac	CH_2OAc	β-OH, α-H	H
8c :	Ac	CH_2OAc	β-OAc, α-H	H
8d :	Ac	CH_2OAc	O	H
8e :	Me	CH_2OTr	β-OMe, α-H	Me
8f :	Me	COOH	β-OMe, α-H	Me
8g :	Me	α-&β-OAc	β-OMe, α-H	Me



12 : $R^1=R^2=H$
12a : R^1=Me, R^2=H
12b : R^1=Me, R^2=Ac



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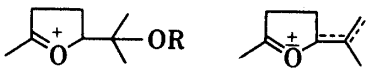
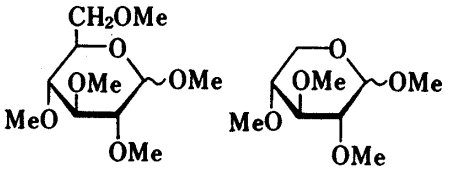
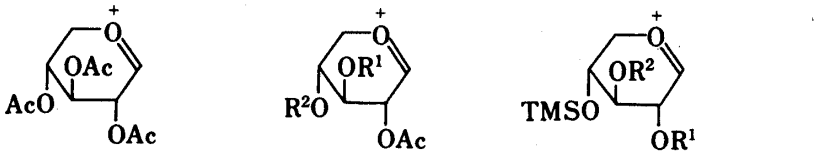


i : R=H
iii : R=Me

ii



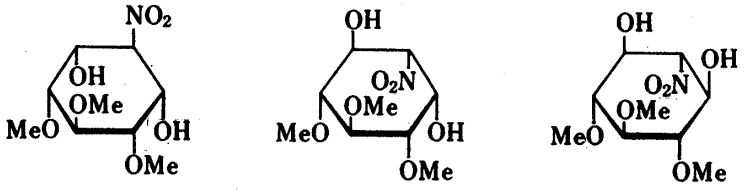
a **b**



iv

va : R^1=Ac, R^2=TMS
vb : R^1=TMS, R^2=Ac

via : R^1=Ac, R^2=TMS
vib : R^1=TMS, R^2=Ac



13a (*muco*) **13b** (*myo*) **13c** (*scyllo*)

Chart 3

indicated the presence of the trityl function, whereas the MS gave a fragment ion **iii**. The ^{1}H-NMR spectrum of **8e** exhibited signals due to a cyclopropane moiety, eight methoxyl groups, a trityl residue, and two β-anomeric proton signals at δ4.26 and 4.34 (1H each, both d, J=8 Hz). Thus, the structure **8e** was supported. Detritylation followed by chromium trioxide oxidation provided the desired glucuronide (**8f**), which was subjected to lead tetraacetate degradation.[8,9]

Lead tetraacetate oxidation of **8f** by heating under reflux in benzene furnished the decarboxylation product (**8g**) which was a 1:1 mixture of the 5″α- and 5″β-acetoxyl derivatives. Treatment of the mixture **8g** with nitromethane and sodium methoxide in methanol yielded the penta-*O*-methyl-3-*O*-xyloside (**12a**) and a nitrocyclitol mixture: **13a** (*muco*), **13b** (*myo*),and 13c (*scyllo*).[9b] The ^{1}H-NMR spectrum of **12a** showed the β-anomeric proton signal at δ4.25 (d, J=7 Hz). Methanolysis of **12a** liberated methyl 2,3,4-tri-*O*-methylxylopyranoside (**b**). Acetylation of **12a** gave the monoacetate (**12b**), and the ^{1}H-NMR spectrum of **12b** clearly indicated the occurrence of acetylation at the 6-OH function as judged from the chemical shift and the coupling pattern of the 6β-H.

Consequently, the location of the 6-*O*-glucopyranoside moiety in **8** was confirmed and that of the 3-*O*-xylopyranoside moiety was also clarified. Based on the above-mentioned evidence, the structure of astragaloside IV was determined to be 3-*O*-β-D-xylopyranosyl-6-*O*-β-D-glucopyranosyl-cycloastragenol (**8**). Recently, Saitoh and his group carried out the X-ray crystallographic analysis of the nona-*O*-methyl derivative of astragaloside IV (**8a**)[10] and the result was in good accord with our proposal.

The selective cleavage method for the glucuronide linkage has already been shown to be useful for the structural study of glucuronide-saponins which contain glucuronic acid as the carbohydrate constituent of the reducing terminal.[8,9] As described above, the lead tetraacetate degradation,which is one of four selective cleavage methods, has now been demonstrated to be useful also for the structural study of an oligoglycoside which possesses a

TABLE I. ^{13}C-NMR Data for Astragalosides (in d_5-pyridine, δc)[a]

		1	**3**	**4**	**5**	**6**	**7**	**8**	**10**	**12**
Aglycone	C-3	78.4	89.5	89.4	89.3	89.2	88.8	88.7	78.6	88.7
	C-6	68.5	79.3	79.4	79.5	79.4	79.2	79.2	79.9	68.2
	C-16	73.6	73.5	73.6	73.6	73.6	73.4	73.5	73.7	73.4
	C-25	71.4	71.3	71.5	71.5	71.4	71.3	71.2	71.6	71.1
D-Xylose moiety	C-1′		103.4	104.1	104.0	104.8	106.6	107.1		107.0
	C-2′		72.5	73.4	75.6[b]	76.4	72.8	75.2		75.1
	C-3′		72.9	77.1	72.7	75.8	78.7	77.7		77.8
	C-4′		70.0	69.0	73.1	71.4	69.1	71.3		71.1
	C-5′		62.6	66.8	63.1	67.1	66.2	66.6		66.5
D-Glucose moiety	C-1″		105.0	105.0	105.0	105.0	104.9	105.0	105.0	
	C-2″		75.5	75.6	75.5[b]	75.7	75.5	75.6	75.7	
	C-3″		79.1	79.1	79.1	79.1	78.9	79.0	79.1	
	C-4″		72.3	72.3	72.3	72.3	72.3	72.2	72.3	
	C-5″		77.7	77.8	77.7	77.8	77.6	77.9	77.8	
	C-6″		63.4	63.5	63.5	63.4	63.4	63.4	63.5	
Acetoxyl group			169.5	169.8	170.5	170.1	170.7			
			170.0	170.6	(2c)	21.4	21.1			
			170.1	20.9	20.9					
			20.5	21.4	21.4					
			20.7							
			21.4							

a) The signals due to the carbons bearing an acetoxyl group are underlined.
b) Assignments may be interchanged.

TABLE II. Physical Data for Acetylated Astragalosides

	Acetylastragaloside I (3)	Astragaloside I (4)	Isoastragaloside I (5)	Astragaloside II (6)	Isoastragaloside II (7)
Molecular formula	$C_{47}H_{74}O_{17}$	$C_{45}H_{72}O_{16}\cdot H_2O$	$C_{45}H_{72}O_{16}\cdot H_2O$	$C_{43}H_{70}O_{15}\cdot H_2O$	$C_{43}H_{70}O_{15}\cdot H_2O$
mp	280—281 °C	184—186 °C	218—220 °C	251—253 °C	223—224 °C
$[\alpha]_D^{18}$ (MeOH)	+1.8° (c=1.0)	+12.7° (c=0.64)	+17.9° (c=1.0)	+31.2° (c=1.4)	+15.0° (c=1.1)
IR (KBr) cm^{-1}	3400, 1750, 1225, 1030	3400, 1734, 1258, 1045	3400, 1740, 1230, 1050	3400, 1739, 1236, 1039	3400, 1738, 1235, 1040
^1H NMR (d_5-pyridine, 90 MHz, δ)	0.24, 0.57 (1H each, both br s) 1.95, 1.98, 2.00 (3H each, all s)	0.22, 0.53 (1H each, both br s) 1.98, 2.01 (3H each, both s)	0.22, 0.54 (1H each, both br s) 1.93, 1.97 (3H each, both s)	0.21, 0.55 (1H each, both br s) 1.98 (3H, s)	0.22, 0.54 (1H each, both br s) 1.97 (3H, s)
EI-MS for TMS derivative m/z (%)	259 (**iv**, 5)	289 (**va**, 27)	289 (**vb**, 24)	319 (**via**, 49)	319 (**vib**, 45)
FD-MS m/z	910 (M^+)	869 $(M+1)^+$	868 (M^+)	849 $(M+Na)^+$	826 (M^+)

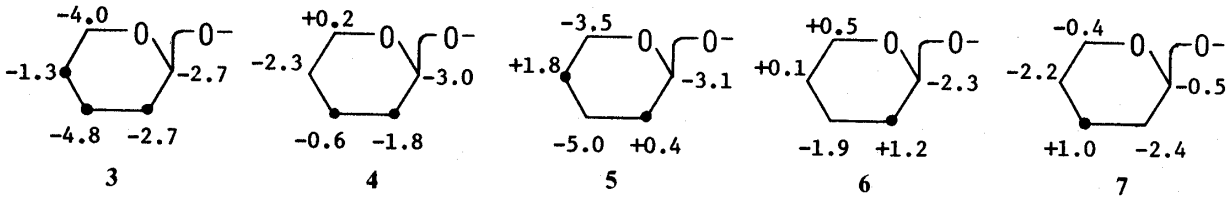


Chart 4. Acetylation Shift Values (in ppm) for Xyloside Carbons of Acetylastragalosides

[astragaloside IV (**8**) as the standard; ● denotes acetoxylated carbons.]

glucopyranoside moiety. In addition, the method has been found to be valuable in the degradation of an oligoglycoside such as astragaloside IV (**8**) which possesses an acid-labile aglycone, cycloastragenol (**1**).

Acetylastragaloside I (3), Isoastragalosides I (5) and II (7) and Astragalosides I (4) and II (6)

Methanolic sodium methoxide treatment of acetylastragaloside I (**3**), isoastragalosides I (**5**) and II (**7**) and astragalosides I (**4**) and II (**6**) yielded astragaloside IV (**8**) as the common deacetylation product. The ^1H-NMR and FD-MS examinations of those astragalosides demonstrated that **3** possessed three acetoxyl groups whereas **4** and **5** had two acetoxyl groups and **6** and **7** had one acetoxyl group (Table II).

The MS of **3** and trimethylsilylated (TMS) derivatives of **4**, **5**, **6** and **7** gave notable fragment ion peaks derivable from the respective xyloside moieties: **iv** from **3** (weak intensity in this case), **va** from **4**, **vb** from **5**, **via** from **6**, and **vib** from **7**. Lead tetraacetate oxidation followed by sodium borohydride reduction[11] of **4** provided 3-*O*-xylopyranosyl-cycloastragenol (**12**) in excellent yield. Thus, the location of two acetoxyl functions in **4** was shown to be in the xyloside moiety. The structure of **12** was supported by its ^{13}C-NMR data and by methanolysis, which liberated methyl xyloside.

The locations of acetoxyl groups in the xyloside moieties of **3**, **4**, **5**, **6** and **7** were determined from their ^{13}C-NMR data in comparison with those for **8**, **10** and **12** As shown in Table I,significant acetylation shifts[12] were observed for the signals due to 2′-, 3′- and 4′-C of **3**, 2′-C and 3′-C of **4**, 2′-C and 4′-C of **5**, 2′-C of **6** and 3′-C of **7**. Consequently, the structures of the five acetylated astragalosides (**3**, **4**, **5**, **6** and **7**) were elucidated.

Detailed thin-layer chromatographic (TLC) examinations of the parent extract of Korean Astragali Radix and of the fractions in the isolation procedure demonstrated that **3**, **4**, **5**, **6**, **7**

and **8** were in fact contained in Astragali Radix. It was also shown by the TLC examinations that, under the conditions used for the extraction and the chromatographic separation of those astragalosides, the occurrence of acetyl migration during the isolation procedure was rather unlikely.[13] Furthermore, the cold *n*-butanol extract of Korean Astragali Radix was also shown to contain **3**, **4**, **5**, **6**, **7** and **8**. Therefore, it was considered that these astragalosides are naturally occurring oligoglycosides of Korean Astragali Radix.

Experimental[14]

Isolation of Twelve Triterpene-oligoglycosides——The *n*-BuOH extract (200 g), which was obtained by *n*-BuOH–H_2O partition of the MeOH extract of Korean Astragali Radix as reported previously,[1] was subjected to column chromatography (SiO_2 4 kg; $CHCl_3$–MeOH–H_2O=10:3:1, lower phase as the eluant) to furnish six fractions: Fr-1 (22 g), Fr-2 (7.5 g), Fr-3 (10 g), Fr-4 (7.5 g), Fr-5 (6.8 g) and Fr-6 (9.2 g). Fr-1 (22 g) was purified on a Bondapak C_{18} column (200 g, MeOH–H_2O=5:4—5:1) to afford a mixture of acetylastragaloside I (**3**), astragaloside I (**4**) and isoastragaloside I (**5**) which was further purified by column chromatography (SiO_2 200 g, $CHCl_3$–MeOH–H_2O=10:3:1, lower phase) to afford **3** (0.3 g), **4** (3.5 g) and **5** (0.3 g). Fr-2 (7.5 g) was purified successively on a Bondapak C_{18} column (100 g) and an SiO_2 column (100 g) as carried out for Fr-1 to afford astragaloside II (**6**, 2.3 g) and isoastragaloside II (**7**, 0.1 g). Fr-3 (10 g) and Fr-4 (7.5 g) were purified on a Bondapak C_{18} column (100 g for each, MeOH–H_2O=5:4—5:1) to afford astragaloside III (1.0 g) and astragaloside IV (**8**, 0.8 g), respectively. Purification of Fr-5 (6.8 g) with a Bondapak C_{18} column (as described for Fr-3) and an SiO_2 column (100 g; $CHCl_3$–MeOH–H_2O=7:3:1,lower phase) furnished astragalosides V (0.1 g), VI (0.3 g) and VII (0.1 g). Fr-6 (9.2 g) was purified on a Bondapak C_{18} column (as described for Fr-3) and the product was dissolved in MeOH and treated with ethereal diazomethane. The methyl ester mixture was subjected to centrifugal liquid chromatography (Hitachi CLC-5 centrifugal liquid chromatograph, KT-gel 2061 120 g; $CHCl_3$–MeOH–H_2O=20:3:1, lower phase) to furnish astragaloside VIII methyl ester (0.65 g) and soyasaponin I methyl ester (0.63 g). Each methyl ester was dissolved in aq. 5% K_2CO_3–MeOH (1:2,10 ml) and the whole solution was heated under reflux for 1 h then neutralized with Dowex 50w×8 (H^+ form). After removal of the resin by filtration, the solvent was evaporated from the filtrate under reduced pressure to give astragaloside VIII (0.6 g) and soyasaponin I (**9**, 0.6 g). The physical data for astragaloside I (**3**), isoastragalosides I (**5**) and II (**7**) and astragalosides I (**4**) and II (**6**) are listed in Tables I and II. **3**: *Anal.*Calcd for $C_{47}H_{74}O_{17}$: C, 61.96; H, 8.19. Found: C, 61.56; H, 8.15. **4**, **5**: *Anal.* Calcd for $C_{45}H_{72}O_{16}\cdot H_2O$: C, 60.93; H, 8.41. Found **4**: C, 60.82; H, 8.40, **5**: C, 60.89; H, 8.40. **6**, **7**: *Anal.* Calcd for $C_{43}H_{70}O_{15}\cdot H_2O$: C, 61.12; H, 8.45. Found **6**: C, 61.19; H, 8.45, **7**: C, 61.02; H, 8.56.

Astragaloside IV (**8**), mp 299—301 °C (colorless needles from MeOH), $[\alpha]_D^{18}$ +24.4° (c=0.23, MeOH). *Anal.* Calcd for $C_{41}H_{68}O_{14}\cdot 2H_2O$: C, 59.98; H, 8.84. Found: C, 59.95; H, 8.70. IR ν_{max}^{KBr} cm^{-1}: 3380, 2930, 1040. ^{1}H-NMR (d_5-pyridine, δ): 0.23, 0.52 (1H each, both br d, 19-H_2), 0.98 (3H), 1.29 (12H), 1.53 (3H), 1.82 (3H) (all s, *tert*-CH_3×7). ^{13}C-NMR: as given in Table I. MS (m/z, %): 143 (**i**, 100), 125 (**ii**, 16). FD-MS (m/z): 785 $(M+1)^+$, 807 $(M+Na)^+$. Soyasaponin I (**9**) was shown to be identical with an authentic sample[2] by mixed mp determination, and TLC (SiO_2 plates were pre-sprayed with aq. 5% oxalic acid and activated at 110 °C for 1 h; solvent: $CHCl_3$–MeOH–H_2O=65:35:10, lower phase and *n*-BuOH–AcOH–H_2O=4:1:5, upper phase) and IR (KBr) comparisons.

Methanolysis of Astragaloside IV (8)——A solution of astragaloside IV (**8**, 2 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 1 h. After neutralization with Ag_2CO_3 powder, the reaction mixture was filtered to remove inorganic material. Removal of the solvent from the filtrate under reduced pressure gave the product,which was dried *in vacuo* and dissolved in pyridine (0.1 ml). The solution was treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (0.2 ml) then allowed to stand for 10 min to afford the TMS derivatives. The reaction products were identified by gas-liquid chromatography (GLC) comparisons with TMS derivatives of methyl glucoside and methyl xyloside. GLC: 1) 5% silicone SE-52 Chromosorb WAW DMCS (80—100 mesh), 2m×3mm glass column; column temp., 190 °C; carrier gas N_2, flow rate 35 ml/min. t_R: TMS-methyl glucoside 3′21″ (major), 3′33″; TMS-methyl xyloside 7′30″ (major), 7′59″.

Acidic Hydrolysis of 8——A solution of **8** (100 mg) in aq. 20% H_2SO_4–MeOH (1:1, 30 ml) was heated under reflux for 10 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed successively with aq. sat. $NaHCO_3$ and H_2O and dried over $MgSO_4$ powder. Evaporation of the solvent from the filtrate under reduced pressure afforded the product, which was purified by preparative TLC ($CHCl_3$–MEOH=10:1) to give astragenol (**2**, 34 mg). **2** was shown to be identical with an authentic sample[1] by mixed mp determination and TLC ($CHCl_3$–MeOH=20:1; *n*-hexane–AcOEt=1:5) and IR (KBr) comparisons.

Heterogeneous Acidic Hydrolysis of 8——A solution of **8** (100 mg) in EtOH (10 ml) was mixed with aq. 10% HCl (5 ml) and benzene (20 ml) and the whole mixture was heated under reflux for 24 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract as

described for the acidic hydrolysis of **8** gave the product, which was purified by preparative TLC ($CHCl_3$–MeOH=10:1) to furnish cycloastragenol (**1**, 30 mg). **1** was shown to be identical with an authentic sample by mixed mp determination, and TLC (as described for **2**) and IR (KBr) comparisons.

Methylation of 8 giving 8a———A solution of **8** (70 mg) in dimethyl sulfoxide (DMSO) (6 ml) was treated with dimsyl carbanion[2,5] (10 ml) and the mixture was stirred at room temperature under an N_2 atmosphere for 1 h, then treated with CH_3I (5 ml). The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed successively with aq. 10% $Na_2S_2O_3$ and water, and dried over $MgSO_4$ powder. The product, obtained by evaporation of the solvent under reduced pressure, was purified by column chromatography (SiO_2 5 g; benzene–acetone=9:1) to furnish the nona-*O*-methyl derivative (**8a**, 65 mg). **8a** white powder, $[\alpha]_D^{17}$ +32.1° (*c*=0.7, $CHCl_3$). *Anal.* Calcd for $C_{50}H_{86}O_{14}$: C, 65.90; H, 9.51. Found: C, 65.70; H, 9.66. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 2930, 1090. ^{1}H-NMR ($CDCl_3$, δ): 0.26, 0.54 (1H each, both d, *J*=5 Hz, 19-H_2), 0.95, 0.99, 1.09, 1.16 (3H each), 1.26 (9H) (all s, *tert*-CH_3×7), 2.39 (1H, d, *J*=8 Hz, 17-H), 3.11, 3.25, 3.38, 3.45 (3H each), 3.52 (6H), 3.60 (9H) (all s, OCH_3×9), 4.28, 4.30 (1H each, both d, *J*=7 Hz, anomeric H×2). MS (*m/z*, %): 187 (61), 175 (30), 157 (**iii**, 100), 143 (21), 125 (**ii**, 23).

Methanolysis of 8a———A solution of **8a** (2 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 3 h. After neutralization with Ag_2CO_3 powder, the whole mixture was filtered. The products obtained from the filtrate were identified as methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**a**) and methyl 2,3,4-tri-*O*-methylxylopyranoside (**b**) by TLC (benzene–acetone=4:1; *n*-hexane–AcOEt=1:1) and GLC comparisons with authentic samples. GLC: 2) 15% polyneopentyl glycol 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). 3) 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).

Enzymatic Hydrolysis of 8 with Crude Hesperidinase———A solution of **8** (1 g) in water (250 ml) was treated with crude hesperidinase (2 g)[1] and the whole mixture was stirred at 30 °C for 5 d. The reaction mixture was extracted with *n*-BuOH and the *n*-BuOH extract was passed through a Celite 535 column. Removal of the solvent from the eluate under reduced pressure gave the residue, which was purified by column chromatography (SiO_2 30 g; $CHCl_3$–MeOH=20:1—5:1) to furnish cycloastragenol (**1**, 134 mg), **10** (196 mg) and **8** (102 mg, recovered). **1** and **8** were shown to be identical with authentic samples by TLC comparisons (**1** as described above; **8** with $CHCl_3$–MeOH–H_2O=7:3:1, lower phase). **10**, mp 261—262 °C (colorless needles from acetone), $[\alpha]_D^{17}$ +41.9° (*c*=0.32, MeOH). *Anal.* Calcd for $C_{36}H_{60}O_{10}\cdot H_2O$: C, 64.45; H, 9.32. Found: C, 64.34; H, 9.17. IR ν_{max}^{KBr} cm^{-1}: 3400, 2935, 1080. ^{13}C-NMR: as given in Table I.

Methylation of 10———A solution of **10** (69 mg) in DMSO (5 ml) was treated with dimsyl carbanion (10 ml) and the mixture was stirred under N_2 atmosphere for 2 h. The reaction mixture was then treated with CH_3I (10 ml) and the whole was stirred in the dark for a further 3 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract as described for the methylation of **8** gave the product,which was purified by column chromatography (SiO_2 5 g; benzene–acetone=15:1) to furnish the hepta-*O*-methyl derivative (**10a**, 65 mg). **10a**, mp 163—164 °C (colorless needles from MeOH), $[\alpha]_D^{18}$ +56.1° (*c*=0.33, $CHCl_3$). *Anal.* Calcd. for $C_{43}H_{74}O_{10}$: C, 68.76; H, 9.93. Found: C, 68.39; H, 10 17. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 2920, 1095. ^{1}H-NMR ($CDCl_3$, δ): 0.26, 0.54 (1H, each, both d, *J*=5 Hz, 19-H_2), 0.91, 0.93, 1.09, 1.16 (3H each), 1.21 (6H), 1.27 (3H) (all s, *tert*-CH_3×7), 2.38 (1H, d, *J*=8 Hz, 17-H), 3.10, 3.24, 3.35, 3.37 (3H each), 3.50 (6H), 3.61 (3H) (all s, OCH_3×7), 4.27 (1H, d, *J*=7 Hz, anomeric H). MS (*m/z*, %): 187 (66), 157 (**iii**, 100), 125 (**ii**, 63).

Methanolysis of 10a———A solution of **10a** (2 mg) in 9% HCl–dry MeOH (0.5 ml) was heated under reflux for 2 h. Work-up of the reaction mixture as described for the methanolysis of **8a** gave the product, from which methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**a**) was identified by GLC and TLC comparisons (as described above).

Acetylation of 8———A solution of **8** (300 mg) in Ac_2O–pyridine (1:1, 20 ml) was left standing at 18 °C for 12 h. The reaction mixture was poured into ice-water and the precipitated product was collected by filtration. Purification of the product by column chromatography (SiO_2 50 g; $CHCl_3$–MeOH=20:1) furnished the hepta-*O*-acetate (**8b**, 345 mg) and the octa-*O*-acetate (**8c**, 40 mg). **8b**, mp 231—232 °C (colorless needles from $CHCl_3$–MeOH), $[\alpha]_D^{17}$ +1.4° (*c*=0.56, $CHCl_3$). *Anal.* Calcd for $C_{55}H_{82}O_{21}$: C, 61.21; H, 7.66. Found: C, 60.89; H, 7.28. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3425, 2930, 1765, 1220, 1035. ^{1}H-NMR ($CDCl_3$, δ): 0.28, 0.51 (1H each, both d, *J*=5 Hz, 19-H_2), 0.87 (3H), 0.98 (6H), 1.08, 1.20 (3H each), 1.28 (6H)(all s, *tert*-CH_3×7), 1.95 (6H), 1.99 (12H), 2.05 (3H) (all s, OAc×7). **8c**, mp 227—228 °C (colorless needles from $CHCl_3$–MeOH) $[\alpha]_D^{17}$ +12.6° (*c*=0.4, $CHCl_3$). *Anal.* Calcd for $C_{57}H_{84}O_{22}$: C, 61.05; H, 7.55. Found: C, 60.82; H, 7.49. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3475 2935, 1765, 1220, 1040. ^{1}H NMR ($CDCl_3$, δ): 0.29, 0.51 (1H each, both br d, 19-H_2), 0.88 (3H), 0.97 (6H), 1.05 (3H), 1.22 (6H), 1.28 (3H) (all s, *tert*-CH_3×7), 1.97 (3H), 2.00 (15H), 2.06, 2.14 (3H each) (all s, OAc×8).

PCC Oxidation of 8b giving 8d———A solution of **8b** (180 mg) in CH_2Cl_2 (10 ml) was treated with PCC (350 mg) and the whole mixture was stirred at 21 °C for 12 h. After dilution with ether, the reaction mixture

was purified on a Florisil column (100—200 mesh, 10 g) to furnish the 16-keto-hepta-*O*-acetate (**8d**, 178 mg). **8d**, white powder,[16] $[\alpha]_D^{17}$ −40.3° (c=0.8, $CHCl_3$). *Anal.*Calcd for $C_{55}H_{80}O_{21}$: C, 61.32; H, 7.49. Found: C, 59.87; H, 7.20. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450, 2930, 1765, 1740, 1220, 1035. CD (c=1.544×10^{-1}, $CHCl_3$): $[\theta]_{336}$ 0, $[\theta]_{310}$ −17000 (neg. max.), $[\theta]_{268}$, 0. ^{1}H-NMR ($CDCl_3$, δ): 0.25, 0.59 (1H each, both br d, 19-H_2), 0.88 (3H), 0.94 (3H), 1.17 (9H), 1.23 (6H) (all s, *tert*-CH_3×7), 2.01—2.05 (total 21H, OAc×7), 2.93 (br s, $W_{h/2}$=4 Hz, 17-H). MS (m/z, %): 143 (**i**, 70), 125 (**ii**, 16), 43 (100).

Alkaline Treatment followed by Acidic Hydrolysis of 8d———A solution of **8d** (150 mg) in 0.1% NaOMe–MeOH (5 ml) was stirred at 20°C for 10 h. After neutralization with Dowex 50w×8 (H^+ form), the whole mixture was filtered. Evaporation of the solvent under reduced pressure from the filtrate gave the product (100 mg). A solution of the product (80 mg) in EtOH (10 ml) was mixed with aq. 10% HCl (5 ml) and benzene (20 ml) and the whole mixture was heated under reflux for 24 h, then extracted with AcOEt. Work-up of the AcOEt extract as described for the acidic hydrolysis of **8** yielded the product, which was purified by preparative TLC (n-hexane–AcOEt=2:9) to furnish 16-keto-cycloastragenol (**1a**, 15 mg) and the enone (**11**, 8 mg). **1a** was shown to be identical with an authentic sample[1] by mixed mp determination, and TLC ($CHCl_3$–MeOH=20:1, n-hexane–AcOEt=1:5) and IR (KBr) comparisons. **11** was shown to be identical with an authentic sample[1] by TLC as described for **1a** and ^{1}H-NMR ($CDCl_3$) comparison.

Tritylation followed by Methylation of 8 giving 8e———A solution of **8** (800 mg) in pyridine (18 ml) was treated with trityl chloride (1.5 g) and the whole mixture was heated at 100°C for 2 h. The reaction mixture was poured into ice-water and the precipitate was collected by filtration. The filtrate was extracted with AcOEt and the residue, obtained by work-up of the AcOEt extract in the usual manner, was combined with the above precipitate. Purification of the combined product by column chromatography (SiO_2 100 g; $CHCl_3$–MeOH=8:1—3:1) furnished the monotritylate (780 mg). ^{1}H-NMR ($CDCl_3$–CD_3OD, δ): 0.27, 0.63 (1H each, both d, J=5 Hz, 19-H_2), 0.95, 1.05, 1.15 (3H each), 1.21, 1.30 (6H each) (all s, *tert*-CH_3×7), 7.17—7.53 (15H, aromatic H of the trityl group). A solution of the monotritylate (780 mg) in DMSO (15 ml) was treated with dimsyl carbanion (20 ml) and the mixture was stirred under an N_2 atmosphere for 2 h. The reaction mixture was then treated with CH_3I (10 ml) and the whole was stirred in the dark for 3 h, then poured into ice-water. Extraction with AcOEt and work-up of the AcOEt extract as described for the methylation of **8** gave the product, which was purified by column chromatography (SiO_2 70 g, n-hexane–AcOEt=3:1) to furnish the octa-*O*-methyl tritylate (**8e**, 520 mg). **8e**, white powder, $[\alpha]_D^{17}$ +21.4° (c=1.0, $CHCl_3$). *Anal.* Calcd for $C_{68}H_{98}O_{14}$: C, 71.67; H, 8.67. Found: C, 71.46; H, 8.90. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 2940, 1490, 1450, 1095. ^{1}H-NMR ($CDCl_3$, δ): 0.25, 0.58 (1H each, both br d, 19-H_2), 0.98 (3H), 1.08, 1.19, 1.25 (6H each) (all s, *tert*-CH_3×7), 3.25 (6H), 3.44 (3H), 3.60 (15H) (all s, OCH_3×8), 4.26, 4.34 (1H each, both d, J=8 Hz, anomeric H×2). MS (m/z, %): 243 (ϕ_3C^+, 75), 157 (**iii**, 100), 125 (**ii**, 14).

Detritylation followed by CrO_3 Oxidation of 8e giving 8f———A solution of **8e** (200 mg) in MeOH (15 ml) was treated with 95% H_2SO_4–MeOH (4:96, 2 ml) and the whole solution was left standing at 50°C for 10 h. After neutralization with aq. K_2CO_3, the reaction mixture was diluted with water and extracted with AcOEt. Usual work-up of the AcOEt extract gave the product, which was purified by column chromatography (SiO_2 10 g, benzene–acetone=5:1) to furnish the detritylation product (142 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 2930, 1085. ^{1}H-NMR ($CDCl_3$, δ): 0.23, 0.53 (1H each, both d, J=5 Hz, 19-H_2), 0.98 (6H), 1.07, 1.14 (3H each), 1.23 (9H) (all s, *tert*-CH_3×7), 2.37 (1H, d, J=8 Hz, 17-H), 3.09, 3.23, 3.43 (3H each), 3.51 (6H), 3.58 (9H) (all s, OCH_3×8), 4.26, 4.34 (1H each, both d, J=8 Hz, anomeric H×2). An ice-cooled solution of the detritylation product (130 mg) in acetone (10 ml) was treated dropwise with CrO_3–H_2SO_4 reagent (0.6 ml) (prepared from CrO_3 7.0 g, H_2O 30 ml and conc. H_2SO_4 11.2 g) and the whole mixture was stirred at 20°C for 1 h. After quenching of the reaction mixture with isopropanol, the acetone was evaporated off under reduced pressure. The reaction mixture was then diluted with water and the precipitated product was collected by filtration. Crystallization of the product from MeOH furnished **8f** (127 mg). **8f**, mp 209—211°C (colorless needles from MeOH), $[\alpha]_D^{17}$ +11.7° (c=0.4, $CHCl_3$). *Anal.* Calcd for $C_{49}H_{82}O_{15}$: C, 64.59; H, 9.07. Found: C, 64.65; H, 9.28. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1740, 1085. ^{1}H-NMR ($CDCl_3$, δ): 0.22, 0.52 (1H each, both d, J=4 Hz, 19-H_2), 0.95, 0.98, 1.09, 1.17 (3H each), 1.22 (6H), 1.26 (3H) (all s, *tert*-CH_3×7), 2.37 (1H, d, J=8 Hz, 17-H), 3.10, 3.20, 3.45 (3H each), 3.52 (6H), 3.60 (9H) (all s, OCH_3×8), 4.25, 4.44 (1H each, both d, J=8 Hz, anomeric H×2).

Pb $(OAc)_4$ Oxidation followed by CH_3NO_2–NaOMe Treatment of 8f———A solution of **8f** (100 mg) in benzene (10 ml) was treated with Pb $(OAc)_4$ (200 mg) and the whole mixture was heated under reflux for 2 h. After dilution with AcOEt, the reaction mixture was passed through a Celite 535 column and the eluate was washed with water and dried over $MgSO_4$ powder. Removal of the solvent under reduced pressure provided the decarboxylation product (**8g**, 112 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: no OH, 1760, 1240, 1090. ^{1}H-NMR (CD_3OD, δ): 0.30, 0.58 (1H each, both br d, 19-H_2), 5.45 (*ca.* 1/2H, d, J=8 Hz, 5″α-H), 6.21 (*ca.* 1/2H, d, J=3 Hz, 5″β-H). A solution of the decarboxylation product (**8g**, 110 mg) in MeOH (4 ml) was mixed with CH_3NO_2 (6 ml) and 10% NaOMe–MeOH (1.5 ml) and the whole solution was stirred at 17°C for 6 h. After neutralization with Dowex 50w×8 (H^+ form), the reaction mixture was diluted with water and extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by preparative TLC (n-hexane–

AcOEt=2:9) to furnish **12a** (43 mg) and a nitrocyclitol mixture (**13**, 19 mg). **12a**, mp 169—171 °C (colorless needles from MeOH), $[\alpha]_D^{17}$ +38.2° (*c*=0.4, $CHCl_3$). *Anal.* Calcd for $C_{40}H_{68}O_9$: C, 69.33; H, 9.89. Found: C, 68.93; H, 10.06. ^{1}H-NMR ($CDCl_3$, δ): 0.35, 0.53 (1H each, both d, *J*=5 Hz, 19-H_2), 0.95, 1.03, 1.10, 1.17 (3H each), 1.28 (9H) (all s, *tert*-CH_3×7), 2.39 (1H, d, *J*=8 Hz, 17-H), 3.09, 3.25, 3.45 (3H each), 3.60 (6H) (all s, OCH_3×5), 4.25 (1H, d, *J*=7 Hz, anomeric H). A solution of the nitrocyclitol mixture (**13**, 1 mg) in pyridine (0.1 ml) was treated with *N,O*-bis (trimethylsilyl) trifluoroacetamide (0.2 ml) and the mixture was left standing for 10 min. The mixture was shown to consist of TMS derivatives of 3-deoxy-1,5,6-tri-*O*-methyl-3-nitro-*muco*-inositol (**13a**), DL-1-deoxy-3,4,5-tri-*O*-methyl-1-nitro-*myo*-inositol (**13b**) and 5-deoxy-1,2,3-tri-*O*-methyl-5-nitro-*scyllo*-inositol (**13c**) (in *ca.* 1:2:2 ratio) by GLC analysis. GLC: 4) 2% silicone OV-17 on Chromosorb WAW DMCS (80—100 mesh), 1 m×3 mm glass column; column temp., 150 °C; N_2 flow rate, 25 ml/min. t_R: **13a** 5′42″, **13b** 3′33″, **13c** 4′11″. 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, 37 ml/min. t_R: **13a** 7′20″, **13b** 6′04″, **13c** 7′20″.

Acetylation of 12a giving 12b——A solution of **12a** (37 mg) in Ac_2O–pyridie (1:1, 4 ml) was left standing at 21 °C for 6 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product (**12b**, 38 mg). **12b**, white powder, $[\alpha]_D^{17}$ +39.7° (*c*=1.0, $CHCl_3$). *Anal.* Calcd for $C_{42}H_{70}O_{10}$: C, 68.63; H, 9.60. Found: C, 68.75; H, 9.60. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1735, 1245, 1090. ^{1}H-NMR ($CDCl_3$,δ): 0.30, 0.60 (1H each, both d, *J*=5 Hz, 19-H_2), 0.92, 0.98, 1.04, 1.09, 1.16 (3H each), 1.26 (6H) (all s, *tert*-CH_3×7), 1.98 (3H, s, OAc), 2.37 (1H, d, *J*=7 Hz, 17-H), 3.07, 3.24, 3.44 (3H each), 3.59 (6H) (all s, *tert*-OCH_3×5), 4.23 (1H, d, *J*=7 Hz, anomeric H), 4.75 (1H, ddd, *J*=4, 8, 8 Hz, 6-H).

Methanolysis of 12a——A solution of **12a** (2 mg) in 9% HCl–dry MeOH (0.5 ml) was heated under reflux for 1 h. Work-up of the reaction mixture as described for the methanolysis of **10a** gave the product, from which methyl 2,3,4-tri-*O*-methylxylopyranoside (**b**) was identified by GLC and TLC analyses as described above for **8a**.

Deacetylation of Acetylastragaloside I (3), Isoastragalosides I (5) and II (7) and Astragalosides I (4) and II (6)——A solution of **3** or **6** (20 mg each) in MeOH (1 ml) was treated with 10% NaOMe–MeOH (0.5 ml). A solution of **5** or **7** (50 mg each) in MeOH (2 ml) was treated with 10% NaOMe–MeOH (1 ml). A solution of **4** (100 mg) in MeOH (5 ml) was treated with 10% NaOMe–MeOH (2.5 ml). Each solution was then heated under reflux for 15 min, neutralized with Dowex 50w×8 (H^+ form) and filtered. Evaporation of the solvent from the filtrate under reduced pressure furnished astragaloside IV (**8**: 19 mg from **3** or **6**; 45 mg from **5** or **7**; 90 mg from **4**). **8** was shown to be identical with an authentic sample by mixed mp determination, and TLC ($CHCl_3$–MeOH–H_2O=7:3:1, lower phase; $CHCl_3$–MeOH–AcOEt–H_2O=9:15:23:3; *n*-BuOH–AcOEt–H_2O=4:1:5,upper phase) and IR (KBr) comparisons.

$Pb(OAc)_4$ Oxidation followed by $NaBH_4$ Reduction of Astragaloside I (4) giving 12——A solution of **4** (230 mg) in pyridine (4 ml) was treated with $Pb(OAc)_4$ (471 mg) and the whole solution was stirred at 16 °C for 14 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed with water and dried over Na_2SO_4 powder. The product (220 mg), obtained by evaporation of the solvent under reduced pressure, was dissolved in EtOH (5 ml) and the solution was treated with $NaBH_4$ (350 mg) stirred at 16 °C for 10 h, and then quenched with acetone. The solvents were evaporated off under reduced pressure and the residue was diluted with water. The whole mixture was extracted with AcOEt and the AcOEt extract was washed with water and dried over Na_2SO_4 powder. Removal of the solvent under reduced pressure furnished the product (220 mg). A solution of the product (120 mg) in MeOH (10 ml) was treated with aq. 10% HCl (1 ml) and the whole solution was left standing at 16 °C for 7 h. After neutralization with aq. 5% K_2CO_3, the reaction mixture was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was crystallized from acetone–MeOH to furnish **12** (80 mg). **12**, mp 293—294 °C (colorless needles from acetone–MeOH), $[\alpha]_D^{18}$ +35.5° (*c*=0.3, MeOH). *Anal.* Calcd for $C_{35}H_{58}O_9$: C, 67.49; H, 9.39. Found: C, 67.24; H, 9.61. IR ν_{max}^{KBr} cm^{-1}: 3420, 2935, 1040. ^{13}C-NMR: as given in Table I.

Methanolysis of 12——A solution of **12** (8 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 1 h. Work-up of the reaction mixture as described for the methanolysis of 8 gave the product. Methyl xyloside was identified in the product by GLC analysis of the TMS derivative (as described for **8**).

Examinations of Acetyl Migration of Acetylated Astragalosides——i) Powdered Korean Astragali Radix (20 g) was stirred with *n*-BuOH (50 ml) at 25 °C for 24 h. Removal of the solvent from the filtrate under reduced pressure furnished the *n*-BuOH extract. Reversed-phase column chromatography (Waters Bondapak C_{18} 10 g; MeOH–H_2O=1:1—5:1) of the *n*-BuOH extract gave an oligoglycosidic mixture. TLC examinations of the mixture ($CHCl_3$–MeOH–H_2O=7:3:1, lower phase; $CHCl_3$–MeOH–AcOEt–H_2O=15:9:23:3) showed the presence of acetylastragaloside I (**3**), isoastragalosides I (**5**) and II (**7**), astragalosides I (**4**) and II (**6**) and astragaloside IV (**8**).

ii) A solution of **3**, **4**, **5**, **6** or **7** (5 mg)in a mixture of $CHCl_3$–MeOH–H_2O (65:35:10, lower phase) was treated with SiO_2 (1.0 g) and the mixture was stirred at 25 °C for 2 d. TLC examination (as described above) of each reaction mixture confirmed that there was no change of any of the astragalosides during the procedure.

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13) Those astragalosides (**3**, **4**, **5**, **6** and **7**) were unaffected either by heating in methanol under reflux or by treatment with Bondapak C_{18} in aqueous methanol with stirring at room temperature for 24 h.
14) The instruments used to obtain physical data and the experimental conditions for chromatography were the same as reported in our previous paper.[15] The ^{13}C NMR spectra were measured in d_5-pyridine with a JEOL JNM-FX 100 (25.05 MHz) NMR spectrometer.
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16) All attempts at crystallization were without success. These compounds are described as "white powder" hereafter.