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Saponin and Sapogenol. XXXII.[1] Chemical Constituents of the Seeds of *Vigna angularis* (Willd.) Ohwi *et* Ohashi. (2). Azukisaponins I, II, III, and IV

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Six oleanene-oligoglycosides named azukisaponins I (**1**), II (**2**),III (**3**), IV (**4**), V, and VI were isolated from azuki beans, the seeds of *Vigna angularis* (Willd.) Ohwi *et* Ohashi (Leguminosae). Among them, the structures of azukisaponins I, II, III, and IV were elucidated as 3-*O*-[*β*-D-glucopyranosyl(1→2)-*β*-D-glucuronopyranosyl]sophoradiol (**1**), 3-*O*-[*β*-D-glucopyranosyl(1→2)-*β*-D-glucuronopyranosyl]soyasapogenol B (**2**), 3-*O*[*β*-D-glucopyranosyl(1→2)-*β*-D-glucuronopyranosyl]azukisapogenol (**3**), and 3-*O*-(*β*-D-glucopyranosyl)-28-*O*-[*β*-D-glucopyranosyl(1→6)-*β*-D-glucopyranosyl]gypsogenic acid (**4**), respectively on the basis of chemical and physicochemical evidence.

Keywords——azuki bean; *Vigna angularis;* azukisaponin; oleanene-oligoglycoside; glucuronide-saponin; photolysis; cleavage of glucuronide linkage; centrifugal liquid chromatography; azukisapogenol

In the preceding paper,[1] we reported the isolation and the structure elucidation of two glucosides, *i.e.* 3-furanmethanol *β*-D-glucopyranoside and (+)-catechin 7-*O*-*β*-D-glucopyranoside, from azuki beans, the seeds of *Vigna angularis* (Willd.) Ohwi *et* Ohashi (Leguminosae). In addition, we isolated the saponin constituent of azuki beans (named total azukisaponin) and identified the four genuine sapogenols, *i.e.* sophoradiol (**5**), soyasapogenol B (**6**), azukisapogenol (**7**), and gypsogenic acid (**8**).

Although the isolation of crystalline saponin of azuki beans was reported a long time ago,[2] its purity was obscure and chemical characterization has not been reported. We carried out the separation of ingredient saponins of total azukisaponin. By a combination of ordinary column chromatography, centrifugal liquid chromatography (CLC), and some other means, six oleanene-oligoglycosides named azukisaponins I (**1**), II (**2**), III (**3**), IV (**4**), V, and VI were isolated from total azukisaponin as shown in Chart 1. This paper reports the structure elucidation of azukisaponins I (**1**), II (**2**), III (**3**), and IV (**4**).[3,4]

Azukisaponin I (1)

The infrared (IR) spectrum of azukisaponin I (**1**) showed the carboxylic absorption band together with strong hydroxyl absorption bands which are characteristic of glycosidic nature. Methanolysis of azukisaponin I (**1**) yielded sophoradiol (**5**) as the sapogenol and D-glucose and D-glucuronic acid in a 1:1 ratio as the carbohydrate components. Since azukisaponin I was found to contain D-glucuronic acid in its molecule, it was subjected to photochemical degradation,[5] which is a selective cleavage method for the glucuronide linkage.[6] Irradiation of a methanolic solution of azukisaponin I (**1**) with a 500 W high pressure mercury lamp for one hour liberated sophoradiol (**5**) in good yield. Thus, azukisaponin I (**1**) was shown to be a D-glucuronide of sophoradiol (**5**) having an additional glucoside residue attached to the glucuronide moiety.

Diazomethane methylation of azukisaponin I (**1**) gave the monomethyl ester (**1a**), which, on further methylation with methyl iodide and dimsyl carbanion,[7] was converted to the octa-

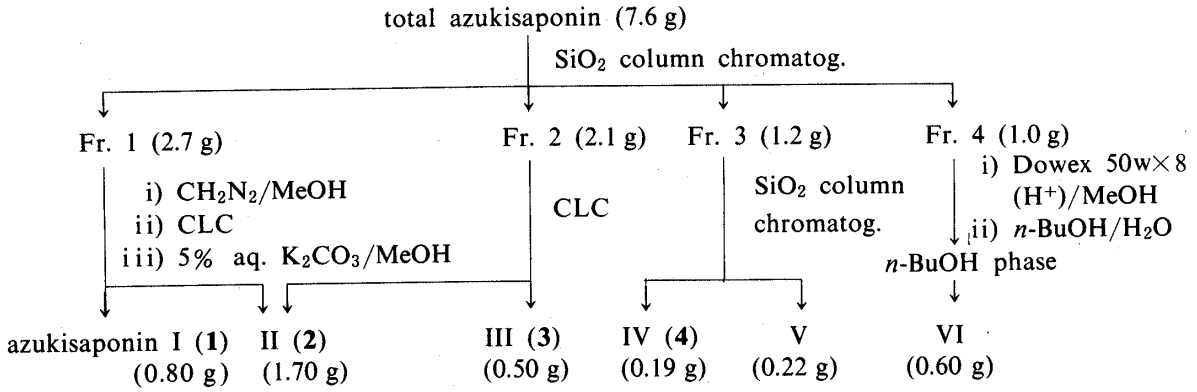


Chart 1

O-methyl derivative (**1b**). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1b** showed two anomeric proton doublets of J=8 Hz,which clearly indicated the β-glycosidic linkage of two sugar moieties in **1b**. Lithium aluminum hydride reduction followed by methanolysis of **1b** liberated methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**a**) and methyl 3,4-di-*O*-methylglucopyranoside (**b**) from the carbohydrate moiety and 22-*O*-methylsophoradiol (**5a**) as the sapogenol. Thus, the sugar moiety in azukisaponin I (**1**) was shown to be 2-*O*-β-D-glucopyranosylglucuronic acid. The structure of **5a** was supported by its spectral properties. The ^{1}H-NMR spectrum showed one methoxyl singlet, while the mass spectrum (MS) gave the fragment ion peaks **i** (base peak, from the *D*/*E* ring) and **ii** (from the *A*/*B* ring) which were presumably derived through the characteristic retro Diels–Alder fragmentation of the olean-12-ene skeleton.[8,9] The latter results are comparable to the mass fragmentation patterns of **5**, **5b**, and **5c**.[1]

Based on the above-mentioned evidence, the structure of azukisaponin I (**1**) was concluded to be 3-*O*-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]sophoradiol (**1**).

Azukisaponin II (2)

The IR spectrum of azukisaponin II (**2**) was quite similar to the spectrum of azukisaponin I (**1**). Methanolysis of **2** liberated soyasapogenol B (**6**) together with D-glucose and D-glucuronic acid in a 1:1 ratio, while photolysis of **2** as carried out for **1** furnished **6**. Thus, azukisaponin II (**2**) was shown to be the D-glucopyranosyl-D-glucuronide of soyasapogenol B.

Diazomethane methylation of **2** gave the monomethyl ester (**2a**), which was further methylated with methyl iodide and dimsyl carbanion to afford the nona-*O*-methyl derivative (**2b**). Two anomeric proton doublets of J=8 Hz, observed in the ^{1}H-NMR spectrum of **2b**, demonstrated again the β-glycosidic nature of the two sugar moieties in **2b**. Lithium hydride reduction followed by methanolysis of **2b** yielded 22,24-di-*O*-methylsoyasapogenol B (**6a**)[9] and two methyl glucopyranoside derivatives (**a**, **b**) as obtained in the similar degradation of **1b** mentioned above.

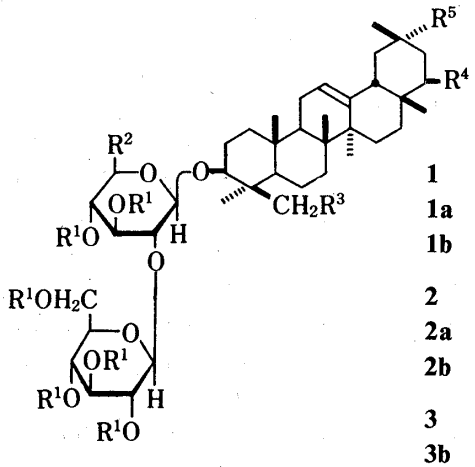
Consequently, the structure of azukisaponin II was proved to be 3-*O*-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]soyasapogenol B (**2**).

Azukisapoin III (3)

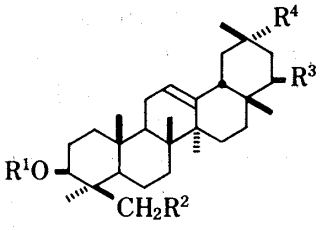
Methanolysis of azukisaponin III (**3**) yielded azukisapogenol methyl ester (**7a**) from the sapogenol portion and D-glucose and D-glucuronic acid in a 1:1 ratio from the carbohydrate portion. However, enzymatic hydrolysis of **3** with crude hesperidinase liberated the genuine sapogenol azukisapogenol (**7**). Complete methylation of **3** with methyl iodide and dimsyl carbanion gave the nona-*O*-methyl derivative (**3b**), which showed two anomeric proton doublets (J=8 Hz each) in the ^{1}H-NMR spectrum, indicating both to be β-glycosidic linkages.

Selective reduction of the methoxycarbonyl group in the glucuronide moiety of **3b** with sodium borohydride[5,9a] furnished the diglucoside derivative (**3c**). The IR spectrum of **3c** showed absorption bands ascribable to hydroxyl group and ester group, while the ^{1}H-NMR spectrum confirmed the retention of one methoxycarbonyl group. Methanolysis of **3c** afforded 24-*O*-methylazukisapogenol methyl ester (**7b**) from the sapogenol portion and two methylated methyl glucopyranosides (**a**, **b**) from the sugar portion. The structure of **7b** was substantiated by the following evidence. The IR spectrum of **7b** showed hydroxyl and ester absorption bands, while the ^{1}H-NMR spectrum showed signals ascribable to one methoxycarbonyl residue and the 4β-methoxymethyl residue. Furthermore, acetylation of **7b** furnished the monoacetate (**7c**), which provided a characteristic doublet of doublets ascribable to 3α-H geminal to the 3β-hydroxyl group in the ^{1}H-NMR spectrum. Therefore, the carbohydrate chain in azukisaponin III (**3**) was demonstrated to be linked to the 3β-hydroxyl function of azukisapogenol (**7**).

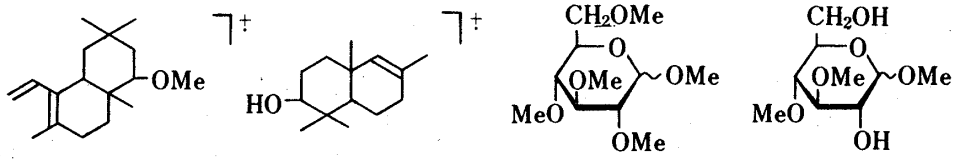
Based on the above-mentioned evidence, the structure of azukisaponin III was concluded to be 3-O-[β-D-glucopyranosyl(1→1)-β-D-glucuronopyranosyl]azukisapogenol (**3**).



	R^1	R^2	R^3	R^4	R^5	
1	H	COOH	H	OH	Me	(azukisaponin I)
1a	H	COOMe	H	OH	Me	
1b	Me	COOMe	H	OMe	Me	
2	H	COOH	OH	OH	Me	(azukisaponin II)
2a	H	COOMe	OH	OH	Me	
2b	Me	COOMe	OMe	OMe	Me	
3	H	COOH	OH	H	COOH	(azukisaponin III)
3b	Me	COOMe	OMe	H	COOMe	
3c	Me	CH_2OH	OMe	H	COOMe	



	R^1	R^2	R^3	R^4	
5	H	H	OH	Me	(sophoradiol)
5a	H	H	OMe	Me	
5b	Ac	H	OH	Me	
5c	H	H	OAc	Me	
6	H	OH	OH	Me	(soyasapogenol B)
6a	H	OMe	OMe	Me	
7	H	OH	H	COOH	(azukisapogenol)
7a	H	OH	H	COOMe	
7b	H	OMe	H	COOMe	
7c	Ac	OMe	H	COOMe	



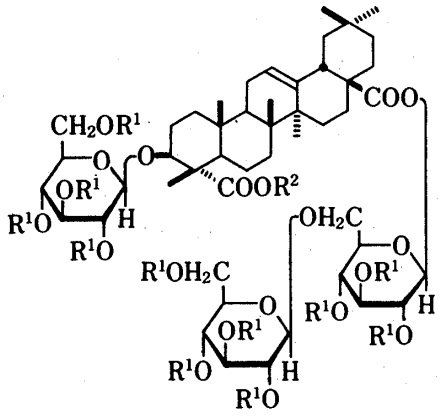
i **ii** **a** **b**

Chart 2

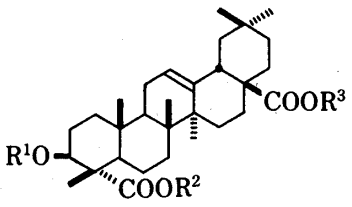
Azukisapoin IV (4)

Methanolysis of azukisaponin IV (**4**) yielded gypsogenic acid monomethyl ester (**8a**) from the sapogenol portion and D-glucose as the sole carbohydrate. Since **8a** was easily formed by methanolysis of gypsogenic acid (**8**) and the MS of **8a** showed the fragment ion peaks **iii** (base peak) and **iv**, the presence in **8a** of the 4α-methoxycarbonyl residue was presumed. Finally, the structure of **8a** was confirmed by the conversion of **8a** to the monoacetate (**8b**).[10]

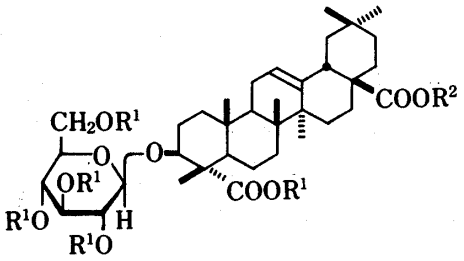
The IR spectrum of azukisaponin IV (**4**) showed an ester absorption band. Alkaline hydrolysis of **3** with potassium carbonate provided the prosapogenol (**9**), which, on further enzymatic hydrolysis with almond emulsin, liberated gypsogenic acid (**8**). Complete methylation of **9** with methyl iodide and dimsyl carbanion afforded the hexa-*O*-methyl derivative (**9a**), which showed an anomeric proton doublet (J=8 Hz) in its ^{1}H-NMR spectrum and liberated upon methanolysis gypsogenic acid dimethyl ester (**8c**)[11] and methyl 2,3,4,6-



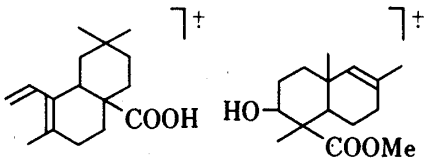
4 : $R^1=R^2=H$ (azukisaponin IV)
4a : $R^1=H$, $R^2=Me$
4b : $R^1=R^2=Me$
4c : $R^1=Ac$, $R^2=H$



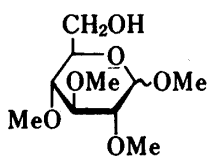
8 : $R^1=R^2=R^3=H$ (gypsogenic acid)
8a : $R^1=R^3=H$, $R^2=Me$
8b : $R^1=Ac$, $R^2=Me$, $R^3=H$
8c : $R^1=H$, $R^2=R^3=Me$



9 : $R^1=R^2=H$
9a : $R^1=R^2=Me$
9b : $R^1=Me$, $R^2=H$



iii **iv**



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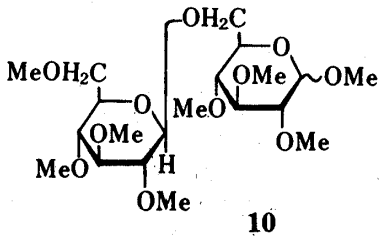

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Chart 3

tetra-*O*-methylglucopyranoside (**a**). Thus, the prosapogenol was proved to be 3-*O*-*β*-D-glucopyranosylgypsogenic acid (**9**).

Next, the location of the ester glycosidic linkage in azukisaponin IV (**4**) was clarified in the following manner. Methylation of **4** with methyl iodide and silver oxide[12] yielded the dodeca-*O*-methyl derivative (**4b**), which, upon complete methanolysis, liberated gypsogenic acid 23-monomethyl ester (**8a**) as the sapogenol and two methyl glucopyranoside derivatives. The ingredients of the methylated glucosides were demonstrated to be **a** and methyl 2,3,4-tri-*O*-methylglucopyranoside (**c**) in a 2:1 ratio. On the other hand, methanolysis of **4b** under milder reaction conditions provided the prosapogenol tetramethyl ether monomethyl ester (**9b**) and methyl hepta-*O*-methylgentiobioside (**10**). Thus, the sugar moiety linked through the ester glycoside linkage was shown to be gentiobiose.

The IR spectrum of **9b** showed ester and carboxyl absorption bands, while the ^{1}H-NMR spectrum showed signals due to six tertiary methyl groups, four methoxyl groups, one methoxycarbonyl group, and an anomeric proton as a doublet of J=8 Hz. The MS of **9b** gave the prominent fragment ion peak **iii** which suggested the presence of the 17-carboxylic residue. Diazomethane methylation of azukisaponin IV (**4**) gave the monomethyl ester (**4a**), which, on enzymatic hydrolysis with crude hesperidinase, provided gypsogenic acid 23-monomethyl ester (**8a**) as the sapogenol. Therefore, the gentiobiose moiety in **4** was concluded to be attached to the 17-carboxyl residue of gypsogenic acid (**8**). Furthermore, acetylation of azukisaponin IV (**4**) yielded the undeca-*O*-acetyl derivative (**4c**). The ^{1}H-NMR spectrum of **4c** showed a one-proton doublet (J=8 Hz) at δ 5.58 which was attributable to the anomeric proton on the *β*-ester-glycoside linkage.

Based on the accumulated evidence mentioned above, the structure of azukisaponin IV was concluded to be 3-*O*-[*β*-D-glucopyranosyl]-28-*O*-[*β*-D-glucopyranosyl(1→6)-*β*-D-glucopyranosyl]gypsogenic acid (**4**).

Azukisaponin IV (**4**) is a bisdesmoside of gypsogenic acid (**8**), whereas azukisaponins I (**1**), II (**2**), and III (**3**) were demonstrated to be the *β*-D-glucopyranosyl(1→2)-*β*-D-glucuronopyranosides of sophoradiol (**5**), soyasapogenol B (**6**), and azukisapogenol (**7**), respectively.

Experimental[13]

Isolation of Azukisaponins——Total azukisaponin (7.6 g)[1] was subjected to column chromatography (SiO_2 500 g, $CHCl_3$–MeOH–H_2O=65:35:10, lower phase as the eluant) to afford four fractions after removal of the solvent under reduced pressure: Fr. 1 (2.7 g), Fr. 2 (2.1 g), Fr. 3 (1.2 g), and Fr. 4 (1.0 g).

A solution of Fr. 1 (2.7 g) in methanol (50 ml) was treated with excess ethereal diazomethane and the reaction mixture was allowed to stand overnight. The product obtained after removal of the solvent under reduced pressure was purified by CLC [KT gel 2061 (Fuji gel) 120 g; $CHCl_3$–MeOH–H_2O=20:3:1, lower phase] to give azukisaponin I methyl ester (**1a**, 0.85 g) and azukisaponin II methyl ester (**2a**, 1.53 g). Treatment of **1a** or **2a** with 5% aq. K_2CO_3–MeOH (1:1, 10 ml) by heating under reflux for 1 h yielded azukisaponin I (**1**, 0.80 g) or azukisaponin II (**2**, 1.50 g), respectively.

Purification of Fr. 2 (2.1 g) by CLC (KT gel 2061 100 g; $CHCl_3$–MeOH–H_2O=10:3:1, lower phase) gave azukisaponin III (**3**, 0.50 g) and an additional amount (0.20 g) of azukisaponin II (**2**). Fr. 3 (1.2 g) was purified by column chromatography (SiO_2 100 g; *n*-BuOH–AcOEt–H_2O=4:1:5, upper phase) to afford azukisaponin IV (**4**, 0.19 g) and azukisaponin V (0.22 g). A solution of Fr. 4 (1.0 g) in MeOH (50 ml) was treated with Dowex 50 w×8 (H^+ form) with stirring at room temp. (25 °C) for 1 h. After removal of the resin by filtration, the solvent was evaporated off under reduced pressure and the residue was partitioned into *n*-BuOH–H_2O (1:1). The *n*-BuOH phase was separated and washed with water. Removal of the solvent under reduced pressure furnished azukisaponin VI (0.60 g).

Azukisaponin I (**1**), mp 215—217 °C (colorless fine crystals from EtOH), $[\alpha]_D^{28}$ +16.0°, (c=0.3, MeOH). *Anal.* Calcd for $C_{42}H_{68}O_{13}$: C, 64.59; H, 8.78. Found: C, 64.26; H, 8.43. IR ν_{max}^{KBr} cm^{-1}: 3400, 2940, 1720, 1075, 1040. Azukisaponin I methyl ester (**1a**), mp 231—232 °C (colorless needles from MeOH), $[\alpha]_D^{20}$ +15.5° (c=1.0, MeOH). *Anal.* Calcd. for $C_{43}H_{70}O_{13}\cdot 2H_2O$: C, 62.15; H, 8.98. Found: C, 61.94; H, 8.95. IR ν_{max}^{KBr} cm^{-1}: 3440, 1725, 1070, 1040. Azukisaponin II (**2**), mp 216—217 °C (colorless needles from MeOH), $[\alpha]_D^{25}$ +27.5° (c=0.2, MeOH). *Anal.*Calcd for $C_{42}H_{68}O_{14}\cdot 2H_2O$: C, 60.56; H, 8.71. Found: C,

60.94; H, 8.77. IR ν_{max}^{KBr} cm^{-1}: 3410, 1730, 1045. Azukisaponin II methyl ester (**2a**), mp 247—250°C (colorless needles from MeOH), $[\alpha]_D^{18}$ +19.5° (c=0.3, MeOH). *Anal.* Calcd for $C_{43}H_{70}O_{14}\cdot 2H_2O$: C, 60.97; H, 8.81. Found: C, 60.95; H, 8.81. IR ν_{max}^{KBr} cm^{-1}: 3465, 1735, 1045. Azukisaponin III (**3**), mp 218—221°C (colorless fine crystals from MeOH–H_2O), $[\alpha]_D^{28}$ +2.5° (c=1.1, MeOH). *Anal.* Calcd for $C_{42}H_{70}O_{15}\cdot H_2O$: C, 60.56: H, 8.71. Found: C, 60.22; H, 8.79. IR ν_{max}^{KBr} cm^{-1}: 3400, 1705, 1065, 1040. Azukisaponin IV (**4**), mp 235—237°C (colorless fine crystals from MeOH), $[\alpha]_D^{25}$ −1.8° (c=1.1, MeOH). *Anal.* Calcd for $C_{48}H_{76}O_{20}\cdot 2H_2O$: C, 55.17; H, 8.05. Found: C, 54.95; H, 7.76. IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1070.

Methanolysis of Azukisaponin I (1)———A solution of **1** (5 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 2 h. After neutralization with Ag_2CO_3 powder, the reaction mixture was filtered to remove inorganic material. Removal of the solvent from the filtrate gave the product, from which sophoradiol (**5**) was identified by thin-layer chromatography (TLC) comparisons (benzene–acetone=4:1, $CHCl_3$–MeOH=20:1) with an authentic sample. The product was then dissolved in pyridine (0.1 ml) and treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (0.2 ml) for 10 min. The reaction product was subjected to gas–liquid chromatography (GLC) analyses and the TMS derivatives of methyl glucoside and methyl glucuronide were identified: 1) 3% silicone SE-30 on Chromosorb WAW DMCS (80—100 mesh), 3 mm×1 m glass column; column temp., 130°C; carrier gas,N_2; flow rate, 35 ml/min; t_R,TMS-methyl glucoside 15′50″, 18′07″, TMS-methyl glucuronide 7′15″, 13′00″, 17′37″. 2) 5% silicone SE-52 on Chromosorb WAW DMCS (80—100 mesh), 3 mm×2 m glass column; column temp., 170°C; carrier gas,N_2; flow rate,35 ml/min; t_R, TMS-methyl glucoside 12′00″, 13′02″, TMS-methyl glucuronide 7′19″, 8′22″, 13′53″. The ratio of two methyl glycosides was 1:1 as judged from the peak areas.

Photolysis of 1———A solution of **1** (50 mg) in MeOH (50 ml) was irradiated externally through a Vycor filter with a 500 W high pressure mercury lamp (Eikosha PIH-500) for 1 h. After neutralization with 5% aq. K_2CO_3, the solvent was removed under reduced pressure. The product was then purified by preparative TLC ($CHCl_3$–MeOH=15:1) to furnish sophoradiol (**5**, 12 mg), which was shown to be identical with an authentic sample by mixed mp determination, and TLC ($CHCl_3$–MeOH=20:1, benzene–acetone=4:1, *n*-hexane–AcOEt=1:1) and IR (KBr) comparisons.

Methylation of 1———A solution of **1** (50 mg) in MeOH (50 ml) was treated with excess ethereal diazomethane and the whole reaction mixture was allowed to stand for 12 h. Removal of the solvent under reduced pressure gave the methyl ester (**1a**, 51 mg). A solution of **1a** (400 mg) in dimethyl sulfoxide (DMSO)(5 ml) was treated with dimsyl carbanion solution (5 ml)[7,9] and the whole mixture was stirred under an N_2 atmosphere for 1 h. The reaction mixture was then treated with methyl iodide (10 ml) and the whole mixture was stirred in the dark for 10 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed with 10% aq. $Na_2S_2O_3$ 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 20 g, benzene–acetone=10:1) to furnish the octa-*O*-methyl derivative (**1b**, 250 mg). **1b**, white powder,[14] $[\alpha]_D^{23}$ +9.2° (c=0.7, $CHCl_3$). *Anal.* Calcd for $C_{50}H_{84}O_{13}$: C, 67.24; H, 9.48. Found: C, 67.49; H, 9.83. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1750, 1090. ^{1}H-NMR ($CDCl_3$, δ): 0.83, 0.86, 0.90, 0.93, 0.97 (3H each), 1.02 (6H), 1.10 (3H) (all s, *tert*-CH_3×8), 3.26, 3.34 (3H each), 3.49 (6H), 3.55 (3H), 3.61 (6H), 3.78 (3H) (all s, OCH_3×7, $COOCH_3$×1), 4.39, 4.63 (1H each, both d, J=8 Hz, anomeric protons), 5.22 (1H, br s, 12-H).

$LiAlH_4$ Reduction followed by Methanolysis of 1b———A solution of **1b** (25 mg) in dry ether (1 ml) was treated with a suspension of $LiAlH_4$ (25 mg) in dry ether (1 ml),and the whole mixture was stirred at room temp. (25°C) for 1 h. After treatment with wet ether, the reaction mixture was made acidic with 5% aq. H_2SO_4. Work-up of the ether soluble portion in the usual manner yielded the reduction product as a white powder (20 mg), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), no $COOCH_3$. A solution of the reduction product (50 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 2 h. The reaction mixture was neutralized with Ag_2CO_3 powder and filtered. Evaporation of the solvent from the filtrate under reduced pressure yielded **5a** (23 mg) as colorless needles. **5a**, mp 195—197°C (colorless needles from $CHCl_3$–MeOH), $[\alpha]_D^{25}$ +76.9° (c=0.8, $CHCl_3$). *Anal.* Calcd for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found: C, 81.56; H, 11.43. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630, 1095. ^{1}H-NMR ($CDCl_3$, δ): 0.78, 0.85, 0.88, 0.94, 0.97 (3H each), 0.99 (6H), 1.11 (3H) (all s, *tert*-CH_3×8), 2.79 (1H, dd, J=3.5 Hz, 6 Hz, 22-H), 3.21 (3H, s, OCH_3),[15] 5.21 (1H, t-like, 12-H). MS m/z (%): 456 (M^+, 4), 248 (**i**, 100), 208 (**ii**, 7). High resolution MS: Found 456.397, 248.213, 208.181. Calcd for $C_{31}H_{52}O_2$ (M^+) 456.397, $C_{17}H_{28}O$ (**i**) 248.214, $C_{14}H_{24}O$ (**ii**) 208.183.

The mother liquor, after separation of **5a**, furnished methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**a**) and methyl 3,4-di-*O*-methylglucopyranoside (**b**) which were shown to be identical with authentic samples by TLC comparisons (benzene–acetone=3:1, benzene–MeOH=5:1) and GLC analyses. GLC: 3) 5% butane-1,4-diol succinate on Uniport B (80—100 mesh),3 mm×2 m glass column; column temp., 170°C; carrier gas,N_2; flow rate,35 ml/min; t_R,**a** 3′23″ (major), 4′33″, **b** 10′30″ (major), 12′18″. 4) 15% diethylene glycol succinate on Chromosorb WAW (80—100 mesh), 3 mm×1 m glass column; column temp., 200°C; carrier gas, N_2; flow rate,33 ml/min; t_R, **a** 1′27″ (major), 1′55″, **b** 10′12″ (major), 12′10″.

Methanolysis of Azukisaponin II (2)———A solution of **2** (5 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 2 h. Work-up of the reaction mixture as described in the case of **1** yielded methyl glucoside

and methyl glucuronide, which were identified by GLC analyses of their TMS derivatives, and soyasapogenol B (**6**), which was identified by TLC comparisons as described for **5**.

Photolysis of 2———A solution of **2** (50 mg) in MeOH (40 ml) was irradiated with a 500 W high pressure mercury lamp and worked up as described for the photolysis of **1**. Preparative TLC purification of the reaction product gave soyasapogenol B (**6**, 10 mg) which was shown to be identical with an authentic sample by mixed mp determination, and TLC ($CHCl_3$–MeOH=15:1, benzene–acetone=4:1, *n*-hexane–AcOEt=1:1) and IR (KBr) comparisons.

Methylation of 2———A solution of **2** (50 mg) in MeOH (50 ml) was treated with ethereal diazomethane as described in the case of **1** to yield the methyl ester (**2a**, 50 mg). A solution of **2a** (102 mg) in DMSO (5 ml) was treated with dimsyl carbanion (5 ml) and stirred for 1 h. The reaction mixture was then treated with methyl iodide (2 ml) and stirred in the dark under an N_2 atmosphere for 10 h. Work-up of the reaction mixture and chromatographic purification (SiO_2) of the product as described above furnished the nona-*O*-methyl derivative (**2b**, 83 mg). **2b**, white powder, $[\alpha]_D^{18}$ +13.2° (*c*=1.2, $CHCl_3$). *Anal.* Calcd for $C_{51}H_{86}O_{14}$: C, 66.35; H, 9.39. Found: C, 65.95; H, 9.39. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1760, 1095. ^{1}H-NMR ($CDCl_3$, δ): 0.86, 0.91, 0.98 (3H each), 1.01 (6H), 1.09, 1.18 (3H each) (all s, *tert*-CH_3×7), 3.28 (6H), 3.39 (3H), 3.50 (6H), 3.58 (3H), 3.62 (6H), 3.79 (3H) (all s, OCH_3×8, $COOCH_3$×1), 4.40, 4.67 (1H each, both d, *J*=8 Hz, anomeric protons), 5.23 (1H, br s, 12-H).

$LiAlH_4$ Reduction followed by Methanolysis of 2b———A solution of **2b** (50 mg) in dry ether (5 ml) was added dropwise to a suspension of $LiAlH_4$ (50 mg) in dry ether (5 ml). The whole mixture was stirred at room temp. (25°C) for 1 h and worked up as described in the case of **1b** to yield the product (white powder,45 mg), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610, no $COOCH_3$. The reduction product (20 mg) was dissolved in 9% HCl–dry MeOH (1 ml) and the whole mixture was heated under reflux for 1 h. Work-up of the reaction mixture as described above furnished 22,24-di-*O*-methylsoyasapogenol B (**6a**, 8 mg), which was shown to be identical with an authentic sample[9] by mixed mp determination, and TLC (benzene–acetone=15:1, benzene–MeOH=30:1, *n*-hexane–AcOEt=4:1) and IR (KBr) comparisons. The mother liquor furnished methylated sugars **a** and **b** which were identified by TLC and GLC comparisons as described above.

Methanolysis of Azukisaponin III (3)———A solution of **3** (5 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 2 h. The products, obtained by work-up as in the case of **1**, were identified as azukisapogenol methyl ester (**7a**) by TLC comparison ($CHCl_3$–MeOH=20:1), and as methyl glucoside and methyl glucuronide by GLC analyses of the TMS derivatives.

Enzymatic Hydrolysis of 3 with Crude Hesperidinase———A solution of **3** (50 mg) in water (10 ml) was treated with crude hesperidinase (100 mg) and the whole mixture was incubated with stirring at 37°C for 3 days. The reaction mixture was extracted with $CHCl_3$–MeOH (10:1) and the extract was worked up in the usual manner. Crystallization of the product from $CHCl_3$–MeOH furnished azukisapogenol (**7**, 21 mg) which was shown to be identical with an authentic sample[1] by mixed mp determination, and TLC ($CHCl_3$–MeOH=10:1, benzene–acetone=2:1, benzene–MeOH=10:1) and IR (KBr) comparisons.

Methylation of 3———A solution of **3** (140 mg) in DMSO (5 ml) was treated with dimsyl carbanion (5 ml). After being stirred under an N_2 atmosphere for 1 h, the whole mixture was treated with methyl iodide (2 ml) and stirred in the dark at room temp. (25°C) for 10 h. Work-up of the reaction mixture as described above and chromatographic purification of the product (SiO_2 20 g, benzene–acetone=10:1) furnished the nona-*O*-methyl derivative (**3b**, 110 mg). **3b**, white powder,$[\alpha]_D^{22}$ +6.6° (*c*=0.6, $CHCl_3$). *Anal.* Calcd for $C_{51}H_{84}O_{15}$: C, 65.36; H, 9.03. Found: C, 65.64; H, 9.41. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1750, 1730, 1110. ^{1}H-NMR ($CDCl_3$, δ): 0.84, 0.95, 1.00, 1.11, 1.16, 1.19 (3H each, all s, *tert*-CH_3×6), 3.25, 3.57 (3H each), 3.48 (6H), 3.56 (3H), 3.60 (6H), 3.64, 3.77 (3H each) (all s, OCH_3×7, $COOCH_3$×2), 4.39, 4.64 (1H each, both d, *J*=8 Hz, anomeric protons), 5.20 (1H, br s, 12-H).

$NaBH_4$ Reduction of 3b———A solution of **3b** (54 mg) in dry ether (2 ml) was added to a solution of $NaBH_4$ (100 mg) in dry MeOH (2 ml) and the whole mixture was stirred at room temp. (26°C) for 1 h. After treatment with acetone to decompose excess $NaBH_4$, the reaction mixture was treated successively with Dowex 50w×8 (H^+) (5 g) and Amberlite IRA-400 (OH^-) (5 g). Removal of the solvent from the filtrate under reduced pressure furnished **3c** (45 mg). **3c**, white powder, $[\alpha]_D^{22}$ +23.4° (*c*=1.2, $CHCl_3$). *Anal.* Calcd for $C_{50}H_{84}O_{14}$: C, 66.05; H, 9.31. Found: C, 65.79; H, 9.59. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 1730 1110. ^{1}H-NMR ($CDCl_3$, δ): 0.85, 0.96, 1.01, 1.11 (3H each), 1.20 (6H) (all s, *tert*-CH_3×6), 3.27, 3.40, 3.49, 3.53, 3.58 (3H each), 3.62 (6H), 3.64 (3H) (all s, OCH_3×7, $COOCH_3$×1), 4.35, 4.78 (1H each, both d, *J*=8 Hz, anomeric protons), 5.21 (1H, br s, 12-H).

Methanolysis of 3c———A solution of **3c** (15 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 1 h. Work-up of the reaction mixture as described in the case of **1b** provided **7b** (7 mg) as colorless needles. **7b**, mp 209—211°C (colorless needles from $CHCl_3$–MeOH),$[\alpha]_D^{18}$ +33.0° (*c*=1.8, $CHCl_3$). *Anal.* Calcd for $C_{32}H_{52}O_4$: C, 76.75; H, 10.47. Found: C, 76.71; H, 10.39. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500, 1730, 1105. ^{1}H-NMR ($CDCl_3$, δ): 0.85, 0.92, 0.94, 1.13, 1.19, 1.21 (3H each, all s, *tert*-CH_3×6), 3.30 (3H, s, OCH_3), 3.65 (3H, s, $COOCH_3$), 3.20, 3.88 (2H, ABq, *J*=10 Hz, 24-H_2), 5.21 (1H, t-like, 12-H). MS *m/z*(%): 500 (M^+, 3), 262 (100), 238 (13). From the mother liquor after separation of **7b**, **a** and **b** were isolated and shown to be identical with authetic samples by TLC comparisons and GLC analyses as described above.

Acetylation of 7b———A solution of **7b** (50 mg) in Ac_2O–pyridine (1:1, 1 ml) was allowed to stand at room temp. (26°C) for 10 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 **7c** (52 mg). **7c**, mp 229—231°C (colorless needles from $CHCl_3$–MeOH), $[\alpha]_D^{25}$ +58.3° (*c*=2.2, $CHCl_3$). *Anal.* Calcd for $C_{34}H_{54}O_5$: C, 75.23; H, 10.03. Found: C, 75.07; H, 9.95. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1725, 1240, 1110. ^{1}H-NMR ($CDCl_3$, δ): 0.84, 0.96 (3H each), 1.00 (6H), 1.14, 1.19 (3H each) (all s, *tert*-CH_3×6), 2.01 (3H, s, OAc), 3.28, 3.65 (3H each, both s, OCH_3, $COOCH_3$), 3.45 (2H, m, 24-H_2), 4.53 (1H, dd, *J*=4 Hz, 8 Hz, 3-H), 5.20 (1H, t-like, 12-H). MS *m/z*(%): 542 (M^+, 3), 262 (100), 280 (9).

Methanolysis of 4———A solution of **4** (100 mg) in 9% HCl–dry MeOH (10 ml) was heated under reflux for 2 h. Work-up of the reaction mixture as in the case of **1** furnished gypsogenic acid methyl ester (**8a**, 40 mg) and the mother liquor gave methyl glucoside, which was shown to be identical with an authentic sample by GLC analyses of the TMS derivative. **8a**, mp 251—252°C (colorless needles from $CHCl_3$–MeOH), $[\alpha]_D^{21}$ +50.1° (*c*=0.5, $CHCl_3$). High resolution MS: Found 500.351, 252.174, 248.178. Calcd. for $C_{31}H_{48}O_5$: (M^+) 500.350, $C_{15}H_{24}O_3$: (**iv**) 252.173, $C_{16}H_{24}O_2$: (**iii**) 248.178. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610, 1718, 1695, 1240. ^{1}H-NMR ($CDCl_3$, δ): 0.75 (3H), 0.96 (6H), 1.15 (3H), 1.26 (6H) (all s, *tert*-CH_3×6), 3.65 (3H, s, $COOCH_3$), 5.16 (1H, br s, 12-H). MS *m/z*(%): 500 (M^+, 3) 252 (**iv**, 8), 248 (**iii**, 100).

Acetylatoin of 8a———A solution of **8a** (10 mg) in Ac_2O–pyridine (1:1, 1 ml) was allowed to stand at 35°C for 5 h. Work-up of the reaction mixture in the usual manner yielded **8b** (10 mg). **8b**, mp 258—259°C (colorless needles from $CHCl_3$–MeOH), $[\alpha]_D^{21}$ +49.6° (*c*=0.9, $CHCl_3$). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400-2500 (br), 1735, 1695, 1245. ^{1}H-NMR ($CDCl_3$, δ): 0.74, 0.93, 0.97, 1.14, 1.20, 1.26 (3H each, all s, *tert*-CH_3×6) 1.94 (3H, s, OAc), 3.60 (3H, s, $COOCH_3$), 5.04 (1H, t-like, 3-H), 5.15 (1H, br s, 12-H) [lit.[10] mp 258—259°C ($CHCl_3$–MeOH), $[\alpha]_D$ +72° (*c*=0.89, $CHCl_3$)].

Alkaline Hydrolysis of 4———A solution of **4** (250 mg) in MeOH (5 ml) was treated with 5% aq. K_2CO_3 (5 ml) and the whole mixture was heated under reflux for 2 h. The reaction mixture was then neutralized with Dowex 50w×8(H^+) and filtered. Work-up of the filtrate in the usual manner yielded the prosapogenol (**9**, 160 mg). **9**, mp 223—225°C (colorless fine crystals from MeOH), $[\alpha]_D^{24}$ +14.4° (*c*=0.6, MeOH). *Anal.* Calcd for $C_{36}H_{56}O_{10}$: C, 66.64; H, 8.70. Found: C, 66.79; H, 8.81. IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1050.

Enzymatic Hydrolysis of Prosapogenol (9) with Almond Emulsin———A solution of **9** (100 mg) in water (10 ml) was treated with almond emulsin (Sigma 100 mg) and the whole mixture was incubated with stirring at 34°C for 36 h. The reaction mixture was extracted with $CHCl_3$–MeOH and the extract was worked up in the usual manner to furnish gypsogenic acid (**8**, 45 mg), which was shown to be identical with an authentic sample by mixed mp determination, and TLC (as described for **7**) and IR (KBr) comparisons.

Methylation of 9———A solution of **9** (160 mg) in DMSO (5 ml) was methylated with dimsyl carbanion (5 ml) and methyl iodide (10 ml) as described in the case of **1a**. Chromatographic purification of the product (SiO_2 20 g, benzene–acetone=20:1) furnished **9a** (120 mg). **9a**, white powder, $[\alpha]_D^{24}$ +29.9° (*c*=2.3, $CHCl_3$). *Anal.* Calcd for $C_{42}H_{68}O_{10}$: C, 68.82; H, 9.35. Found: C, 68.71; H, 9.57. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1725, 1095. ^{1}H-NMR ($CDCl_3$, δ): 0.71 (3H), 0.94 (9H), 1.13, 1.17 (3H each) (all s, *tert*-CH_3×6), 3.39, 3.42, 3.51, 3.59 (3H each, all s, OCH_3×4), 3.61, 3.70 (3H each, both s, $COOCH_3$), 4.16 (1H, d, *J*=8 Hz, anomeric proton), 5.28 (1H, br s, 12-H).

Methanolysis of 9a———A solution of **9a** (28 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 2 h. Work-up of the reaction mixture as described in the case of **1b** provided **8c** as colorless needles. The mother liquor furnished **a** as the methylated sugar,which was identified by TLC comparisons and GLC analyses as described above. **8c**, mp 251—252°C (colorless needles from MeOH), $[\alpha]_D^{24}$ +49.6° (*c*=0.6, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610, 1715, 1255. ^{1}H-NMR ($CDCl_3$, δ): 0.71 (3H), 0.93 (9H), 1.14 (6H) (all s, *tert*-CH_3×6), 3.61, 3.70 (3H each, both s, $COOCH_3$×2), 5.27 (1H, t-like, 12-H). MS *m/z* (%): 514 (M^+, 6), 262 (100), 252 (3). [lit.[11] mp 251—253°C (MeOH),$[\alpha]_D^{15}$ +77.4° ($CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 3448, 1715, 1165].

Methylation of 4 with Methyl Iodide and Silver Oxide———A solution of **4** (150 mg) in dimethylformamide (4 ml) was treated with silver oxide (1.5 g) and methyl iodide (6 ml) and the whole mixture was stirred in the dark at room temp. (29°C). The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was worked up in the usual manner and the product was purified by column chromatography (SiO_2 20 g, benzene–acetone=8:1) to furnish the dodeca-*O*-methyl derivative (**4b**, 138 mg). **4b**, white powder, $[\alpha]_D^{19}$ +32.9° (*c*=0.14, $CHCl_3$). *Anal.* Calcd for $C_{60}H_{100}O_{20}$: C, 63.14; H, 8.83. Found: C, 63.35; H, 8.81. IR $\nu_{max}^{CCl_4}$ cm^{-1}: no OH, 1730, 1095. ^{1}H-NMR ($CDCl_3$, δ): 0.72 (3H), 0.87 (9H), 1.07 (3H), 1.12 (3H) (all s, *tert*-CH_3×6), 3.37 (9H), 3.43 (3H), 3.48 (9H), 3.51 (3H), 3.57 (6H), 3.61 (3H), 3.68 (3H) (all s, OCH_3×11, $COOCH_3$×1), 5.28 (1H, br s, 12-H), 5.34 (1H, d, *J*=8 Hz, anomeric proton on the ester-glycoside linkage).

Methanolysis of 4b———A solution of 4b (20 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 3 h. Work-up of the reaction mixture as described in the case of **1b** and crystallization from MeOH furnished gypsogenic acid 23-monomethyl ester (**8a**, 6 mg), which was shown to be identical with an authentic sample by mixed mp determination, and TLC ($CHCl_3$–MeOH=20:1, benzene–acetone=3:1, benzene–MeOH=20:1) and IR ($CHCl_3$) comparisons. The mother liquor, after separation of **8a**, furnished **a** and **c** as methylated sugars,which were shown to be identical with authentic samples by TLC comparisons (benzene–acetone=2:1, benzene–MeOH=5:1) and GLC analyses. GLC: 5) 15% polyneopentyl glycol succinate on Chromosorb WAW (80—100 mesh), 3 mm×2 m glass column; column temp., 190°C; carrier gas,N_2; flow rate,35 ml/min; t_R,**a** 5′53″

(major), 7'43", **c** 12'10" (major), 16'04". 6) 15% diethylene glycol succinate on Chromosorb WAW (80—100 mesh), 3 mm×2 m glass column; column temp., 170°C; carrier gas, N_2; flow rate, 35 ml/min; t_R, **a** 5'42" (major), 8'07", **c** 15'6" (major), 22'35". The proportions of **a** and **c** were determined to be 2:1 from the peak areas.

Partial Methanolysis of 4b———A solution of **4b** (74 mg) in 4.5% HCl–dry MeOH (3 ml) was heated under reflux for 1 h. Work-up of the reaction mixture in the usual manner followed by preparative TLC (benzene–acetone=4:1) furnished **9b** (35 mg) and **10** (20 mg). **9b**, white powder, $[\alpha]_D^{25}$ +27.1° (c=1.3, $CHCl_3$). *Anal.* Calcd for $C_{41}H_{66}O_{10}$: C, 68.49; H, 9.25. Found: C, 68.18; H, 9.64. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550, 1735, 1725, 1095, 1090. ^{1}H-NMR ($CDCl_3$, δ): 0.73 (3H), 0.93 (9H), 1.13, 1.17 (3H each) (all s, *tert*-CH_3×6), 3.38, 3.46, 3.50, 3.59, 3.70 (3H each, all s, OCH_3×5), 4.16 (1H, d, J=8 Hz, anomeric H) 5.28 (1H, br s, 12-H). MS m/z(%): 718 (M^+, <1), 483 ($C_{31}H_{47}O_4$ from the aglycone part, 100), 248 (**iii**, 38). **10** was shown to be identical with authentic methyl hepta-*O*-methylgentiobioside by TLC comparisons (benzene–acetone=4:1, benzene–MeOH=8:1, $CHCl_3$–MeOH=15:1) and GLC analyses. GLC: 7) column temp. 195°C, and other conditions as described for 1); **10** 4'50" (β-anomer), 5'41" (α-anomer). 8) column temp. 200°C, and other conditions as described for 2); **10** 24'16" (β-anomer), 28'50" (α-anomer).

Diazomethane Methylation of 4———A solution of **4** (50 mg) in MeOH (10 ml) was treated with excess ethereal diazomethane as described above. Work-up of the reaction mixture in the usual manner furnished **4a** (50 mg). **4a**, mp 242—243°C (colorless needles from MeOH), $[\alpha]_D^{25}$ −1.5° (c=0.6, MeOH). *Anal.* Calcd for $C_{49}H_{78}O_{20}$: C, 59.62; H, 7.96. Found: C, 59.86; H, 8.09. IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1670, 1070.

Enzymatic Hydrolysis of 4a with Crude Hesperidinase———A solution of **4a** (25 mg) in water (10 ml) was treated with crude hesperidinase (50 mg) and the whole mixture was incubated with stirring at 37°C for 7 days. Work-up of the reaction mixture as described above and crystallization of the product from MeOH furnished **8a** (8 mg), which was shown to be identical with an authentic sample by mixed mp determination, and TLC (as described above) and IR ($CHCl_3$) comparisons.

Acetylation of 4———A solution of **4** (120 mg) in Ac_2O–pyridine (1:1, 4 ml) was allowed to stand at room temp. (25°C) for 10 h. Work-up of the reaction mixture in the usual manner furnished the undeca-acetate (**4c**, 70 mg). **4c**, white powder, $[\alpha]_D^{24}$ +5.4° (c=2.0, $CHCl_3$). *Anal.* Calcd for $C_{70}H_{98}O_{31}$: C, 58.57; H, 6.88. Found: C, 58.88; H, 6.97. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1750, 1225, 1035. ^{1}H-NMR ($CDCl_3$, δ): 0.76, 0.92, 0.96 (3H each), 1.11 (6H), 1.27 (3H) (all s, *tert*-CH_3×6), 1.99 (9H), 2.01 (6H), 2.02 (6H), 2.08 (12H) (all s, OAc×11), 5.58 (1H, d, J=8 Hz, anomeric H on the ester-glycoside linkage).

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References and Notes

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4) The structure elucidation of azukisaponin V and VI will be reported in Part XXXIII. I. Kitagawa, H. K. Wang, M. Saito, and M. Yoshikawa, *Chem. Pharm. Bull.*, **31**, 683 (1983).
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13) The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in the preceding paper.[1]
14) All attempts at crystallization were without success. These compounds are described as "white powder" hereafter.
15) The signal due to 3-H was overlapped by this methoxyl signal.