[Chem. Pharm. Bull. 31(2) 683—688 (1983)]

Saponin and Sapogenol. XXXIII.[1] Chemical Constituents of the Seeds of *Vigna angularis* (Willd.) Ohwi *et* Ohashi. (3). Azukisaponins V and VI

Isao Kitagawa,* Hui Kang Wang, Masayuki Saito, and Masayuki Yoshikawa

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

(Received August 30, 1982)

The chemical structures of azukisaponins V (**1**) and VI (**5**), two of the six oligoglycosidic ingredients of total azukisaponin isolated from azuki beans, the seeds of *Vigna angularis* (Willd.) Ohwi *et* Ohashi (Leguminosae), were investigated. By means of photochemical degradation and chemical analyses, the structures of azukisaponins V and VI were elucidated to be 3-*O*-[α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]-soyasapogenol B (**1**) and 3-*O*-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]-29-*O*-[β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl]azukisapogenol (**5**), respectively. Azukisaponin VI (**5**) is the first reported example of a 3,29-bisdesmoside of an oleanene oligoglycoside.

Keywords——azuki bean; *Vigna angularis;* azukisaponin; oleanene bisdesmoside; glucuronide-saponin; photochemical degradation; cleavage of glucuronide linkage; azukisapogenol

In one of the two foregoing papers,[2] we reported the structural elucidation of two aromatic glucosides and four genuine sapogenols [sophoradiol, soyasapogenol B (**2**), gypsogenic acid, and azukisapogenol (**6**)] of total azukisaponin, which was isolated from azuki beans, the seeds of *Vigna angularis* (Willd.) Ohwi *et* Ohashi (Leguminosae). In the preceding paper,[1] we described the isolation of six oleanene-oligoglycoside components (azukisaponins I, II, III, IV, V, and VI) from total azukisaponin and the structural elucidation of azukisaponins I, II (**4**), III (**7**), and IV. The present paper presents chemical evidence leading to the structure elucidation of azukisaponin V (**1**) and azukisaponin VI (**5**).[3]

Azukisaponin V (1)

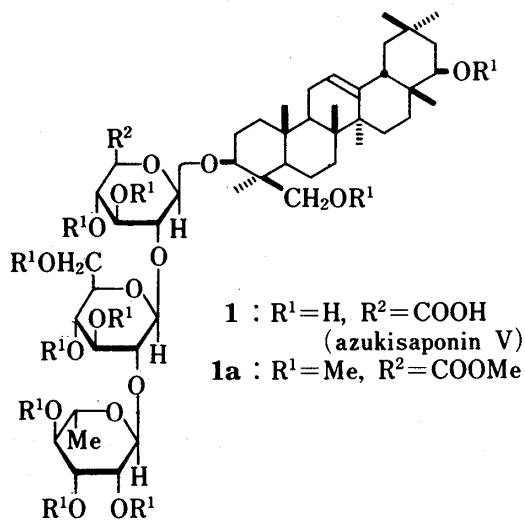
Methanolysis of azukisaponin V (**1**) with 9% hydrogen chloride in dry methanol provided soyasapogenol B (**2**)[2,4] as the sapogenol and D-glucose, D-glucuronic acid, and L-rhamnose in 1:1:1 ratio as the carbohydrate ingredients. On the other hand, acidic hydrolysis of **1** with a 1:2 mixture of 10% aqueous sulfuric acid and methanol yielded soyasapogenol B (**2**) and soyasapogenol C (**3**),[2] which was secondarily formed from **2**.

Since azukisaponin V (**1**) was found to contain a glucuronic acid residue in the molecule, **1** was subjected to photochemical degradation,[5] which is one of four selective cleavage methods for the glucuronide linkage in glucuronide-saponin.[6] Irradiation of **1** in methanol with a 500 W high pressure mercury lamp through a Vycor filter provided soyasapogenol B (**2**) as the sole sapogenol. Therefore, azukisaponin V (**1**) was shown to be a glucuronide-saponin which possessed D-glucose and L-rhamnose residues attached to the glucuronide moiety.

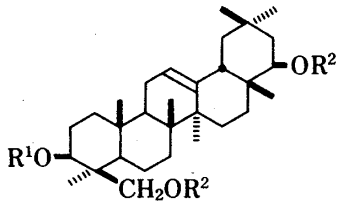
Complete methylation of azukisaponin V (**1**) with methyl iodide and dimsyl carbanion[7] furnished the undeca-*O*-methyl derivative (**1a**). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1a** showed three anomeric proton signals at δ 4.45 and 4.91 (1H each, both d, J=7 Hz) and δ 5.48 (1H, s), among which the two doublets suggested the β-glycosidic nature of the D-glucoside and D-glucuronide moieties in **1a**. Lithium aluminum hydride reduction

followed by methanolysis of **1a** afforded 22,24-di-*O*-methylsoyasapogenol B (**2a**)[2,4] as the sapogenol and methyl 3,4-di-*O*-methylglucopyranoside (**a**), methyl 3,4,6-tri-*O*-methylglucopyranoside (**b**), and methyl 2,3,4-tri-*O*-methylrhamnopyranoside (**c**) from the carbohydrate moiety.

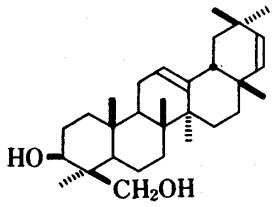
Based on the above-mentioned evidence, the chemical structure of azukisaponin V was concluded to be 3-*O*-[α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]soyasapogenol B (**1**). The rhamnoside linkage at the non-reducing terminal of azukisaponin V (**1**) was determined to be α by application of Klyne's rule[8] to the molecular rotation difference between **1** and azukisaponin II (**4**).[2]



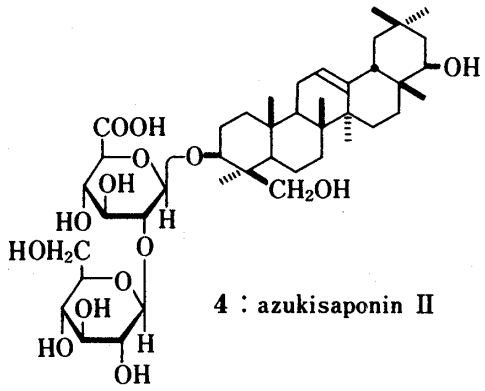
1 : R^1=H, R^2=COOH (azukisaponin V)
1a : R^1=Me, R^2=COOMe



2 : R^1=R^2=H (soyasapogenol B)
2a : R^1=H, R^2=Me



3 : soyasapogenol C



4 : azukisaponin II

Chart 1

Azukisaponin VI (5)

The infrared (IR) spectrum of azukisaponin VI (**5**) showed strong hydroxyl absorption bands characteristic of the glycosidic structure. It also showed absorption bands ascribable to carboxyl and ester functions. The carbon nuclear magnetic resonance (^{13}C-NMR) spectrum of **5** showed signals attributable to four anomeric carbons and two carbonyl carbons, one in a carboxyl moiety and the other in an ester moiety.

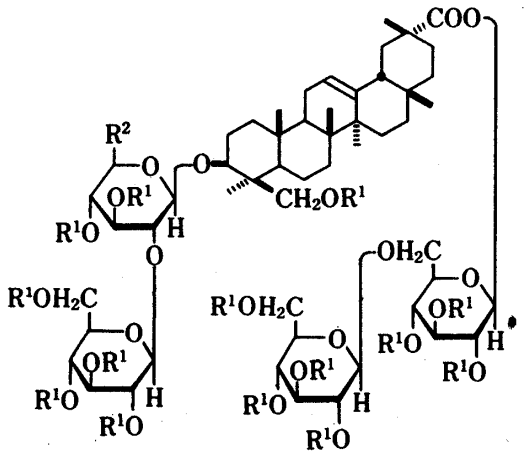
Methanolysis of azukisaponin VI (**5**) provided azukisapogenol methyl ester (**6a**)[2] from the sapogenol portion and methyl glucoside and methyl glucuronide in a 3:1 ratio from the carbohydrate portion. Methanolic sulfuric acid hydrolysis of **5** also yielded **6a**, while enzymatic hydrolysis of **5** with crude hesperidinase liberated the genuine sapogenol azukisapogenol (**6**).

Since azukisaponin VI (**5**) contained an ester function, **5** was subjected to alkaline hydrolysis with methanolic potassium carbonate to give azukisaponin III (**7**)[2] and gentiobiose (**9**). On the other hand, methylation of azukisaponin VI (**5**) with methyl iodide and dimsyl carbanion furnished methylated products derived through cleavage of the ester-glycosidic linkage in **5**: the nona-*O*-methyl derivative (**7a**) of **7**, methyl hepta-*O*-methyl-α-gentiobioside

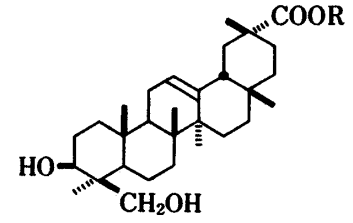
(**9a**), and methyl hepta-*O*-methyl-β-gentiobioside (**9b**). Thus, azukisaponin VI (**5**) was suggested to be a gentiobioside of azukisaponin III (**7**), in which the biose is connected through an ester-glycosidic linkage.

Acetylation of azukisaponin VI (**5**) furnished the tetradeca-*O*-acetyl derivative (**5a**). The ^{1}H-NMR spectrum of **5a** exhibited a one-proton doublet at δ 5.65 (J=7 Hz) which was assignable to the anomeric proton on the ester-glycoside linkage. Thus, the gentiobiose moiety in **5** was demonstrated to be connected to the carboxyl group through a β-glycoside linkage. Furthermore, a carbon signal observed at δ 95.0, which was one of four anomeric carbon signals, is rationally attributable to the anomeric carbon of the β-ester-glycoside linkage.[9]

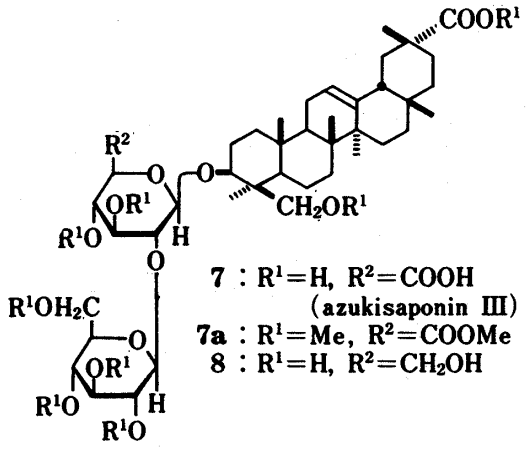
Diazomethane methylation and subsequent sodium borohydride reduction of azukisaponin VI (**5**) provided a tetraglucoside (**5b**). The IR spectrum of **5b** lacked the carboxyl absorption band but exhibited the ester absorption band. The ^{13}C-NMR spectrum of **5b** showed signals due to four anomeric carbons and one ester carbonyl carbon. Since the methoxycarbonyl moiety in the glucuronide residue was selectively affected by sodium borohydride reduction, while the ester glycoside linkage was unaffected,[2,4] **5b** was considered to be formed *via* conversion of the glucuronide moiety in azukisaponin VI (**5**) into the glucoside moiety.



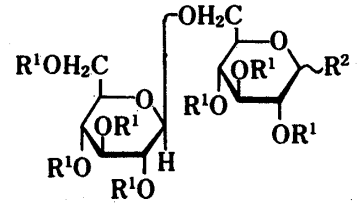
5 : R^1=H, R^2=COOH (azukisaponin VI)
5a : R^1=Ac, R^2=COOH
5b : R^1=H, R^2=CH_2OH



6 : R=H (azukisapogenol)
6a : R=Me



7 : R^1=H, R^2=COOH (azukisaponin III)
7a : R^1=Me, R^2=COOMe
8 : R^1=H, R^2=CH_2OH



9 : R^1=H, R^2=OH
9a : R^1=Me, R^2=α-OMe
9b : R^1=Me, R^2=β-OMe

Chart 2

Alkaline hydrolysis of **5b** liberated the prosapogenol **8** and gentiobiose (**9**). Methanolysis of **8** provided azukisapogenol methyl ester (**6a**) and methyl glucoside as the sole carbohydrate. Thus, the structure of the prosapogenol **8** and the tetraglucoside **5b** became evident. The gentiobiose moiety in azukisaponin VI (**5**) was demonstrated to be attached through a β-glycoside linkage to the 20α-carboxyl function of azukisapogenol (**6**) and not to the carboxyl function of the glucuronide moiety.

On the basis of the accumulated evidence mentioned above, the structure of azukisaponin VI was concluded to be 3-*O*-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]-29-*O*-[β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl]azukisapogenol (**5**). Azukisaponin VI seems to be the first example of an oleanene-bisdesmoside which possesses a carbohydrate chain connected to the C-29 oxygen function.

Experimental[10]

Azukisaponin V (1)———Obtained by chromatographic separation of total azukisaponin as described in the preceding paper.[1] Azukisaponin V (**1**), mp 228—229°C (colorless fine crystals from MeOH), $[\alpha]_D^{28}$ +0.4° (c=1.1, MeOH). *Anal.* Calcd for $C_{48}H_{78}O_{18}\cdot 2H_2O$: C, 58.88; H, 8.44. Found: C, 58.60; H, 8.29. IR ν_{max}^{KBr} cm^{-1}: 3386, 1726.

Methanolysis of 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. From the filtrate, soyasapogenol B (**2**) was identified by thin-layer chromatography (TLC) comparisons ($CHCl_3$–MeOH=15:1, benzene–acetone=4:1, *n*-hexane–AcOEt=1:1). After removal of the solvent from the filtrate under reduced pressure, the residue was dissolved in pyridine (0.1 ml) and the solution was treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (0.2 ml) for 10 min. Gas–liquid chromatography (GLC) analyses [1), 2)] of the products resulted in the identification of the TMS derivatives of methyl glucoside, methyl glucuronide, and methyl rhamnoside. GLC: 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: methyl glucoside 15′50″, 18′07″, methyl glucuronide 7′15″, 13′00″, 17′37″, methyl rhamnoside 3′21″. 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: methyl glucoside 12′00″, 13′02″, methyl glucuronide 7′19″, 8′22″, 13′53″, methyl rhamnoside 3′22″.

Acidic Hydrolysis of 1———A solution of **1** (100 mg) in MeOH (10 ml) was treated with 10% aq. H_2SO_4 (5 ml), and the whole mixture was heated under reflux for 12 h. The reaction mixture was extracted with AcOEt and the AcOEt extract was washed with sat. aq. $NaHCO_3$ and water, then dried over $MgSO_4$ powder. The product obtained by evaporation of the solvent under reduced pressure was purified by preparative TLC ($CHCl_3$–MeOH=15:1) to furnish soyasapogenol B (**2**, 23 mg) and soyasapogenol C (**3**, 5 mg), which were shown to be identical with authentic samples by mixed mp determination, and TLC (as described above) and IR (KBr) comparisons.

Photolysis of 1———A solution of **1** (20 mg) in MeOH (50 ml) in a Vycor tube was irradiated with a 500 W high pressure mercury lamp (Eikosha PIH-500) for 3 h. The reaction mixture was neutralized with 5% aq. K_2CO_3, then the solvent was removed under reduced pressure and the product was purified by preparative TLC ($CHCl_3$–MeOH=15:1) to give soyasapogenol B (**2**, 3 mg), which was shown to be identical with an authentic sample by TLC and IR (KBr) comparisons as described above.

Complete Methylation of 1———A solution of **1** (200 mg) in dimethyl sulfoxide (DMSO)(10 ml) was treated with dimsyl carbanion solution (10 ml)[4,7] with stirring under an N_2 atmosphere at room temperature (28°C) for 2 h. Methyl iodide (8 ml) was then added to the reaction mixture and the whole mixture was stirred in the dark for 2 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed with aq. $Na_2S_2O_3$ and water and dried. Removal of the solvent under reduced pressure gave the product,which was purified by column chromatography (SiO_2 25 g, benzene–acetone=12:1) to afford the undeca-*O*-methyl derivative (**1a**, 132 mg). **1a**, white powder,[11] $[\alpha]_D^{28}$ +2.8° (c=0.9, $CHCl_3$). *Anal.* Calcd for $C_{59}H_{100}O_{18}$: C, 64.57; H, 9.19. Found: C, 64.13; H, 9.20. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: no OH, 1738. ^{1}H-NMR (d_6-benzene, δ): 0.93 (3H), 1.07 (9H), 1.13, 1.22, 1.40 (3H each) (all s, *tert*-CH_3×7), 1.44 (3H, d, J=6 Hz, *sec*-CH_3), 3.16 (3H), 3.30 (6H), 3.41 (9H), 3.50 (6H), 3.56, 3.67, 3.76 (3H each) (all s, OCH_3×11), and anomeric proton signals as given in the text.

$LiAlH_4$ Reduction followed by Methanolysis of 1a———A solution of **1a** (87 mg) in dry ether (4 ml) was added to a suspension of $LiAlH_4$ (80 mg) in dry ether (4 ml) and the whole mixture was kept stirring at room temp. (28°C) for 1 h. The reaction mixture was treated with wet ether, washed with water and dried. Removal of the solvent gave the reduction product (77 mg), IR $\nu_{max}^{CCl_4}$cm^{-1}: 3600, no $COOCH_3$. The reduction product (77 mg) was dissolved in 9% HCl–dry MeOH (2 ml) and the solution was heated under reflux

for 2 h. After neutralization with Ag_2CO_3 powder, the whole mixture was filtered to remove inorganic material and the filtrate was concentrated then left to stand. The resultant colorless needles (30 mg) were collected by filtration and shown to be identical with 22,24-di-*O*-methylsoyasapogenol B (**2a**) by mixed mp determination, and TLC ($CHCl_3$, benzene–acetone=15:1, benzene–AcOEt=4:1) and IR (CCl_4) comparisons. From the mother liquor after separation of **2a**, methyl 3,4-di-*O*-methylglucopyranoside (**a**), methyl 3,4,6-tri-*O*-methylglucopyranoside (**b**), and methyl 2,3,4-tri-*O*-methylrhamnopyranoside (**c**) were identified by GLC [3), 4)] analyses and TLC comparisons (benzene–acetone=2:1, benzene–MeOH=5:1). 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** 38′28″, 45′08″, **b** 14′23″, 17′16″, **c** 2′27″. 4) 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,37 ml/min. t_R: **a** 27′45″, 31′55″, **b** 12′20″, 14′08″, **c** 2′44″.

Application of Klyne's Rule———$[M]_D$ of azukisaponin V (**1**)—$[M]_D$ of azukisaponin II (**4**)=−155.8°. $[M]_D$ of methyl α-L-rhamnopyranoside=−109°, $[M]_D$ of methyl β-L-rhamnopyranoside=+169°.[4a)]

Azukisaponin VI (5)———Obtained by chromatographic separation of total azukisaponin as described in the preceding paper.[1)] Azukisaponin VI (**5**), mp 223—226°C (colorless fine crystals from MeOH), $[\alpha]_D^{20}$ −5.9° (c=1.1, MeOH). *Anal.* Calcd for $C_{54}H_{86}O_{25}$: C, 57.13; H, 7.64. Found: C, 57.49; H, 7.84. IR ν_{max}^{KBr} cm^{-1}: 3400, 1725 (br), 1055. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1733, 1718. ^{13}C-NMR (d_5-pyridine, δc, off-resonance pattern): 95.0 (d), 103.7 (d), 104.0 (d, 2C), 170.8 (s), 176.3 (s).

Methanolysis of 5———A solution of **5** (2 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 1 h. After work-up of the reaction mixture as described for the methanolysis of **1**, the product was shown by TLC comparisons (as described for **2**) to be identical with azukisapogenol methyl ester (**6a**),and GLC analyses (as TMS derivatives) demonstrated the presence of methyl glucoside and methyl glucuronide.

Acidic Hydrolysis of 5———A solution of **5** (100 mg) in MeOH (25 ml) was treated with 10% aq. H_2SO_4 (2.5 ml) and the whole solution was heated under reflux for 14 h. Work-up of the reaction mixture as described in the case of **1** gave the product. Purification of the product by preparative TLC ($CHCl_3$–MeOH=10:1) furnished **6a** (16 mg), which was shown to be identical with an authentic sample by mixed mp determination, and TLC (as described for **2**) and IR (KBr) comparisons.

Enzymatic Hydrolysis of 5 with Crude Hesperidinase———A solution of **5** (100 mg) in water (20 ml) was treated with crude hesperidinase (200 mg) and the whole mixture was incubated with stirring at 35°C for 3 days. The reaction mixture was extracted with $CHCl_3$–MeOH (20:1) and the extract was washed with water and dried. The product, obtained by removal of the solvent under reduced pressure, was crystallized from $CHCl_3$–MeOH to furnish azukisapogenol (**6**, 34 mg),which was shown to be identical with an authentic sample by mixed mp determination, and TLC ($CHCl_3$–MeOH=10:1, benzene–acetone=2:1, benzene–MeOH=10:1) and IR (KBr) comparisons.

Alkaline Hydrolysis of 5———A solution of **5** (200 mg) in MeOH (10 ml) was treated with 5% aq. K_2CO_3 (6 ml) and the whole mixture was heated under reflux for 5 h. After neutralization with Dowex 50w ×8 (H^+), the filtrate was concentrated under reduced pressure. Colorless fine crystals of **7** (120 mg) separated out and were collected by filtration. The product was shown to be identical with authentic azukisaponin III (**7**)[2)] by mixed mp determination, and TLC ($CHCl_3$–MeOH–H_2O=6:4:1, *n*-BuOH–AcOH–H_2O =4:1:5, upper phase) and IR (KBr) comparisons. From the mother liquor after separation of **7**, gentiobiose (**9**) was identified by TLC comparisons ($CHCl_3$–MeOH=1:1, *n*-propanol–H_2O= 4:1).

Methylation of 5———A solution of **5** (280 mg) in DMSO (10 ml) was treated with dimsyl carbanion (10 ml), and the whole solution was stirred under an N_2 atmosphere at room temp. (18°C) for 1 h. After addition of methyl iodide (5 ml), the reaction mixture was stirred in the dark for a further 1 h. The product, obtained by working up the reaction mixture as described above, was subjected to column chromatography to furnish **7a** (173 mg), **9a** (10 mg), and **9b** (26 mg). **7a** was shown to be identical with an authentic sample[2)] by TLC (benzene–acetone= 10:1, *n*-hexane–AcOEt= 1:1), IR (CCl_4), and ^{1}H-NMR ($CDCl_3$) comparisons. **9a** and **9b** were also shown to be identical with the respective authentic samples by TLC (benzene–acetone= 4:1, benzene–MeOH=8:1, $CHCl_3$–MeOH=15:1) and IR (CCl_4) comparisons and GLC analyses [5), 6)]. GLC: 5) column temp. 195°C and other conditions were the same as described in 1). t_R: **9a** 5′41″, **9b** 4′50″, 6) column temp. 200°C and other conditions were the same as described in 2). t_R: **9a** 28′50″, **9b** 24′16″.

Acetylation of 5———A solution of **5** (190 mg) in Ac_2O–pyridine (1:1, 2 ml) was allowed to stand at 34°C for 7 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. The AcOEt extract was washed successively with 1% aq. HCl, sat. aq. $NaHCO_3$, and water, and dried over $MgSO_4$. Removal of the solvent under reduced pressure furnished **5a** (116 mg). **5a**, white powder, $[\alpha]_D^{27}$ +4.5° (c=0.8, $CHCl_3$). *Anal.* Calcd for $C_{82}H_{114}O_{39}$: C, 57.13; H, 6.67. Found: C, 56.87; H, 6.72. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1225. ^{1}H-NMR ($CDCl_3$, δ): 0.85 (3H), 0.96 (9H), 1.04, 1.12, 1.20 (3H each)(all s, *tert*-CH_3×7), 1.98, 2.00, 2.06, 2.08 (all s, totally 42H, OAc×14), 5.65 (1H, d, J=7 Hz, anomeric H on the ester-glycoside linkage).

Diazomethane Methylation followed by $NaBH_4$ Reduction of 5———A solution of **5** (500 mg) in MeOH (100 ml) was treated with excess ethereal diazomethane and the yellow solution was left standing for 12 h. The product, obtained by removal of the solvent, was dissolved in MeOH (40 ml) and the solution was treated with

$NaBH_4$ (100 mg). The mixture was stirred at room temp. (20°C) for 1 h, then neutralized with Dowex 50w×8 (H^+). The solvent was evaporated off under reduced pressure. Purification of the product by column chromatography (SiO_2 25 g, $CHCl_3$–MeOH–H_2O=65:35:10, lower phase) furnished **5b** (250 mg). **5b**, white powder, $[\alpha]_D^{25}$ −6.1° (c=0.9, MeOH). *Anal.* Calcd for $C_{54}H_{88}O_{24}$: C, 57.84; H, 7.91. Found: C, 57.65; H, 7.78. IR ν_{max}^{KBr} cm^{-1}: 3400, 1735, 1070. ^{13}C-NMR (d_5-pyridine, δc, off-resonance pattern): 95.8 (d), 104.4 (d), 104.9 (d), 105.0 (d), 177.7 (s).

Alkaline Hydrolysis of 5b——A solution of **5b** (250 mg) in MeOH (10 ml) was treated with 2% NaOH-MeOH (2 ml) and the whole solution was heated under reflux for 2 h, then neutralized with Dowex 50w×8 (H^+), and filtrated. The filtrate was concentrated under reduced pressure to yield a white precipitate (**8**, 70 mg),which was collected by filtration. **8**, white powder, $[\alpha]_D^{25}$ +3.1° (c=0.8, MeOH). *Anal.* Calcd for $C_{42}H_{72}O_{14}$: C, 62.98; H, 9.06. Found: C, 62.63; H, 9.17. IR ν_{max}^{KBr} cm^{-1}: 3400, 1735, 1070, 1020. From the mother liquor after separation of **8**, gentiobiose(**9**) was identified by TLC comparisons (as described above).

Methanolysis of 8——A solution of **8** (2 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 **1** furnished **6a** and methyl glucoside, which was identified by TLC comparisons and GLC analyses of the TMS derivative as described above.

Acknowledgement The authors are grateful to the Suzuken, Kenzo Memorial Foundation for a grant. One of the authors (M.Y.) is grateful to the Ministry of Education, Science, and Culture of Japan for a Grant-in-Aid for Scientific Research (No. 56570720) and one of the authors (H.K.W.) would also like to express his thanks to the same Ministry for providing the scholarship for his research work at Osaka University.

References and Notes

1) Part XXXII: I. Kitagawa, H. K. Wang, M. Saito, and M. Yoshikawa, *Chem. Pharm. Bull.*, **31**, 674 (1983).
2) Part XXXI: I. Kitagawa, H. K. Wang, M. Saito, and M. Yoshikawa, *Chem. Pharm. Bull.*, **31**, 664 (1983).
3) I. Kitagawa, H. K. Wang, M. Saito, and M. Yoshikawa, presented at the 27th Annual Meeting of the Japanese Society of Pharmacognosy Abstract. p. 21 (Sept. 1980, Nagoya).
4) *a*) I. Kitagawa, M. Yoshikawa, and I. Yosioka, *Chem. Pharm. Bull.*, **24**, 121 (1976); *b*) I. Kitagawa, M. Yoshikawa, H. K. Wang, M. Saito, V. Tosirisuk, T. Fujiwara, and K. Tomita, *Chem. Pharm. Bull.*, **30**, 2294 (1982).
5) I. Kitagawa, M. Yoshikawa, Y. Imakura, and I. Yosioka, *Chem. Pharm. Bull.*, **22**, 1339 (1974).
6) I. Kitagawa and M. Yoshikawa, *Heterocycles*, **8**, 783 (1977).
7) S. Hakomori, *J. Biochem.*(Tokyo), **55**, 205 (1964).
8) W. Klyne, *Biochem. J.*, **47**, xli (1950).
9) K. Yamasaki, H. Kohda, T. Kobayashi, N. Kaneda, O. Tanaka, and K. Nishi, *Chem. Pharm. Bull.*, **25**, 2895 (1977).
10) The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in our previous paper.[2]
11) All attempts at crystallization were without success. These compounds are described as "white powder" hereafter.