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Saponin and Sapogenol. XXXIV.[1] Chemical Constituents of Astragali Radix, the Root of *Astragalus membranaceus* Bunge. (1). Cycloastragenol, the 9,19-Cyclolanostane-type Aglycone of Astragalosides, and the Artifact Aglycone Astragenol

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Triterpene-oligoglycoside constituents of Astragali Radix, the root of Korean *Astragalus membranaceus* Bunge (Leguminosae), were isolated. By means of enzymatic and chemical degradations, the 9,19-cyclolanostane-type triterpene named cycloastragenol (**1**), which was the common genuine aglycone of ten of eleven astragalosides, and the lanost-9(11)-ene-type counterpart named astragenol (**5**), which was an artifact aglycone secondarily formed from **1**, were isolated. On the basis of chemical and physicochemical evidence, the structures of cycloastragenol and astragenol were elucidated as (20R,24S)-3β,6α,16β,25-tetrahydroxy-20,24-epoxy-9,19-cyclolanostane (**1**) and (20R,24S)-3β,6α,16β,25-tetrahydroxy-20,24-epoxy-lanost-9(11)-ene (**5**), respectively.

Keywords——*Astragalus membranaceus;* Leguminosae; astragaloside; cycloastragenol; 9,19-cyclolanostane; astragenol; lanost-9(11)-ene; genuine aglycone; artifact aglycone

Astragali Radix is a commonly used Chinese crude drug, which is processed from the root of *Astragalus membranaceus* Bunge and other *Astragalus spp.* (Leguminosae)[2a)] and is prescribed in Chinese traditional medicine as an antiperspirant, a diuretic, or a tonic.[2b)] As for the chemical constituents of Astragali Radix, lipid,[3)] flavonoids,[4,5)] γ-aminobutyric acid (isolated as an antihypertensive ingredient),[6)] L-canavanine (isolated as an inhibitory constituent against silkworm metamorphosis)[7)] and polysaccharides[8)] have so far been characterized. However, no work was reported on the principal bioactive constituents of Astragali Radix.

During studies on the bioactive constituents of naturally occurring drug materials originated from leguminous plants, we isolated various bioactive triterpene-oligoglycosides from soybeans (the seeds of *Glycine max* Merrill)[9)] and azuki beans (the seeds of *Vigna angularis* (Willd.) Ohwi *et* Ohashi).[1)] As a continuing study, we investigated the glycosidic constituents of Astragali Radix, the root of Korean *Astragalus membranaceus* Bunge and isolated eleven new triterpene-oligoglycosides (named astragalosides) together with soyasaponin I.[9)] This paper describes the structure elucidation of a 9,19-cyclolanostane aglycone named cycloastragenol (**1**) and a lanost-9(11)-ene aglycone named astragenol (**5**). Cycloastragenol (**1**) was a common genuine aglycone of ten of eleven astragalosides, while astragenol (**5**) was an artifact aglycone which was secondarily formed from **1** during the acidic degradation of astragalosides.[10)]

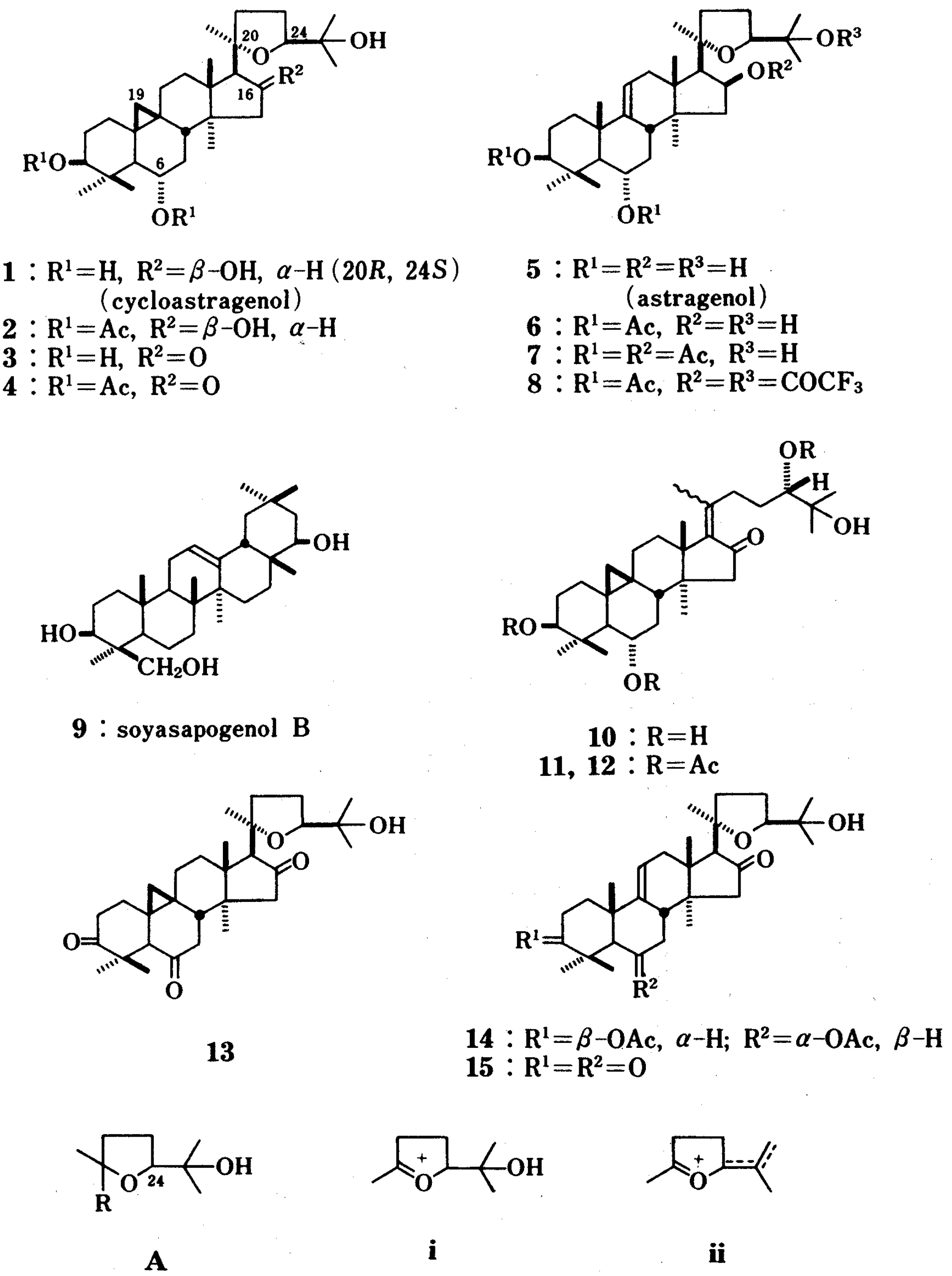
The n-butanol-soluble portion, which was obtained by n-butanol–water partition of the methanol extract of the crude drug, was subjected to reversed-phase column chromatography to afford the glycosidic constituents, which comprised soyasaponin I and the astragaloside mixture. Enzymatic hydrolysis with crude hesperidinase[11)] or heterogeneous acidic hydrolysis using an aqueous hydrochloric acid–ethanol–benzene mixture[12] of the total glycoside provided cycloastragenol (**1**) as the major aglycone together with a minor quantity of soyasapogenol B (**9**).[9] On the other hand, acidic hydrolysis of the same glycosidic mixture with aqueous sulfuric acid–methanol furnished astragenol (**5**) as the major aglycone.[13]

Cycloastragenol (**1**) and astragenol (**5**) had the same molecular composition $C_{30}H_{50}O_5$. The high resolution mass spectra (high MS) of both compounds gave two fragment ions **i** and **ii**, which were characteristic of the partial structure **A** in tetracarbocyclic triterpenes.[14] The proton nuclear magnetic resonance (^{1}H-NMR) spectra of **1** and **5** showed a double doublet at δ 3.87 ($J=5, 9$ Hz for **1** and $J=7, 9$ Hz for **5**) which was assignable to 24-H in **A**.[14b] Comparisons of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) data for **1** and **5** with those for the ocotillone triterpenes,[14c] also disclosed the presence of the partial structure **A** (a 25-hydroxy-20,24-epoxy residue) in **1** and **5** (Table I). Furthermore, detailed ^{1}H- and ^{13}C-NMR examinations of **1** and **5** revealed that, along with the presence of **A** and three *sec*-hydroxyl groups in both compounds, **1** possessed seven *tert*-methyl groups and one cyclopropane ring whereas **5** lacked the cyclopropane moiety but contained eight *tert*-methyl groups and a trisubstituted olefin in its molecule. Therefore, taking into consideration their molecular compositions, both **1** and **5** were shown to be tetracarbocyclic triterpenes (with an additional cyclopropane ring in the former) having the tetrahydrofuran residue **A** and three *sec*-hydroxyl groups (Tables I, II). The chemical correlation of **1** and **5** was readily achieved by acidic treatment of **1**, which yielded **5** as the major product. This correlation was reminiscent of a conversion from a 9,19-cyclolanostane triterpene to the isomeric lanost-9(11)-ene counterpart.[15] The circular dichroism (CD) spectrum of **5** showed a positive maximum, $[\theta]_{200}$ +45500, which is characteristic of the 9(11)-double bond chirality in lanost-9(11)-ene triterpenes.[16] The presence of the 9(11)-double bond in **5** was further supported by the 11-H signal, the chemical shift of which was in good accord with that for the 11-H of lanost-9(11)-ene triterpenes.[16,17] Finally, examinations of the ^{13}C-NMR data for **1** and **5**, in comparison with the data for 9,19-cyclolanostane[18] and lanost-9(11)-ene[19] triterpenes, led us to consider that cycloastragenol (**1**) was a 9,19-cyclolanostane triterpene while astragenol (**5**) was a corresponding lanost-9(11)-ene triterpene, both possessing three *sec*-hydroxyl groups at C-3, -6, and -16.

Acetylation of cycloastragenol (**1**) gave the diacetate (**2**), which, on pyridinium chlorochromate (PCC) oxidation,[20] was converted to the diacetyl-monoketone (**4**). The mass spectra (MS) of both **2** and **4** provided two fragment ions **i** and **ii**, indicating the retention of **A**, while the ^{1}H-NMR spectra confirmed the retention of the cyclopropane moiety[21] in **2** and **4** and showed signals due to two acetoxyl functions, seven *tert*-methyl groups, and the 24-H for both compounds. Since the signal due to the 17-H in **2** was observed at δ 2.44 (d, $J=8$ Hz) while that in **4** was at δ 2.97 (s), the free *sec*-hydroxyl group in **2** was shown to be at C-16. Furthermore, a negative CD maximum, $[\theta]_{308}$ -15800, of **4** indicated the location of the ketone group at C-16 in the 9,19-cyclolanostane triterpene.[21]

In order to ascertain the chemical environment around the 16-CO function and the 17-residue **A**, the diacetyl-monoketone (**4**) was treated with sodium methoxide in methanol at room temperature to yield two products: **3** (major) and **10** (minor). The major product **3** was the normal deacetylation product as shown by its physicochemical properties and by reacetylation to recover **4**. The signal due to the 17-H of **3** was observed at δ 2.90 (s). The infrared (IR) spectrum showed the presence of a five-membered ring ketone in **3**, whereas the CD spectrum indicated the location of the ketone function at C-16 by a negative maximum: $[\theta]_{308}$ -14600.

The CD and ultraviolet (UV) spectra of the minor product **10** indicated the formation of an enone chromophore[16] which was supported by the IR spectrum. The ^{1}H-NMR spectrum of **10** showed signals ascribable to a cyclopropane methylene moiety, six *tert*-methyl groups, and a vinylic methyl group (total intensity of 3H at δ 1.89 and 2.14 in *ca.* 2:1 peak



1 : $R^1=H$, $R^2=\beta$-OH, α-H (20*R*, 24*S*)
(cycloastragenol)
2 : $R^1=Ac$, $R^2=\beta$-OH, α-H
3 : $R^1=H$, $R^2=O$
4 : $R^1=Ac$, $R^2=O$

5 : $R^1=R^2=R^3=H$
(astragenol)
6 : $R^1=Ac$, $R^2=R^3=H$
7 : $R^1=R^2=Ac$, $R^3=H$
8 : $R^1=Ac$, $R^2=R^3=COCF_3$

9 : soyasapogenol B

10 : R=H
11, 12 : R=Ac

13

14 : $R^1=\beta$-OAc, α-H; $R^2=\alpha$-OAc, β-H
15 : $R^1=R^2=O$

A **i** **ii**

Chart 1

ratio). Since acetylation of **10** provided two triacetates **11** and **12**[22] in *ca.* 2:1 ratio, **10** was considered to be a mixture of 17(20)-geometric isomers. Based on this evidence, the enone **10** was considered to be formed *via* a 20,24-epoxide ring opening in the residue **A**, initiated by a base attack at the 17-H as depicted in Chart 2.[23] A similar enone formation was experienced in the structural study of echinoderm oligoglycosides such as holotoxins **A** and **B**.[16] In those cases, the γ-lactone ring was opened during the methylation of **B** under basic reaction conditions to provide **C**.

Consequently, one of three *sec*-hydroxyl groups in **1** was demonstrated to be at C-16 and the 16-OH group was considered to be in *cis* relation to the 17-residue **A**, since it resisted ordinary acetylation.

Chromium trioxide oxidation of cycloastragenol (**1**) furnished the triketone (**13**), which was shown to possess one five-membered and two independent six-membered ring ketone functions by its IR spectrum. The MS of **13** gave ion peaks **i** and **ii**, while the ^{1}H-NMR

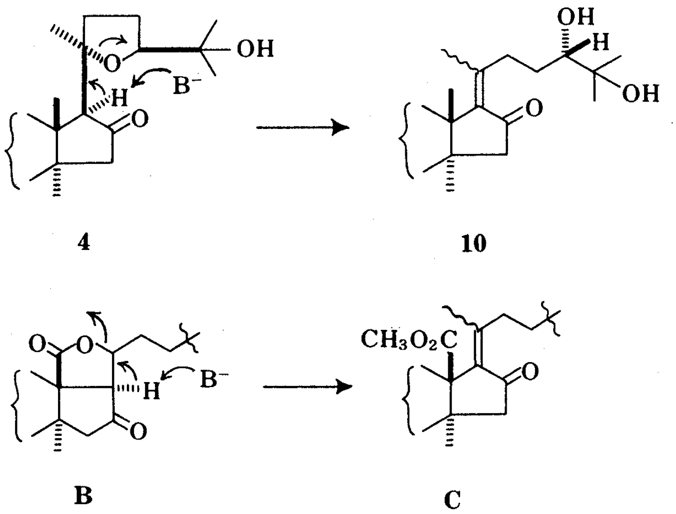


Chart 2

TABLE I. ^{13}C-NMR Data for Cycloastragenol (**1**), Astragenol (**5**) and Its Derivatives (100 MHz, δc)[a]

Carbon	**1**	**5**	**6**	**14**	**15**
1	35.1 (t)	37.2 (t)[b]	36.0 (t) [−1.2][d]	36.0 (t)	37.1 (t)
2	32.9 (t)	28.4 (t)	23.8 (t) [−4.6]	23.8 (t)	34.2 (t) [+5.8]
3	78.4 (d)	78.7 (d)	80.7 (d) [+2.0]	80.6 (d)	213.9 (s)[b] [+135.2]
4	42.5 (s)	40.3 (s)	37.9 (s) [−2.4]	38.1 (s)	47.0 (s) [+6.7]
5	54.0 (d)	57.9 (d)	55.0 (d) [−2.9]	55.1 (d)	62.2 (d) [+4.3]
6	68.5 (d)	69.3 (d)	72.0 (d) [+2.7]	71.7 (d) [+2.4]	209.8 (s)[b] [+140.5]
7	39.0 (t)	39.7 (t)	34.6 (t) [−5.1]	35.9 (t) [−3.8]	48.7 (t) [+9.0]
8	47.5 (d)	41.3 (d)	40.2 (d) [−1.1]	39.5 (d)	42.7 (d)
9	21.1 (s)	147.8 (s)	145.8 (s)	146.1 (s)	144.4 (s)
10	30.1 (s)	44.3 (s)	44.2 (s)	43.7 (s)	44.3 (s)
11	26.5 (t)	115.2 (d)	116.3 (d)	116.6 (d)	118.8 (d)
12	33.6 (t)	37.9 (t)[b]	37.6 (t)	36.5 (t)	36.3 (t)
13	45.2 (s)	44.1 (s)	44.1 (s)	41.4 (s)	41.0 (s)
14	46.3 (s)	41.4 (s)	41.1 (s)	40.8 (s)	43.7 (s)
15	46.9 (t)	45.4 (t)	44.7 (t)	49.4 (t) [+4.0]	49.0 (t) [+3.6]
16	73.6 (d)	73.4 (d)	73.4 (d)	217.3 (s) [+143.9]	216.9 (s) [+143.5]
17	58.5 (d)	57.1 (d)	56.3 (d)	64.3 (d) [+7.2]	64.1 (d) [+7.0]
18	21.8 (q)	18.4 (q)	18.2 (q)	17.1 (q)	17.2 (q)
19	31.5 (t)[b]	23.5 (q)	23.2 (q)	23.3 (q)	23.2 (q)
20	87.4 (s)	87.1 (s)	87.1 (s)	84.6 (s)	84.5 (s)
21	27.3 (q)[c]	27.1 (q)[c]	26.7 (q)[c]	25.2 (q)[c]	24.6 (q)[c]
22	31.3 (t)[b]	30.5 (t)	30.6 (t)	36.2 (t)	35.5 (t)
23	26.6 (t)	26.4 (t)	25.8 (t)	26.5 (t)	26.4 (t)
24	81.8 (d)	81.9 (d)	81.6 (d)	82.8 (d)	82.5 (t)
25	71.4 (s)	71.2 (s)	71.8 (s)	70.9 (s)	70.9 (s)
26	28.3 (q)[c]	28.1 (q)[c]	27.8 (q)[c]	28.1 (q)[c]	25.2 (q)[c]
27	28.7 (q)[c]	28.5 (q)[c]	28.0 (q)[c]	30.2 (q)[c]	28.1 (q)
28	29.3 (q)	32.2 (q)	34.4 (q)	17.2 (q)	22.3 (q)
29	16.3 (q)	16.6 (q)	17.1 (q)	34.7 (q)	25.4 (q)[c]
30	20.4 (q)	19.4 (q)	19.2 (q)	18.9 (q)	18.6 (q)
Ac			170.1, 170.4 21.3, 22.0	170.2, 170.9 21.3, 22.0	

a) Compounds **1** and **5** were measured in d_5-pyridine whereas **6**, **14**, and **15** were measured in $CDCl_3$. Abbreviations given in parentheses denote the signal patterns observed in off-resonance experiments: d=doublet, q=quartet, s=singlet, t=triplet.

b—*c*) The assignments for these signals within the same column may be interchanged.

d) The values in brackets are differences from corresponding chemical shifts for **5**.

spectrum showed signals due to a cyclopropane ring, seven *tert*-methyl groups, the 24-H in **A** and the 17-H (δ 2.78, s). The accumulated data mentioned above suggested that cycloastragenol (**1**) was a 9,19-cyclolanostane triterpene possessing residue **A** at C-17, a 16-OH group, and two hydroxyl groups presumably at C-3 and C-6.

We next investigated the location of two *sec*-hydroxyl groups by examination of astragenol (**5**) which was considered to be a lanost-9(11)-ene counterpart of cycloastragenol (**1**) as mentioned above.

Acetylation of **5** gave the diacetate (**6**) (major) and the triacetate (**7**). Trifluoroacetylation of the diacetate (**6**) provided the diacetyl-difluoroacetate (**8**), while PCC oxidation of **6** furnished the diacetyl-monoketone (**14**). Direct oxidation of **5** with chromium trioxide in pyridine afforded the triketone (**15**). Detailed ^{1}H-NMR examinations of **5** and these four derivatives (**6**, **8**, **14**, **15**) were carried out at 400 MHz, including decoupling experiments and NOE measurements (Table II).

The signals due to the 3α-H in **6** and **8** were readily assigned from their chemical shifts and characteristic coupling patterns. The 16-H signals for **6** and **8** were assigned from their couplings with the 17-H and with the 15-H_2 signals. Here again, the coupling constants ($J_{15\alpha,16}=8$ Hz and $J_{15\beta,16}=5$ Hz for **8**) between 16-H and 15-H_2 supported the *cis*-relationship of the 16-OH group and the 17-residue. The 6-H signals for **6** and **8** were assigned from their coupling patterns with the 5-H signals and the 6β-axial proton was identified by its coupling constant ($J_{5\alpha,6\beta}=11$ Hz). Consequently, the 3β-OH and 6α-OH configurations in astragenol (**5**) were substantiated.

In the ^{1}H-NMR spectrum of the diacetyl-monoketone (**14**), the signals attributable to 3α-H, 15-H_2 and 17-H were assigned analogously. Detailed decouping experiments with of **14** enabled us to assign all signals due to the *B*/*C* ring protons (5-, 6-, 7-, 8-, 11-, and 12-H) as given in Table II. It should be mentioned here that long range couplings between 8β-H and

TABLE II. ^{1}H-NMR Data for Astragenol (**5**) and Its Derivatives (400 MHz, δ)[a]

	5	**6**	**8**	**14**	**15**
3α-H	3.53 (t-like)	4.45 (dd, J=4, 11)	4.52 (dd, J=4, 12)	4.47 (dd, J=4, 11)	—
5α-H	—[i]	1.38 (d, J=11)	1.45 (d, J=11)	1.43 (d, J=11)	2.55 (s)
6β-H	4.45 (ddd, J=3, 11, 11)	5.38 (ddd, J=4, 11, 11)	5.37 (ddd, J=4, 11, 11)	5.37 (ddd, J=4, 11, 12)	—
7α-H	—[i]	—[i]	—[i]	1.50 (ddd, J=12, 12, 12)	2.45 (dd, J=12, 12.5)
7β-H	—[i]	—[i]	—[i]	1.83 (ddd, J=4, 4, 12)	2.23 (dd, J=6, 12.5)
8β-H	—[i]	—[i]	2.55 (m)	2.55 (br ddd, J=2.5[b], 4, 12)[c]	2.88 (m)
11-H	5.37 (br d, J=4)	5.31 (br d, J=5)	5.38 (m)	5.43 (br dd, J=2, 6)[c]	5.63 (br d, J=4)
12α-H	—[i]	—[i]	—[i]	2.39 (ddd, J=2, 2.5[b], 17)	2.47 (m)[f]
12β-H	—[i]	—[i]	—[i]	2.12 (dd, J=6, 17)	2.22 (m)
15α-H	—[i]	—[i]	2.30 (dd, J=8, 14)	2.03 (d, J=18)	2.02 (d, J=18)
15β-H	—[i]	—[i]	1.52 (dd, J=5, 14)	2.17 (d, J=18)[d]	2.16 (d, J=18)
16α-H	4.99 (m)	4.66 (ddd, J=6, 8, 8)	5.51 (ddd, J=5, 8, 8)	—	—
17α-H	2.55 (d, J=7.5)	2.31 (d, J=8)	2.51 (d, J=8)	2.96 (s)[e]	2.93 (s)[h]
24α-H	3.87 (dd, J=7, 9)	3.74 (dd, J=7, 7)	—[i]	3.74 (dd, J=5, 8)	3.74 (dd, J=5, 8)
tert-CH_3	0.84, 1.09, 1.21 1.29, 1.32, 1.52 1.56, 1.93	0.78, 0.93, 0.97 1.04, 1.14, 1.15 1.24, 1.28	0.79, 0.86, 1.03 1.06, 1.17, 1.36 1.53, 1.58	0.84[e], 0.97[d], 0.98 1.06, 1.11, 1.18 1.20, 1.26	0.89[f,h], 1.04[g], 1.10 1.11, 1.21, 1.25 1.34, 1.53

a) **5** was measured in d_5-pyridine whereas **6**, **8**, **14**, and **15** were measured in $CDCl_3$.
b—h) Long-range couplings were observed between the indicated signals.
i) These signals have not yet been assigned so far.

12α-H (J=2.5 Hz) and between 8β-H and 11-H[24] were observed. Therefore, the *B*/*C* ring structure including the 6α-OH function and the 9(11) double bond in astragenol (**5**) was confirmed.

Next, the ^{1}H-NMR spectrum of the triketone (**15**) was examined. It showed signals due to eight *tert*-methyl groups. Among them, the signals of 13β-CH_3 and 14α-CH_3 were assigned on the basis of detailed examination of long-range coupling. Thus, the signal of 13β-CH_3 at δ 0.89 was found to couple[24] with the signals of 17α-H and 12α-H, while the signal of 14α-CH_3 at δ 1.04 was found to couple[24] with that of 15β-H. In addition, the 20% NOE observed between 14α-CH_3 and 17α-H cast light on the stereochemical features of the D ring having the 17β-residue and the 16β-OH function.

Finally, the ^{13}C-NMR examinations of cycloastragenol (**1**), astragenol (**5**), **6**, **14**, and **15** demonstrated that i) significant acetylation shifts[25] were observed in the 2-, 3-, 4-C and 5-, 6-, 7-C signals for **6** and **14**, and ii) the signals due to 16-C in **14** and 3-, 6-, 16-C in **15** were markedly shifted to the lower field as compared with those in their parent compounds (Table I). Thus, the locatios of three *sec*-hydroxyl functions in **1** and **5** were again confirmed.

Based on the above-described findings, the structures of cycloastragenol (**1**) and astragenol (**5**) became evident except for the C-20 and C-24 configurations. Recently, Saitoh and his group carried out an X-ray crystallographic analysis of the octa-*O*-methyl derivative of astragaloside IV,[26] which is identical with one of the eleven astragalosides isolated by us, and possesses cycloastragenol (**1**) as the aglycone.[27] Their result supported the 9,19-cyclolanostane structure of cycloastragenol (**1**) and established the 20*R* and 24*S* configurations. Consequently, the total structures of cycloastragenol and astragenol can be expressed as (20*R*,24*S*)-3β,6α,16β,25-tetrahydroxy-20,24-epoxy-9,19-cyclolanostane (**1**) and (20*R*,24*S*)-3β,6α,16β,25-tetrahydroxy-20,24-epoxy-lanost-9(11)-ene (**5**), respectively.

Experimental[28]

Isolation of Glycosidic Constituents——Korean Astragali Radix (cut, 8 kg, purchased from Mikuni Shoten Co. Osaka) was extracted with hot MeOH and the solvent was evaporated off under reduced pressure to give the MeOH extract (1.1 kg). The MeOH extract was partitioned in an *n*-BuOH–H_2O (1:1) solvent system and removal of the solvent from the *n*-BuOH phase under reduced pressure yielded the *n*-BuOH extract (610 g). Reversed-phase column chromatography (Waters, Bondapak C_{18} 100 g; MeOH–H_2O=1:1—5:1) of the *n*-BuOH extract (100 g) furnished the glycosidic constituents (20 g).

Enzymatic Hydrolysis of Total Glycoside Mixture with Crude Hesperidinase——A solution of the total glycoside mixture (500 mg) in water (200 ml) was treated with crude hesperidinase (2 g)[11] and the whole mixture was incubated with stirring at 36°C for 5 days. The reaction mixture was extracted with $CHCl_3$–MeOH (5:1). The residue, which was obtained by evaporation of the solvent under reduced pressure from the extract, was subjected to column chromatography (SiO_2 20 g, $CHCl_3$–MeOH=30:1—10:1) to furnish cycloastragenol (**1**, 130 mg) and soyasapogenol B (**9**, 5 mg). **9** was shown to be identical with an authentic sample[9] by mixed mp determination, and thin-layer chromatography (TLC) ($CHCl_3$–MeOH=20:1; benzene–acetone=3:1; *n*-hexane–AcOEt=1:2) and infrared (IR) spectrum (KBr) comparisons. Cycloastragenol (**1**), mp 243—244°C (colorless needles from MeOH), $[\alpha]_D^{20}$ +49.0° (c=0.35, MeOH). *Anal.* Calcd for $C_{30}H_{50}O_5$: C, 73.43; H, 10.27. Found: C, 73.30; H, 10.19. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400, 2930, 1090. ^{1}H-NMR (d_5-pyridine, 90 MHz, δ): 0.35, 0.62 (1H each, both d, J=4 Hz, 19-H_2), 1.02 (3H), 1.31 (12H), 1.43, 1.53 (3H each)(all s, *tert*-CH_3×7), 2.48 (1H, d, J=8 Hz, 17-H), 3.87 (1H, dd, J=5, 9 Hz, 24-H). ^{13}C-NMR (d_5-pyridine, 100 MHz, δ c): as given in Table I. MS (m/z, %): 490 (M^+, <1), 143 (**i**, 100), 125 (**ii**, 27). High MS: Found 490.366, 143.107, 125.097. Calcd for $C_{30}H_{50}O_5$(M^+): 490.366, $C_8H_{15}O_2$(**i**): 143.107, $C_8H_{13}O$ (**ii**): 125.097.

Heterogeneous Acidic Hydrolysis of Total Glycoside Mixture——A solution of the total glycoside mixture (1.1 g) in EtOH (50 ml) was mixed with aq. 10% HCl (25 ml) and benzene (100 ml). The heterogeneous mixture was then heated under reflux for 30 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 water, and dried over $MgSO_4$ powder. Removal of the solvent under reduced pressure yielded the product, which was purified by column chromatography (SiO_2 50 g, $CHCl_3$–MeOH=40:1—10:1) to furnish cycloastragenol (**1**, 105 mg) and soyasapogenol B (**9**, 3 mg). **1** was shown to be identical with the sample obtained above by mixed mp determination, and TLC ($CHCl_3$–MeOH=20:1, *n*-hexane–AcOEt=1:5) and IR (KBr) comparisons.

Acidic Hydrolysis of Total Glycoside Mixture with Methanolic Sulfuric Acid——A solution of the total glycoside mixture (2 g) in MeOH (50 ml) was treated with aq. 20% H_2SO_4 (50 ml) and the whole mixture was heated under reflux for 3.5 h. The reaction mixture was poured into ice-water and the resulting product was collected by filtration and purified by column chromatography (SiO_2 200 g, $CHCl_3$, $CHCl_3$-MeOH=50:1—10:1) to furnish astragenol (**5**, 220 mg).[13] Astragenol (**5**), mp 240.5—241°C (colorless needles from MeOH), $[\alpha]_D^{26}$ +57.5° (c=0.8, MeOH). *Anal.* Calcd for $C_{30}H_{50}O_5$: C, 73.43; H, 10.27. Found: C, 73.18; H, 10.19. IR ν_{max}^{KBr} cm^{-1}: 3385, 2930, 1030. CD (c=2.63×10^{-2}, MeOH): $[\theta]_{214}$ 0, $[\theta]_{200}$ +45500 (pos. max.), $[\theta]_{198}$ +43000!. ^{1}H-NMR (d_5-pyridine, 400 MHz, δ): as given in Table II. ^{13}C-NMR (d_5-pyridine, 100 MHz, δ c): as given in Table I. MS (m/z, %): 490 (M^+, 2): 143 (**i**, 100), 125 (**ii**, 26). High MS: Found 490.365, 143.105, 125.097. Calcd for $C_{30}H_{50}O_5$ (M^+): 490.366, $C_8H_{15}O_2$ (**i**): 143.107, $C_8H_{13}O$ (**ii**): 125.097.

Conversion from Cycloastragenol (1) to Astragenol (5)———A solution of **1** (20 mg) in MeOH (5 ml) was treated with aq. 20% H_2SO_4 (1 ml) and the whole solution was heated under reflux for 5 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 water, and dried over $MgSO_4$ powder. The product, which was obtained by evaporation of the solvent under reduced pressure, was purified by preparative TLC ($CHCl_3$-MeOH=10:1) to furnish **5** (12 mg), which was shown to be identical with an authentic sample by mixed mp determination, and TLC ($CHCl_3$-MeOH=20:1; n-hexane-AcOEt=1:5) and IR (KBr) comparisons.

Acetylation of Cycloastragenol (1)———A solution of 1 (40 mg) in Ac_2O-pyridine (1:2, 3 ml) was left standing at 5°C 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. dil. HCl, aq. sat. $NaHCO_3$, and water, and dried over $MgSO_4$ powder. Removal of the solvent under reduced pressure furnished the diacetate (**2**, 40 mg), mp 210—211°C (colorless needles from MeOH), $[\alpha]_D^{20}$ +71.0° (c=0.33, MeOH). *Anal.* Calcd for $C_{34}H_{54}O_7$: C, 71.08; H, 9.48. Found: C, 70.90; H, 9.64. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 2926, 1722, 1200. ^{1}H-NMR ($CDCl_3$, 90 MHz, δ): 0.35, 0.65 (1H each, both d, J=5 Hz, 19-H_2), 0.86, 0.95, 1.00, 1.04 (3H each), 1.15 (6H), 1.20 (3H) (all s, $tert$-CH_3×7), 1.98, 2.04 (3H each, both s, OAc×2), 2.44 (1H, d, J=8 Hz, 17-H), 3.75 (1H, dd, J=7, 7 Hz, 24-H), 4.64 (2H, m, 3,6-H), 5.35 (1H, m, 6-H). MS (m/z, %): 574 (M^+, <1), 143 (**i**, 100), 125 (**ii**, 21).

PCC Oxidation of Diacetate (2)———A solution of **2** (40 mg) in CH_2Cl_2 (2 ml) was treated with PCC (100 mg) and the whole mixture was stirred at 20°C for 5 h. After dilution with ether, the reaction mixture was passed through a Florisil column (80—100 mesh, 5 g). Removal of the solvent from the eluate under reduced pressure gave the diacetyl-monoketone (**4**, 38 mg). **4**, mp 221—223°C (colorless needles from MeOH), $[\alpha]_D^{20}$ +7.0° (c=0.35, $CHCl_3$). High MS: Found 572.371. Calcd for $C_{34}H_{52}O_7$: (M^+): 572.371. CD (c=2.987×10^{-1}, EtOH): $[\theta]_{350}$ 0, $[\theta]_{308}$ −15800, (neg. max.), $[\theta]_{250}$ 0. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3465, 1743, 1245. ^{1}H-NMR ($CDCl_3$, 90 MHz, δ): 0.36, 0.65 (1H each, both d, J=5 Hz, 19-H_2), 0.84, 0.97, 1.07, 1.12 (3H each), 1.15 (6H), 1.21 (3H)(all s, $tert$-CH_3×7), 2.01 (6H, s, OAc×2), 2.97 (1H, s, 17-H), 3.72 (1H, dd, J=7, 7 Hz, 24-H), 4.67 (1H, m, 3-H), 5.56 (1H, m, 6-H). MS (m/z, %): 572 (M^+, <1), 143 (**i**, 76), 125 (**ii**, 60).

Alkaline Treatment of Diacetyl-monoketone (4)———A solution of **4** (45 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 reaction mixture was filtered. Removal of the solvent from the filtrate under reduced pressure gave the product, which was purified by preparative TLC (n-hexane-AcOEt=9:2) to afford **3** (21 mg) and **10** (12 mg). **3**, mp 224—226°C (colorless needles from MeOH), $[\alpha]_D^{20}$ +8.5° (c=0.5, MeOH). High MS: Found 488.350. Calcd for $C_{30}H_{48}O_5$:(M^+): 488.350. CD (c=3.423×10^{-1}, EtOH): $[\theta]_{340}$ 0, $[\theta]_{308}$ −14600 (neg. max.), $[\theta]_{206}$0. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 2936, 1738. ^{1}H-NMR ($CDCl_3$, 90 MHz, δ): 0.42, 0.57 (1H each, both d, J=5 Hz, 19-H_2), 0.97, 1.10 (3H each), 1.15 (6H), 1.17, 1.23, 1.26 (3H each) (all s, $tert$-CH_3×7), 2.90 (1H, s, 17-H). MS (m/z, %): 488 (M^+, 1), 143 (**i**, 82), 125 (**ii**, 67). **10**, white powder,[30] $[\alpha]_D^{19}$ −57.5° (c=0.3, MeOH). High MS: Found 488.348. Calcd for $C_{30}H_{48}O_5$: (M^+): 488.350. UV λ_{max}^{MeOH} nm: 256 (ϵ=8300). CD (c=7.823×10^{-2}, MeOH): $[\theta]_{390}$ 0, $[\theta]_{350}$ −6200 (neg. max.), $[\theta]_{300}$ 0. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1690, 1608. ^{1}H-NMR ($CDCl_3$, 90 MHz, δ): 0.37, 0.56 (1H each, both d, J=5 Hz, 19-H_2), 0.95, 1.01, 1.16, 1.25, 1.31 (total 18 H, all s, $tert$-CH_3×6), 1.89, 2.14 (total 3H, *ca.* 2:1, both s, 20-CH_3). MS (m/z, %): 488 (M^+, 16), 143 (82).

Acetylation of 10 giving 11 and 12———A solution of **10** (15 mg) in Ac_2O-pyridine (1:1, 1 ml) was left standing at 20°C for 4 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 acetylation of **1** gave the product, which was purified by preparative TLC to furnish **11** (5 mg) and **12** (9 mg). **11**, white powder, $[\alpha]_D^{20}$ −4.0° (c=0.5, $CHCl_3$). High MS: Found 614.382. Calcd for $C_{36}H_{54}O_8$: (M^+): 614.382. UV λ_{max}^{MeOH} nm: 254 (ϵ=7800). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610, 1735, 1710, 1615, 1240. ^{1}H-NMR ($CDCl_3$, 90 MHz, δ): 0.37, 0.60 (1H each, both br d, 19-H_2), 0.88 (3H), 1.05, 1.31 (6H each), 1.37 (3H) (all s, $tert$-CH_3×6), 2.12 (3H, s, 20-CH_3), 1.95, 2.02, 2.06 (3H each, all s, OAc×3). MS (m/z, %): 614 (M^+, 4), 43 (100). **12**, white ponder, $[\alpha]_D^{20}$ −10.0° (c=0.9, $CHCl_3$). High MS: Found 614.384. Calcd for $C_{36}H_{54}O_8$ (M^+): 614.382. UV λ_{max}^{MeOH} nm: 254 (ϵ=7400). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3605, 1730, 1705, 1615, 1240. ^{1}H-NMR ($CDCl_3$, 90 MHz, δ): 0.39, 0.69 (1H each, both d, 19-H_2), 0.83, (3H), 0.99 1.18 (6H each), 1.24 (3H) (all s, $tert$-CH_3×6), 1.81 (3H, s, 20-CH_3), 1.93, 1.99, 2.09 (3H each, all s, OAc×3). MS (m/z, %): 614 (M^+, 3), 43 (100).

CrO_3 Oxidation of Cycloastragenol (1)———A solution of **1** (50 mg) in pyridine (2 ml) was treated with a CrO_3 (50 mg)-pyridine (2 ml) solution and the whole mixture was stirred at 25°C for 8 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed successively with aq. dil. HCl, aq. sat. $NaHCO_3$, and water, and dried over $MgSO_4$ powder. Removal of the solvent under reduced pressure furnished the triketone (**13**, 46 mg). **13**, mp 193°C (colorless needles from MeOH), $[\alpha]_D^{20} -13.0°$ ($c=0.35$, MeOH). High MS: Found 484.319. Calcd for $C_{30}H_{44}O_5$ (M^+): 484.319. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3446, 2976, 1727, 1706. ^{1}H-NMR (d_6-benzene, 90 MHz, δ): -0.12 (1H, d, $J=6$ Hz, 19-H), 0.59, 0.75, 1.06, 1.21, 1.29, 1.46, 1.56 (3H each, all s, *tert*-$CH_3 \times 7$), 2.78 (1H, s, 17-H), 3.67 (1H, dd, $J=5$, 7 Hz, 24-H), 4.26 (1H, br s, disappeared on D_2O addition, 25-OH). MS (m/z, %): 425 (M^+,100): 143 (**i**, 46), 125 (**ii**, 50).

Acetylation of Astragenol (5)———A solution of **5** (100 mg) in Ac_2O–pyridine (1:2, 3 ml) was stirred at 35°C for 48 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 acetylation of **1** gave the product, which was purified by preparative TLC (*n*-hexane–AcOEt$=1:1$) to afford the diacetate (**6**, 58 mg) and the triacetate (**7**, 13 mg). **6**, mp 250—250.5°C (colorless prisms from MeOH), $[\alpha]_D^{23} +86.4°$ ($c=0.47$, MeOH). *Anal.* Calcd for $C_{34}H_{54}O_7$: C, 71.08; H,9.48. Found: C, 70.85; H, 9.40. CD ($c=1.628 \times 10^{-1}$, MeOH): $[\theta]_{250}$ 0, $[\theta]_{216}$ -7400 (neg. max.), $[\theta]_{210}$ 0, $[\theta]_{205}$ $+22200$!. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3330, 1731, 1243. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): as given in Table II. ^{13}C-NMR ($CDCl_3$, 100 MHz, δ c): as given in Table I. MS (m/z, %): 574 (M^+, 1), 143 (**i**, 100), 125 (**ii**, 30). High MS: Found 574.388. Calcd for $C_{34}H_{54}O_7$: (M^+) 574.387. **7**, mp 105—106°C (colorless fine crystals, MeOH), $[\alpha]_D^{23} +91.0°$ ($c=0.34$, MeOH). High MS: Found 616.397. Calcd for $C_{36}H_{56}O_8$ (M^+): 616.397. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3578, 1733, 1238. ^{1}H-NMR ($CDCl_3$, 90 MHz, δ): 0.83 (3H), 0.97 (6H), 1.06, 1.10, 1.15, 1.21, 1.31 (3H each) (all s, *tert*-$CH_3 \times 8$), 2.02 (3H), 2.05 (6H)(both s, $OAc \times 3$), 2.48 (1H, d, $J=8$ Hz, 17-H), 3.70 (1H, dd, $J=7$, 7 Hz, 24-H), 4.47 (1H, m, 3-H), 5.35 (3H, m, 6, 11, 16-H). MS (m/z, %): 616 (M^+, <1), 143 (**i**, 100), 125 (**ii**, 39).

Trifluoroacetylation of Diacetate (6)———A solution of **6** (80 mg) in $(CF_3CO)_2O$-pyridine (1:1, 1 ml) was left standing at 30°C for 24 h. The reaction mixture was poured into ice-water and the resulting precipitate was collected by filtration. Column chromatography (SiO_2 5 g, $CHCl_3$) of the product furnished the diacetyldifluoroacetate (**8**, 85 mg). **8**, white powder, $[\alpha]_D^{25} +79.6°$ ($c=0.9$, $CHCl_3$). *Anal.* Calcd for $C_{38}H_{54}O_9F_6$: C, 59.52; H, 6.84; F, 14.87. Found: C, 59.68; H, 6.95; F, 14.62. IR $\nu_{max}^{CCl_4}$cm^{-1}: 1780, 1733, 1225, 1170. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): as given in Table II. MS (m/z, %): 766 (M^+, <1), 706 ($M^+ -$AcOH, 2), 652 (M^+ $-CF_3COOH$, 2), 125 (**ii**, 100).

PCC Oxidation of 6———A solution of **6** (89 mg) in CH_2Cl_2 (2 ml) was treated with PCC (97 mg) and the whole mixture was stirred at 22°C for 2.5 h. After dilution with ether, the reaction mixture was passed through a Florisil column (80—100 mesh, 5 g). Removal of the solvent from the eluate furnished the diacetylmonoketone (**14**, 73 mg). **14**, mp 241—242°C (colorless plates from MeOH), $[\alpha]_D^{20} +8.0°$ ($c=0.39$, MeOH). *Anal.* Calcd for $C_{34}H_{52}O_7$: C, 71.29; H, 9.15. Found: C, 71.04; H, 9.38. CD ($c=1.091 \times 10^{-1}$, MeOH): $[\theta]_{336}$ 0, $[\theta]_{302}$ -12000 (neg. max.), $[\theta]_{260}$ 0, $[\theta]_{238}$ 0, $[\theta]_{210}$ -9700 (neg. max.), $[\theta]_{204}$ 0, $[\theta]_{200}$ $+18000$!. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1727, 1719, 1248. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): as given in Table II. ^{13}C-NMR ($CDCl_3$, 100 MHz, δc): as given in Table I. MS (m/z, %): 572 (M^+, 4), 143 (**i**, 41), 125 (**ii**, 46), 84 (100).

CrO_3 Oxidation of Astragenol (5)———A solution of **5** (30 mg) in pyridine (1 ml) was treated with a solution of CrO_3 (57 mg) in pyridine (2 ml) and the whole mixture was stirred at 25°C for 7.2 h. The reaction mixture was then poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract as described for the oxidation of **1** furnished the triketone (**15**, 45 mg). **15**, mp 213—214°C (colorless needles from MeOH), $[\alpha]_D^{20} -57.9°$ ($c=0.33$, MeOH). High MS: Found 484.319. Calcd for $C_{30}H_{44}O_5$ (M^+): 484.319. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1727, 1719. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ): as given in TableII. ^{13}C-NMR ($CDCl_3$ 100 MHz, δc): as given in Table I. MS (m/z, %): 484 (M^+, 4), 466 (M^+–H_2O, 58), 425 (100), 143 (**i**, 34), 125 (**ii**, 45), 84 (60).

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22) On the bases of the ^{1}H-NMR chemical shifts of the vinylic methyl signals for **10**, **11**, and **12** and the relative yields of **11** and **12** from **10**, **11** was considered to be *Z* and **12** to be *E* at the 17 (20) double bond.

23) The 24*S* configuration in **10** was presumed to be retained from **4** from mechanistic considerations.

24) Long-range coupling between these protons was in fact observed, but the coupling constant was so small that we could not obtain the exact value.

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27) The chemical structures of these eleven astragalosides will be reported in our following three papers.

28) The instruments used to obtain the physical data and the experimental conditions for chromatography were the same as described in our previous paper[29] except for the following. In Tables I and II, the ^{13}C-NMR spectrum of **1** was taken with a JEOL JNM-FX 100 spectrometer and those of the other compounds were measured with a Brucker WH-400 spectrometer. The CD spectra were taken with a JASCO UV/ORD-5 spectrometer (c=g/100 ml).

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30) All attempts to crystallize the product were without success. Such compound are described as "white powder" hereafter.