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Saponin and Sapogenol. XXXVIII.[1] Structure of Soyasaponin A_2, a Bisdesmoside of Soyasapogenol A, from Soybean, the Seeds of *Glycine max* MERRILL

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Two new bisdesmosides of soyasapogenol A (**1**), named soyasaponin A_1 and soyasaponin A_2 (**7**), were isolated from soybean, the seeds of *Glycine max* MERRILL, together with the known soyasaponins I (**4**), II (**5**), and III (**6**). By employing a photochemical degradation method, which is a selective cleavage method for the glucuronide linkage in oligoglycosides, and on the bases of spectral analyses and chemical reactions, the structure of soyasaponin A_2 was elucidated as 3-*O*-[β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl]-22-*O*-[β-D-glucopyranosyl(1→3)-α-L-arabinopyranosyl]soyasapogenol A (**7**).

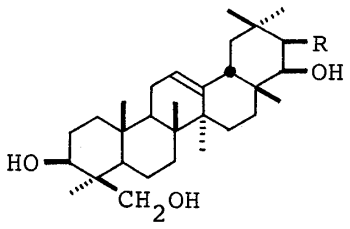
Keywords——soybean; *Glycine max*; soyasaponin A_1; soyasaponin A_2; glucuronide linkage selective cleavage; glucuronide linkage photolysis; oleanene-bisdesmoside; oleanene-bisdesmoside ^{13}C-NMR

During the course of chemical studies of bioactive constituents in Leguminous naturally occurring drug materials,[2] we recently elucidated the glycosidic constituents from the seeds of *Vigna angularis* (WILLD.) OHWI *et* OHASHI (azuki bean)[3] and from Astragali Radix, the root of *Astragalus membranaceus* BUNGE.[1,4] In regard to the oligoglycosidic constituents of soybean, the seeds of *Glycine max* MERRILL, we initially isolated three saponins, named soyasaponins I, II, and III, which have soyasapogenol B as a common sapogenol, and elucidated the structures and locations of their oligosaccharide moieties.[5a] Later, since the structures proposed by previous workers for soybean sapogenols became questionable, we carried out a re-investigation. Finally, we concluded that the structures of soyasapogenols A, B, and E should be revised to **1**, **2**, and **3**, and consequently, the structures of soyasaponins I, II, and III are **4**, **5**, and **6**, respectively.[5b]

In parallel studies on the chemical behavior of glucuronidesaponins,[6] we developed four selective cleavage methods for the glucuronide linkage:[7] photochemical cleavage,[7,8] lead tetraacetate degradation,[7,9] acetic anhydride-pyridine degradation,[7,10] and anodic oxidation.[7,11]

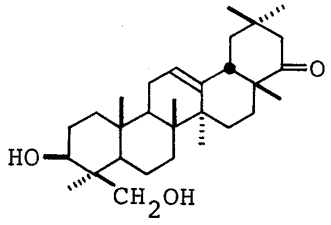
Recently, we investigated the oligoglycosidic constituents of soybean in more detail, and isolated two new bisdesmosides of soyasapogenol A (**1**), named soyasaponin A_1 and soyasaponin A_2 (**7**). By employing the above-mentioned photochemical cleavage method for the glucuronide linkage, the structure of soyasaponin A_2 (**7**) has been elucidated as described in this paper.[12]

Soybean contains various constituents such as sterol glycosides and isoflavone glycosides together with large amounts of lipid and carbohydrate,[2] and this has made the isolation of saponins rather troublesome. In our previous isolation of soyasaponins I (**4**), II (**5**), and III (**6**),[5] the saponin-containing fraction was washed with 1-butanol and 5% aqueous sodium hydroxide to obtain a mixture of three soyasaponins. Afterwards, it was found that the

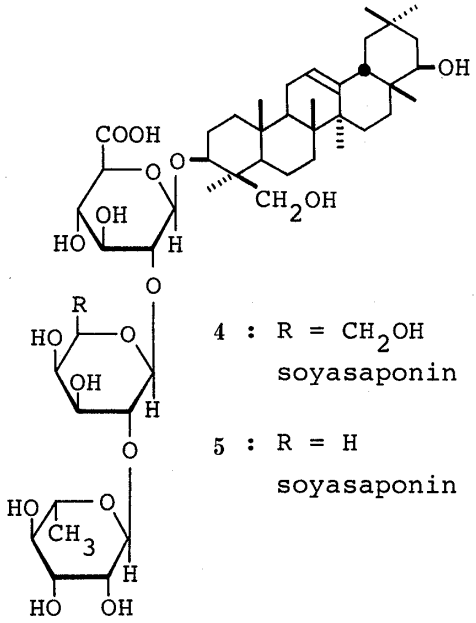


1 : R = OH soyasapogenol A

2 : R = H soyasapogenol B

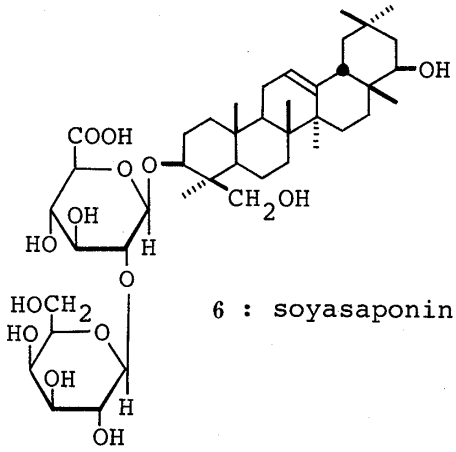


3 : soyasapogenol E



4 : R = CH_2OH soyasaponin I

5 : R = H soyasaponin II



6 : soyasaponin III

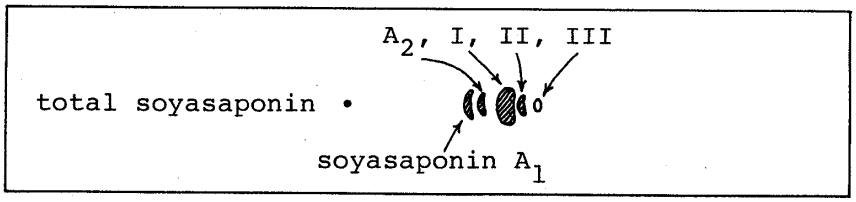
Chart 1

alkaline washings contained new saponins now named soyasaponins A_1 and A_2. However, since those isolation procedures were rather complicated, we devised a refined isolation method for total soyasaponin, which comprised five soyasaponins as a whole. Through subsequent purification of total soyasaponin by employing centrifugal liquid chromatography (CLC) followed by acidic ion-resin treatment, soyasaponin A_1 and soyasaponin A_2 (**7**) were isolated together with soyasaponins I (**4**), II (**5**), and III (**6**), as shown in Chart 2.[13]

The infrared (IR) spectrum of soyasaponin A_2 (**7**) showed carboxyl absorption bands. Acidic hydrolysis of **7** liberated soyasapogenol A (**1**), while acidic methanolysis of **7** yielded, together with **1**, methyl L-arabinoside, methyl D-galactoside, methyl D-glucoside, methyl D-glucuronide in 1 : 1 : 1 : 1 ratio. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **7** showed signals due to four anomeric carbons at δc 104.7, 105.3, 106.0, and 108.3, which suggested the presence of one α-L-arabinoside linkage and three β-linkages of D-galactose, D-glucose, and D-glucuronic acid in **7**.[14]

Since soyasaponin A_2 (**7**) was revealed to contain a glucuronide moiety, **7** was subjected to photochemical cleavage.[8] As reported in our previous papers,[3,8a] the photochemical cleavage method has been employed to liberate the genuine sapogenols from various glucuronide-saponins. Recently, we showed that this photochemical method is also useful for elucidation of the carbohydrate sequence in glucuronide-saponins.[8b] Irradiation of a methanolic solution of soyasaponin A_2 (**7**) with a 500 W high-pressure mercury lamp furnished a prosapogenol (**8**) and D-galactose (identified as the pentaacetate), thus suggesting

soybean (powder, 4.0 kg)
↓ MeOH, Δ
MeOH ext. (0.5 kg)
↓ *n*-hexane
insolu. (160 g) — solu. (340 g)
↓ *n*-BuOH - H_2O (1:1)
H_2O phase (100 g) — isoflavone (2.5 g) — *n*-BuOH phase (50 g)
AcOEt / MeOH
insolu. (35 g) — AcOEt phase (15 g)
↓ silica gel column chromatog.
total soyasaponin (12 g)
2 g
↓ i) centrifugal liquid chromatog.
ii) Dowex 50w X 8 (H^+ form)
soyasaponin III (6, 0.09 g)
soyasaponin II (5, 0.19 g)
soyasaponin I (4, 1.05 g)
soyasaponin A_2 (7, 0.20 g)
soyasaponin A_1 (0.16 g)



TLC diagram for total soyasaponin
adsorbent : Pre-coated silica gel 60 F_{254} (0.25 mm)
solvent : $CHCl_3$-MeOH-H_2O= 6 : 4 : 1

Chart 2

7 to be a galactosyl-glucuronide of **8**.

The IR spectrum of **8** showed hydroxyl absorption bands but lacked carbonyl absorption bands. Acidic hydrolysis of **8** gave soyasapogenol A (**1**), and methanolysis yielded methyl arabinoside and methyl glucoside in 1 : 1 ratio. Here again, the ^{13}C-NMR spectrum of **8** showed the presence of an α-L-arabinoside linkage and a β-D-glucoside linkage in **8** (anomeric carbon signals at δc 106.0 and 108.3).

Methylation of **8** with dimsyl carbanion and methyl iodide[15] afforded a nona-*O*-methyl derivative (**8a**), which lacked hydroxyl absorption bands in its IR spectrum but showed nine methoxyl signals in its proton nuclear magnetic resonance (^{1}H-NMR) spectrum. Methanolysis of **8a** yielded methyl 2,4-di-*O*-methylarabinopyranoside (**a**), methyl 2,3,4,6-

tetra-*O*-methylglucopyranoside (**b**), and a methylated sapogenol. The structure of this sapogenol was concluded to be 3,21,24-tri-*O*-methylsoyasapogenol A (**9**) from the following evidence.

The IR spectrum of **9** showed hydroxyl absorption bands, whereas the ^{1}H-NMR spectrum showed signals due to three methoxyl groups and 3α-H, 21α-H, and 22α-H. In the mass spectrum (MS) of **9**, retro-Diels-Alder type fragment ion peaks[16] due to **i** (base peak, from the D, E rings) and **ii** (from the A, B rings) were observed, suggesting the location of a free hydroxyl group to be at C-21 or C-22 in the E ring. Prolonged acetylation of **9** under ordinary conditions (acetic anhydride and pyridine at 34 °C) afforded a monoacetate (**9a**) in low yield. However, the monoacetate (**9a**) was obtained in high yield by acetylation in the presence of 4-dimethylaminopyridine (DMAP) as a catalyst.[17] This behavior suggested the free hydroxyl group in **9** to be 22β-axial rather than 21β-equatorial.

The IR spectrum of **9a** lacked hydroxyl absorption bands but showed acetoxyl bands.

TABLE I. ^{13}C-NMR Data for Soyasapogenol A (1), Prosapogenol (8), and Soyasaponin A_2 (7) (25 MHz, in d_5-pyridine, δc)[a]

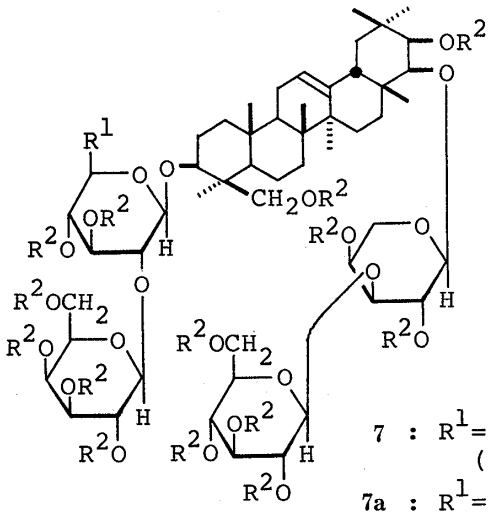
		1	8	7
Sapogenol moiety	C-3	80.1 (d)	80.1 (d)	90.6 (d)
	C-12	122.5 (d)	122.4 (d)	122.6 (d)
	C-13	144.5 (s)	144.1 (s)	144.0 (s)
	C-21	74.6 (d)	72.6 (d)	72.6 (d)
	C-22	79.6 (d)	92.8 (d)	92.7 (d)
	C-24	64.5 (t)	64.3 (t)	64.3 (t)
22-*O*-α-L-Arabino-pyranosyl moiety	C-1′		108.3 (d)	108.3 (d)
	C-2′		69.1 (d)	69.1 (d)
	C-3′		85.2 (d)	85.2 (d)
	C-4′		67.3 (d)	67.2 (d)
	C-5′		64.3 (t)	64.3 (t)
3′-*O*-β-D-Gluco-pyranosyl moiety	C-1″		106.0 (d)	106.0 (d)
	C-2″		75.5 (d)	75.5 (d)
	C-3″		78.2 (d)[b]	78.2 (d)[c]
	C-4″		71.3 (d)	71.3 (d)
	C-5″		78.4 (d)[b]	78.4 (d)[c]
	C-6″		62.5 (t)	62.5 (t)
3-*O*-β-D-Glucurono-pyranosyl moiety	C-1‴			104.7 (d)
	C-2‴			80.8 (d)
	C-3‴			75.5 (d)
	C-4‴			73.4 (d)
	C-5‴			77.0 (d)
	C-6‴			172.0 (s)
2‴-*O*-β-D-Galacto-pyranosyl moiety	C-1⁗			105.3 (d)
	C-2⁗			72.6 (d)
	C-3⁗			75.5 (d)
	C-4⁗			70.9 (d)
	C-5⁗			77.0 (d)
	C-6⁗			62.5 (t)

a) The off-resonance patterns of the signals are given in parentheses with the following abbreviations: d=doublet, s=singlet and t=triplet. The carbon signals affected by glycosidation shifts are underlined.

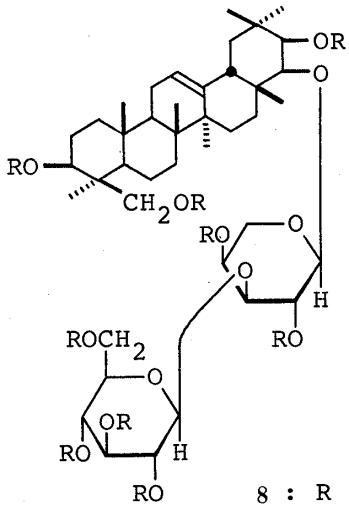
b), *c*) Assignments may be interchangeable within the same column.

The ^{1}H-NMR spectrum of **9a** showed signals due to one acetoxyl group, three methoxyl groups, 3α-H, 21α-H (δ 3.02, d, J=3 Hz), and 22α-H (δ 5.01, d, J=3 Hz). In the MS, two fragment ion peaks due to **ii** and **iii** were observed.

Next, irradiation of **9a** in a hexamethylphosphoramide (HMPA)–water (95 : 5) mixture with a 30 W low-pressure mercury lamp[18] furnished a deacetoxylated product (**10**) in good yield. The IR spectrum of **10** indicated the loss of an acetoxyl function and the MS showed a base peak due to **iv**, derivable from the D, E rings. The ^{1}H-NMR spectrum of **10** showed signals due to three methoxyl groups, 3α-H, and 21α-axial proton (δ 2.95, dd, J=4, 12 Hz). Comparison of these physical properties of **10** with those of 3,22,24-tri-*O*-methylsoyasapogenol B (**11**)[5] finally confirmed the structure of **10**. Consequently, the structures of **9** and **9a** were also established.

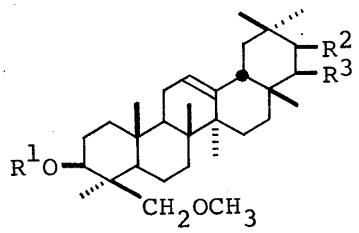


7 : R^1= COOH, R^2= H
(soyasaponin A_2)
7a : R^1= $COOCH_3$, R^2= CH_3
7b : R^1= CH_2OH, R^2= CH_3

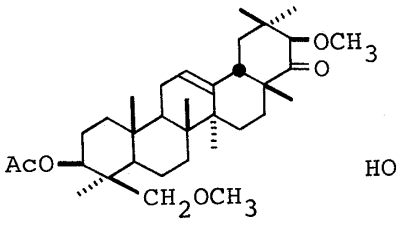


8 : R = H
8a : R = CH_3

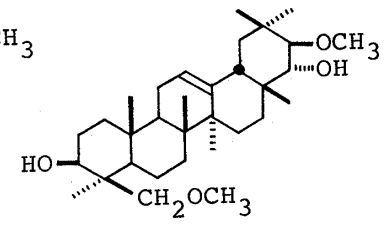
Chart 3-1



9 : R^1= CH_3, R^2= OCH_3, R^3= OH
9a : R^1= CH_3, R^2= OCH_3, R^3= OAc
10 : R^1= CH_3, R^2= OCH_3, R^3= H
11 : R^1= CH_3, R^2= H, R^3= OCH_3
12 : R^1= H, R^2= OCH_3, R^3= OH
12a : R^1= Ac, R^2= OCH_3, R^3= OH
12b : R^1= Ac, R^2= OCH_3, R^3= OAc



12c



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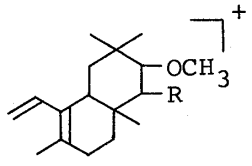
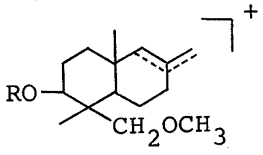


i : R = OH
iii : R = OAc
iv : R = H



ii : R = CH_3
v : R = H
vi : R = Ac

Chart 3-2

Based on these findings, the disaccharide moiety in prosapogenol (**8**) was shown to be attached to 22β-OH of soyasapogenol A (**1**), and from methylation analysis, the structure of **8** was determined to be 22-*O*-[β-D-glucopyranosyl(1→3)-α-L-arabinopyranosyl] soyasapogenol A. Examinations of the ^{13}C-NMR data for **1**, **8**, and methyl glycosides (Table I) supported the carbohydrate sequence in **8** (glycosidation shifts[19] in the C-22 and C-3′ signals).

Finally, the structure of soyasaponin A_2 (**7**) was determined from the following findings. Methylation of **7** with dimsyl carbanion and methyl iodide provided a pentadeca-*O*-methyl derivative (**7a**). The IR spectrum of **7a** lacked hydroxyl absorption bands but showed ester bands. The ^{1}H-NMR spectrum showed signals assignable to three out of four anomeric protons, each as a doublet of $J=7$ Hz.[20] Lithium aluminum hydride ($LiAlH_4$) reduction of **7a** gave **7b** and the IR spectrum of **7b** showed the formation of a carbinol function and the loss of an ester group. Methanolysis of **7b** yielded methyl 2,4-di-*O*-methylarabinopyranoside (**a**), methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**b**), methyl 3,4-di-*O*-methylglucopyranoside (**c**), methyl 2,3,4,6-tetra-*O*-methyl-galactopyranoside (**d**), and a methylated sapogenol (**12**).

The IR spectrum of **12** showed hydroxyl absorption bands, whereas the ^{1}H-NMR spectrum showed signals due to two methoxyl groups, 21α-H (δ 2.96, d, $J=3$ Hz) and 22α-H (δ 3.53, d, $J=3$ Hz). In the MS of **12**, fragmentation peaks due to **i** (base peak) and **v** (from the A, B rings) were observed. Ordinary acetylation of **12** furnished a monoacetate (**12a**) having 3β-OAc and retaining 22β-OH as shown by the IR and ^{1}H-NMR spectra. Acetylation of **12** with acetic anhydride and pyridine in the presence of DMAP provided a diacetate (**12b**) and the indicated structure was supported by its spectral properties, *e.g.*, a 22α-H signal was observed at δ 5.00 as a doublet of $J=3$ Hz and fragment ion peaks due to **iii** and **vi** were seen in the MS. Consequently, the structure of **12b** was determined to be 3,22-di-*O*-acetyl-21,24-di-*O*-methylsoyasapogenol A.

Pyridinium chlorochromate (PCC) oxidation[21] of **12a** provided a ketone (**12c**). The ^{1}H-NMR spectrum of **12c** showed signals due to 21α-H at δ 3.73 as a singlet and due to 3α-H at δ 4.58 (t-like). Sodium borohydride ($NaBH_4$) reduction of **12c** provided **12a** selectively, but $LiAlH_4$ reduction of **12c** yielded **12** and a minor amount of **13**. The structure of **13**, having a 22α-equatorial hydroxyl group, was supported by its MS (fragment ion peaks due to **i** and **v**) and its ^{1}H-NMR spectrum, which showed signals due to two methoxyl groups and 21α-H and 22β-H (δ 2.86, 3.30, ABq, $J=10$ Hz).[16]

Based on these findings, the structure of **12** was determined to be 21,24-di-*O*-methylsoyasapogenol A, and consequently, soyasaponin A_2 was elucidated as 3-*O*-[β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl]-22-*O*-[β-D-glucopyranosyl(1→3)-α-L-arabinopyranosyl]soyasapogenol A (**7**).

Hitherto isolated oleanene-bisdesmosides mostly contain an ester-glycosidic linkage together with an ordinary glycosidic linkage, so that soyasaponin A_2 (**7**) seems to be the first example of an oleanene-bisdesmoside having two ordinary glycosidic linkages.[12]

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as described in our previous paper,[3a] except for ^{13}C-NMR spectra, for which a JEOL JNM-FX 100 (25.05 MHz) FT-NMR spectrometer was used.

Isolation of Soyasaponins I (4), II (5), III (6), A_2 (7), and A_1——Powdered soybeans (cultivated in Akita Prefecture, 4.0 kg) were extracted with MeOH three times (5 l each, with heating under reflux for 5 h). Removal of the solvent from the combined MeOH solutions under reduced pressure gave the MeOH extract (0.5 kg). The MeOH extract was defatted with *n*-hexane several times to afford the *n*-hexane soluble portion (340 g) and the insoluble portion (160 g). The insoluble portion (160 g) was then partitioned into *n*-BuOH–H_2O (1 : 1, 2 l) and a light-yellow precipitate formed during this procedure was collected by filtration and crystallized from MeOH to give an isoflavone mixture (2.5 g). Removal of the solvent from the *n*-BuOH phase and the H_2O phase under reduced pressure provided the *n*-BuOH extract (50 g) and the H_2O extract (100 g), respectively. The *n*-BuOH extract (50 g) was dissolved in

MeOH (50 ml) and the solution was poured dropwise into AcOEt (1 l) with stirring. The precipitate (35 g) was collected by filtration and dried. Removal of the solvent from the filtrate under reduced pressure yielded the AcOEt extract (15 g). Column chromatography (SiO_2 1 kg, $CHCl_3$–MeOH–H_2O = 65 : 35 : 10, lower phase) of the precipitate (35 g) furnished total soyasaponin (12 g). The total soyasaponin (2 g) was then subjected to CLC [KT gel 2061 (Fuji gel) 80 g, i) $CHCl_3$–MeOH–H_2O = 7 : 3 : 1, lower phase; ii) 65 : 35 : 10, lower phase; iii) 6 : 4 : 1] followed by treatment with Dowex 50 W × 8 (H^+ form) in MeOH (20 °C) with stirring for 30 min to furnish soyasaponins III (**6**, 0.09 g), II (**5**, 0.19 g), I (**4**, 1.05 g), A_2 (**7**, 0.20 g), and A_1 (0.16 g).

Soyasaponin A_2 (**7**), mp 231—232 °C (colorless fine crystals from aq. MeOH), $[\alpha]_D^{26}$ +25.3° (c = 1.0, MeOH). *Anal.* Calcd for $C_{53}H_{86}O_{24} \cdot 3H_2O$: C, 54.81; H, 7.99. Found: C, 54.50; H, 8.13. IR ν_{max}^{KBr} cm^{-1}: 3350, 2925, 1740. IR ν_{max}^{Nujol} cm^{-1}: 3350, 1710. ^{13}C-NMR (d_5-pyridine): Table I.

Acidic Hydrolysis of Soyasaponin A_2 (7)——A solution of **7** (20 mg) in MeOH (5 ml) was treated with 20% aq. H_2SO_4 (5 ml) and the whole mixture was heated under reflux for 2 h. After removal of the MeOH under reduced pressure, the reaction mixture was diluted with water and the whole was extracted with AcOEt. The AcOEt extract was washed with sat. aq. $NaHCO_3$ and water, then dried over $MgSO_4$. Removal of the AcOEt under reduced pressure gave the product, which was purified by preparative thin-layer chromatography (TLC) ($CHCl_3$–MeOH = 20 : 1) followed by crystallization from $CHCl_3$–MeOH to furnish soyasapogenol A (**1**, 6 mg). Soyasapogenol A (**1**) thus obtained was shown to be identical with an authentic sample[5] by TLC ($CHCl_3$–MeOH = 20 : 1, benzene–acetone = 5 : 1, *n*-hexane–AcOEt = 2 : 1), mixed mp determination, and IR (KBr), and ^{1}H-NMR ($CDCl_3$–CD_3OD = 1 : 1) comparisons.

Methanolysis of Soyasaponin A_2 (7)——A solution of **7** (1 mg) in 9% HCl–dry MeOH (0.3 ml) was heated under reflux for 1 h. The reaction mixture was neutralized with Ag_2CO_3 powder and the inorganic precipitate was removed by filtration. After identification of **1** in the filtrate by TLC (as above), the solvent was removed from the filtrate under reduced pressure to yield the product. The product was dissolved in pyridine (0.1 ml) and treated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, 0.2 ml) for 10 min. The product was then subjected to gas-liquid chromatography (GLC) to identify the trimethylsilyl (TMS) derivatives of methyl arabinoside, methyl galactoside, methyl glucoside, and methyl glucuronide. The amounts of the four methyl glycosides were determined from their GLC peak areas. GLC: 1) 3% silicone SE-30 on Chromosorb WAW DMCS (80—100 mesh), 3 mm × 1 m glass column; column temp. 140 °C; N_2 flow rate 36 ml/min; t_R, TMS methyl arabinoside 2′50″, 3′15″, TMS-methyl galactoside 9′48″, 11′08″, 12′56″, TMS-methyl glucuronide 6′51″, 15′43″, TMS-methyl glucoside 14′15″, 16′02″. 2) 5% silicone SE-52 on Chromosorb WAW DMCS (80—100 mesh), 3 mm × 2 m glass column; column temp. 170 °C; N_2 flow rate 38 ml/min; t_R, TMS-methyl arabinoside 2′56″, 3′19″, TMS-methyl galactoside 8′03″, 9′18″, 10′36″, TMS-methyl glucuronide 7′07″, 14′33″, TMS-methyl glucoside 11′50″, 12′55″.

In another experiment, a solution of **7** (300 mg) in 9% HCl–dry MeOH (5 ml) was heated under reflux for 1 h. The product, obtained by treatment as described above, was subjected to column chromatography (SiO_2 7 g, $CHCl_3$–MeOH = 10 : 1) to furnish methyl arabinoside (21 mg) and other methyl glycosides. Methyl arabinoside thus obtained was hydrolyzed with 5% aq. HCl (100 °C, 30 min). The reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the resin was removed by filtration. Removal of the water from the filtrate under reduced pressure furnished arabinose, which was shown to be L form by its $[\alpha]_D^{18}$ +98.2° (c = 1.2, H_2O, 2 h after preparing the solution).

Photolysis of Soyasaponin A_2 (7)——A solution of **7** (200 mg) in MeOH (500 ml) in a Vycor tube was irradiated externally with a 500 W high-pressure mercury lamp (Eikosha, PIH-500) for 5 h while keeping the solution temperature below 20 °C. The reaction mixture was neutralized with 10% aq. K_2CO_3 and the solvent was evaporated off under reduced pressure. The product was partitioned into an *n*-BuOH–H_2O mixture (1 : 1). Removal of the solvent from the *n*-BuOH phase under reduced pressure yielded the product, which was purified by preparative TLC ($CHCl_3$–MeOH–H_2O = 7 : 3 : 1, lower phase) and by crystallization from EtOH to furnish a prosapogenol (**8**, 42 mg). The H_2O phase was examined by paper-partition chromatography (PPC) (iso-PrOH–*n*-BuOH–H_2O = 7 : 1 : 2) to identify galactose, then the solvent was evaporated off under reduced pressure. The residue was treated with Ac_2O–pyridine (1 : 2, 3 ml) at 34 °C for 12 h, then the reaction mixture was poured into ice-water and the whole mixture was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by column chromatography (SiO_2 5 g, benzene–acetone = 20 : 1) to furnish 1,2,3,4,6-penta-*O*-acetyl-D-galactopyranose (10 mg). The product was shown to be identical with an authentic sample by TLC (benzene–acetone = 5 : 1, *n*-hexane–AcOEt = 1 : 1, *n*-hexane–acetone = 2 : 1) and GLC: 3) 1.5% silicone SE-30 on Chromosorb WAW DMCS (80—100 mesh), 3 mm × 1 m glass column; column temp. 190 °C; N_2 flow rate 30 ml/min; t_R 3′38″, 4) 2% OV-101 on Uniport HP (80—100 mesh), 3 mm × 2 m glass column; column temp. 270 °C; N_2 flow rate 30 ml/min; t_R 5′10″. Prosapogenol (**8**), mp 284—286 °C (colorless fine crystals), $[\alpha]_D^{18}$ +65.5° (c = 0.70, MeOH). *Anal.* Calcd for $C_{41}H_{68}O_{13} \cdot 2H_2O$: C, 61.17; H, 9.02. Found: C, 61.46; H, 9.17. IR ν_{max}^{KBr} cm^{-1}: 3363, 2950, 2910, 1074, 1026. ^{13}C-NMR (d_5-pyridine): Table I; (d_6-DMSO, δc off-resonance pattern): 143.8 (s, 13-C), 122.0 (d, 12-C), 107.0 (d, anom. C of arabinose moiety), 104.4 (d, anom. C of glucose moiety), 92.0 (d, 22-C), 83.9 (d, 3′-C of arabinose moiety), 79.2 (d, 3-C), 73.9 (d, 21-C).

Acidic Hydrolysis of Prosapogenol (8)——A solution of **8** (20 mg) in MeOH (3 ml) was treated with 20% aq. H_2SO_4 (1 ml) and the whole mixture was heated under reflux for 1 h. Work-up of the reaction mixture as described

for acidic hydrolysis of **7** gave an AcOEt extract, which was purified by preparative TLC followed by crystallization from $CHCl_3$–MeOH to furnish soyasapogenol A (**1**, 10 mg). **1** was shown to be identical with an authentic sample[5] by mixed mp determination, TLC (as above), and IR (KBr) comparisons.

Methanolysis of Prosapogenol (8)——A solution of **8** (1 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 1 h. The product, obtained by work-up as described above for methanolysis of **7**, was subjected to GLC analyses as above and was shown to be a 1 : 1 mixture of methyl arabinoside and methyl galactoside (from the peak areas).

Methylation of Prosapogenol (8)——A solution of **8** (29 mg) in dimethylsulfoxide (DMSO) (3 ml) was treated with dimsyl carbanion (5 ml)[5,15] and the whole mixture was stirred at 20 °C under a nitrogen atmosphere for 1 h. The reaction mixture was then treated with CH_3I (4 ml) in the dark, stirred for a further 16 h, and then poured into ice-water. The whole mixture was extracted with AcOEt and the AcOEt extract was washed with 10% aq. $Na_2S_2O_3$ and water, then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a syrup, which was purified by preparative TLC (benzene–acetone = 3 : 1) and subsequent crystallization from $CHCl_3$–MeOH to furnish **8a** (30 mg). **8a**, mp 177.5—178.5 °C (colorless needles), $[\alpha]_D^{18}$ +46.8° (c = 0.22, $CHCl_3$). *Anal.* Calcd for $C_{50}H_{86}O_3$: C, 67.08; H, 9.68. Found: C, 66.75; H, 9.90. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2920, 1099. ^{1}H-NMR ($CDCl_3$, δ): 0.92 (3H), 0.96 (9H), 1.08, 1.09, 1.25 (3H each) (all s, *tert*-CH_3 × 7), 3.24, 3.33 (3H each), 3.36 (6H), 3.46, 3.50 (3H each), 3.52 (9H) (all s, OCH_3 × 9), 4.50 (1H, d, J = 7 Hz, anom. H),[20] 5.20 (1H, br s, $W_{h/2}$ = 7 Hz, 12-H); (C_6D_6, δ): 1.08 (9H), 1.24, 1.29 (3H each), 1.33 (6H) (all s, *tert*-CH_3 × 7), 3.14 (3H), 3.17 (9H), 3.35, 3.45, 3.60, 3.63, 3.69 (3H each) (all s, OCH_3 × 9), 4.72 (1H, d, J = 7 Hz, anom. H),[20] 5.35 (1H, br s, $W_{h/2}$ = 7 Hz, 12-H).

Methanolysis of 8a——A solution of **8a** (110 mg) in 9% HCl–dry MeOH (8 ml) was heated under reflux for 2 h. After cooling, the precipitate was collected by filtration and crystallized from $CHCl_3$–MeOH to afford **9** (45 mg). 3,21,24-Tri-*O*-methylsoyasapogenol A (**9**), mp 245—247 °C (colorless fine crystals), $[\alpha]_D^{27}$ +109.6° (c = 0.30, $CHCl_3$). *Anal.* Calcd for $C_{33}H_{56}O_4$: C, 76.69; H, 10.92. Found: C, 76.45; H, 10.83. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3535, 2910, 1083. ^{1}H-NMR ($CDCl_3$, δ): 0.93 (3H), 1.00 (12H), 1.01, 1.12 (3H each) (all s, *tert*-CH_3 × 7), 2.72 (1H, dd, J = 4, 12 Hz, 3-H), 3.27, 3.35, 3.40 (3H each, all s, OCH_3 × 3), 3.01 (1H, d, J = 3 Hz, 21-H), 3.57 (1H, d, J = 3 Hz, 22-H), 3.32, 3.56 (2H, ABq, J = 10 Hz, 24-H_2), 5.26 (1H, t-like, 12-H). MS m/z (%): 516 (M^+, 2), 264 (**i**, 100), 252 (**ii**, 13). The filtrate was neutralized with Ag_2CO_3 powder and the inorganic precipitate was removed by filtration. After removal of the solvent from the filtrate under reduced pressure, the product was subjected to TLC and GLC analyses; methyl 2,4-di-*O*-methylarabinopyranoside (**a**) and methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**b**) were identified. TLC: benzene–acetone = 5 : 1, *n*-hexane–AcOEt = 1 : 1, benzene–MeOH = 5 : 1. GLC: 5) 15% polyneopentyl glycol succinate on Chromosorb WAW (80—100 mesh), 3 mm × 2 m glass column; column temp. 180 °C; N_2 flow rate 38 ml/min; t_R, **a** 4′55″, **b** 3′05″, 4′01″, 6) 5% butane-1,4-diol succinate on Uniport B (80—100 mesh), 3 mm × 2 m glass column; column temp. 160 °C; N_2 flow rate 37 ml/min; t_R, **a** 11′25″, 12′03″, **b** 5′31″, 7′48″.

Acetylation of 9 with Ac_2O–Pyridine——A solution of **9** (16 mg) in Ac_2O–pyridine (1 : 1, 1 ml) was stirred at 34 °C for 12 h. Since TLC examination (*n*-hexane–AcOEt = 20 : 1) of the reaction mixture disclosed no change of the starting compound, the mixture was stirred for a further 12 h. The reaction mixture was poured into ice-water, and the whole was extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave the product, which was purified by preparative TLC (*n*-hexane–AcOEt = 20 : 1) to furnish **9a** (4 mg) together with recovered **9** (12 mg). 22-*O*-Acetyl-3,21,24-tri-*O*-methylsoyasapogenol A (**9a**), mp 224—225 °C (colorless needles from $CHCl_3$–MeOH), $[\alpha]_D^{28}$ +100.0° (c = 0.35, $CHCl_3$). *Anal.* Calcd for $C_{35}H_{58}O_5$: C, 75.22; H, 10.46. Found: C, 74.96; H, 10.45. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2935, 1733, 1250, 1096. ^{1}H-NMR ($CDCl_3$, δ): 0.83, 0.97, 0.99 (3H each), 1.01 (6H), 1.14, 1.17 (3H each) (all s, *tert*-CH_3 × 7), 2.06 (3H, s, OAc), 2.73 (1H, dd, J = 4, 12 Hz, 3-H), 3.02 (1H, d, J = 3 Hz, 21-H), 3.27, 3.33, 3.35 (3H each, all s, OCH_3 × 3), 5.01 (1H, d, J = 3 Hz, 22-H), 5.28 (1H, m, 12-H). MS m/z (%): 558 (M^+, 3), 306 (**iii**, 45), 252 (**ii**, 38), 246 (**iii**-AcOH, 100).

Acetylation of 9 with Ac_2O–Pyridine–DMAP——A solution of **9** (10 mg) in Ac_2O–pyridine (1 : 1, 1 ml) was treated with DMAP (1 mg) and the whole mixture was stirred at 34 °C for 7 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 and removal of the AcOEt under reduced pressure yielded the product, which was crystallized from $CHCl_3$–MeOH to furnish **9a** (10 mg). **9a** was shown to be identical with an authentic sample obtained above by TLC (*n*-hexane–AcOEt = 20 : 1, benzene–acetone = 10 : 1, benzene–$CHCl_3$ = 1 : 2) and IR ($CHCl_3$) comparisons.

Photochemical Deacetoxylation of 9a——A solution of **9a** (23 mg) in HMPA–H_2O (95 : 5, 10 ml) in a quartz tube was irradiated externally with a 30 W low-pressure mercury lamp (Eikosha PIL-30) for 134 h while keeping the reaction temperature below 20 °C. After dilution with H_2O (20 ml), the reaction mixture was extracted with ether. The ether extract was washed with water and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the product, which was crystallized from $CHCl_3$–MeOH to furnish **10** (16 mg). **10**, mp 229—230 °C (colorless plates), $[\alpha]_D^{14}$ +106.2° (c = 0.35, $CHCl_3$). High-resolution MS: Found 500.423, 252.207, 248.214. Calcd for $C_{33}H_{56}O_3$ (M^+): 500.423, $C_{16}H_{28}O_2$ (**ii**): 252.205, $C_{17}H_{28}O$ (**iv**): 248.214. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2920, 1095. ^{1}H-NMR ($CDCl_3$, δ): 0.84, 0.87 (3H each) 0.95 (6H), 0.98 (3H), 1.11 (6H) (all s, *tert*-CH_3 × 7), 2.71 (1H, dd, J = 4, 12 Hz, 3-H), 2.95 (1H, dd, J = 4, 12 Hz, 21-H), 3.24 (3H), 3.33 (6H) (both s, OCH_3 × 3), 3.54 (1H, d, J = 10 Hz, 24-H), 5.21 (1H, t-like, 12-H). MS m/z (%): 500 (M^+, 4), 252 (**ii**, 27), 248 (**iv**, 100).

Methylation of Soyasaponin A_2 (7)——A solution of **7** (100 mg) in DMSO (10 ml) was treated with dimsyl carbanion (10 ml) and the whole mixture was stirred under a nitrogen atmosphere for 2 h. The reaction mixture was then treated with CH_3I (10 ml) in the dark and stirred in a similar manner for a further 16 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. Work-up of the AcOEt extract as described above for methylation of **8** gave the product, which was purified by column chromatography (SiO_2 10 g, benzene–acetone = 4 : 1) and crystallized from aq. MeOH to furnish **7a** (58 mg). Pentadeca-*O*-methyl derivative (**7a**), mp 215—216 °C (colorless needles), $[\alpha]_D^{27}$ +13.2° (*c* = 0.93, $CHCl_3$). *Anal.* Calcd for $C_{68}H_{116}O_{24}$: C, 61.98; H, 8.87. Found: C, 61.68; H, 8.87. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2925, 1760, 1100. ^{1}H-NMR ($CDCl_3$, δ): 0.97, 0.99, 1.02 (total 12H), 1.10 (6H), 1.18 (3H) (all s, *tert*-CH_3 × 7), 3.28 (3H), 3.38 (9H), 3.46, 3.50 (3H each), 3.51 (9H), 3.53, 3.59 (3H each), 3.62 (9H) (all s, OCH_3 × 14), 3.79 (3H, s, $COOCH_3$), 4.40, 4.53, 4.61 (1H each, all d, *J* = 7 Hz, anom. H × 3),[20] 5.23 (1H, br s, $W_{h/2}$ = 7 Hz, 12-H).

$LiAlH_4$ Reduction of 7a——A solution of **7a** (98 mg) in dry ether (10 ml) was treated with a suspension of $LiAlH_4$ (100 mg) in dry ether (5 ml) and the whole mixture was stirred at 28 °C for 2 h. After decomposition of excess $LiAlH_4$ with wet ether, the reaction mixture was made weakly acidic with 10% aq. H_2SO_4 and the whole was extracted with ether. Work-up of the ether extract in the usual manner and removal of the solvent under reduced pressure furnished **7b** (95 mg). **7b**, white powder,[22] $[\alpha]_D^{18}$ +53.1° (*c* = 0.65, $CHCl_3$). *Anal.* Calcd for $C_{67}H_{116}O_{24}$: C, 61.63; H, 8.96. Found: 61.28; H, 9.03. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 2923, 1094, 1075. ^{1}H-NMR ($CDCl_3$, δ): 0.96 (9H), 1.01 (3H), 1.09 (6H), 1.19 (3H) (all s, *tert*-CH_3 × 7), 3.29 (3H), 3.36 (9H), 3.45 (3H), 3.50, 3.53, 3.60 (9H each) (all s, OCH_3 × 14), 4.36, 4.53, 4.65 (1H each, all d, *J* = 7 Hz, anom. H × 3),[20] 5.21 (1H, br s, $W_{h/2}$ = 6 Hz, 12-H).

Methanolysis of 7b——A solution of **7b** (22 mg) in 9% HCl–dry MeOH (1 ml) was heated under reflux for 1.5 h, then cooled. The precipitate was collected by filtration and purified by preparative TLC (benzene–acetone = 9 : 1) and subsequent crystallization from MeOH to furnish **12** (9 mg). 21,24-Di-*O*-methylsoyasapogenol A (**12**), mp 256—258 °C (colorless fine crystals), $[\alpha]_D^{27}$ +106.8° (*c* = 0.20, $CHCl_3$). *Anal.* Calcd for $C_{32}H_{54}O_4$: C, 76.44; H, 10.83. Found: C, 76.14; H, 10.67. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 2935, 1093. ^{1}H-NMR ($CDCl_3$, δ): 0.92, 0.97 (6H each), 1.01, 1.13, 1.21 (3H each) (all s, *tert*-CH_3 × 7), 2.96 (1H, d, *J* = 3 Hz, 21-H), 3.31, 3.39 (3H each, both s, OCH_3 × 2), 3.53 (1H, d, *J* = 3 Hz, 22-H), 3.89 (1H, d, *J* = 10 Hz, 24-H), 5.24 (1H, t-like, 12-H). MS *m/z* (%): 502 (M^+, 2), 264 (**i**, 100), 238 (**v**, 10). The filtrate was neutralized with Ag_2CO_3 powder and worked up as described above. The product was subjected to TLC and GLC analyses, and was determined to consist of methyl 2,4-di-*O*-methylarabinopyranoside (**a**), methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**b**), methyl 2,3,4,6-tetra-*O*-methylgalactopyranoside (**c**), and methyl 3,4-di-*O*-methylglucopyranoside (**d**). TLC: benzene–acetone = 5 : 2, *n*-hexane–AcOEt = 1 : 1, benzene–MeOH = 5 : 1. GLC: 7) column temp. 190 °C; N_2 flow rate 38 ml/min, and other conditions were the same as for 6); t_R, **a** 3′34″, **b** 1′54″, 2′27″, **c** 2′51″, **d** 10′46″, 12′37″, 8) 15% ethylene glycol succinate on Chromosorb WAW (80—100 mesh), 3 mm × 1 m glass column; column temp. 170 °C; N_2 flow rate 35 ml/min; t_R, **a** 7′50″, 8′20″, **b** 2′55″, 4′11″, **c** 5′22″, **d** 11′18″, 13′20″.

Acetylation of 12 with Ac_2O–Pyridine——A solution of **12** (27 mg) in Ac_2O–pyridine (1 : 1, 2 ml) was stirred at 32 °C for 7 h. The reaction mixture was poured into ice-water and the precipitate was collected by filtration and crystallized from $CHCl_3$–MeOH to furnish **12a** (25 mg). 3-*O*-Acetyl-22,24-di-*O*-methylsoyasapogenol A (**12a**), mp 277—278 °C (colorless plates), $[\alpha]_D^{26}$ +111.2° (*c* = 0.38, $CHCl_3$). *Anal.* Calcd for $C_{34}H_{56}O_5$: C, 74.95; H, 10.36. Found: C, 74.72; H, 10.63. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 2930, 1730, 1250. ^{1}H-NMR ($CDCl_3$, δ): 0.94 (3H), 1.00 (12H), 1.13, 1.25 (3H each) (all s, *tert*-CH_3 × 7), 2.04 (3H, s, OAc), 2.99 (1H, d, *J* = 3.5 Hz, 21-H), 3.28, 3.41 (3H each, both s, OCH_3 × 2), 3.56 (1H, d, *J* = 3.5 Hz, 22-H), 3.33, 3.63 (2H, ABq, *J* = 10 Hz, 24-H_2), 4.54 (1H, t-like, 3-H), 5.23 (1H, t-like, 12-H). MS *m/z* (%): 544 (M^+, 1), 280 (**vi**, 5), 264 (**i**, 100).

Acetylation of 12 with Ac_2O–Pyridine–DMAP——A solution of **12** (10 mg) in Ac_2O–pyridine (1 : 1, 1 ml) was treated with DMAP (1 ml) and the whole mixture was stirred at 34 °C for 7 h. The reaction mixture was poured into ice-water and the whole was extracted with AcOEt. After work-up of the AcOEt extract in the usual manner, the product was purified by preparative TLC (*n*-hexane–AcOEt = 20 : 1) and crystallization from $CHCl_3$–MeOH to furnish **12b** (9 mg). 3,22-Di-*O*-acetyl-21,24-di-*O*-methylsoyasapogenol A (**12b**), mp 306—308 °C (colorless plates), $[\alpha]_D^{26}$ +107.1° (*c* = 0.68, $CHCl_3$). *Anal.* Calcd for $C_{36}H_{58}O_6$: C, 73.68; H, 9.96. Found: C, 73.45; H, 10.19. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 1731, 1250. ^{1}H-NMR ($CDCl_3$, δ): 0.81, 0.94, 0.98 (3H each), 1.01 (9H), 1.15 (3H) (all s, *tert*-CH_3 × 7), 2.05 (6H, s, OAc × 2), 3.02 (1H, d, *J* = 3 Hz, 21-H), 3.29, 3.32 (3H, each, both s, OCH_3 × 2), 3.36, 3.64 (2H, ABq, *J* = 10 Hz, 24-H_2), 4.57 (1H, t-like, 3-H), 5.00 (1H, d, *J* = 3 Hz, 22-H), 5.25 (1H, t-like, 12-H). MS *m/z* (%): 586 (M^+, 2), 306 (**iii**, 62), 280 (**vi**, 9), 246 (**iii**-AcOH, 100).

PCC Oxidation of 12a——A solution of **12a** (8 mg) in dry $CHCl_3$ (1.2 ml) was treated with PCC (6 mg) and the whole mixture was stirred at 26 °C under a nitrogen atmosphere for 4 h. The product was purified by column chromatography (Florisil 100—200 mesh, 1 g, ether), and subsequent crystallization from $CHCl_3$–MeOH to furnish **12c** (7 mg). **12c**, mp 280—281 °C (colorless needles), $[\alpha]_D^{12}$ +73.7° (*c* = 0.22, $CHCl_3$). *Anal.* Calcd for $C_{34}H_{54}O_2$: C, 75.23; H, 10.03. Found: C, 74.99; H, 9.92. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2925, 1735, 1720, 1254. ^{1}H-NMR ($CDCl_3$, δ): 0.78, 0.97 (3H each), 1.02 (9H), 1.08, 1.25 (3H each) (all s, *tert*-CH_3 × 7), 2.05 (3H, s, OAc), 3.29, 3.42 (3H each, both s, OCH_3 × 2), 3.34, 3.64 (2H, ABq, *J* = 10 Hz, 24-H_2), 3.73 (1H, s, 21-H), 4.58 (1H, t-like, 3-H), 5.29 (1H, m, 12-H).

$NaBH_4$ Reduction of 12c——A solution of **12c** (7 mg) in EtOH (20 ml) was treated with $NaBH_4$ (10 mg) and the whole mixture was stirred at 26 °C for 1 h. The reaction mixture was neutralized with Dowex 50 W × 8 (H^+ form) and

the resin was removed by filtration. Removal of the solvent from the filtrate under reduced pressure gave the product, which was crystallized from $CHCl_3$–MeOH to furnish **12a** (7 mg). **12a** was shown to be identical with an authentic sample (above) by mixed mp determination and TLC (benzene–acetone = 20 : 1, $CHCl_3$, *n*-hexane–ether = 5 : 1), IR ($CHCl_3$), and ^{1}H-NMR ($CDCl_3$) comparisons.

$LiAlH_4$ Reduction of 12c——A solution of **12c** (20 mg) in dry ether (9 ml) was treated with a suspension of $LiAlH_4$ (5 mg) in a small amount of dry ether and the whole mixture was stirred at 21 °C for 30 min. After quenching of the reaction by adding wet ether, the whole mixture was weakly acidified with 10% aq. H_2SO_4 and extracted with AcOEt. Work-up of the AcOEt extract in the usual manner and removal of the solvent under reduced pressure gave the product, which was purified by preparative TLC (benzene–acetone = 10 : 1) and by crystallization from $CHCl_3$–MeOH to furnish **12** (13 mg) and **13** (3 mg). **12** was shown to be identical with an authentic sample (above) by mixed mp determination, and TLC (benzene–acetone = 10 : 1, $CHCl_3$–MeOH = 30 : 1, *n*-hexane–AcOEt = 5 : 1), IR ($CHCl_3$), and ^{1}H-NMR ($CDCl_3$) comparisons. **13**, mp 253—254 °C (colorless plates), $[\alpha]_D^{12}$ +44.1° (c = 0.2, $CHCl_3$). High-resolution MS: Found 502.400, 264.208, 238.193. Calcd for $C_{32}H_{54}O_4$ (M^+): 502.402, $C_{17}H_{28}O_2$ (**i**): 264.208, $C_{15}H_{26}O_2$ (**v**): 238.193. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 2930, 1100. ^{1}H-NMR ($CDCl_3$, δ): 0.86, 0.91, 0.93 (3H each), 0.99 (6H), 1.14, 1.22 (3H each) (all s, *tert*-CH_3 × 7), 2.86, 3.30 (2H, ABq, J = 10 Hz, 21,22-H_2), 3.92 (1H, d, J = 10 Hz, 24-H), 5.23 (1H, m, 12-H). MS m/z (%): 502 (M^+, 2), 264 (**i**, 100), 238 (**v**, 27).

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References and Notes

1) Part XXXVII: I. Kitagawa, H. K. Wang, and M. Yoshikawa, *Chem. Pharm. Bull.*, **31**, 716 (1983).
2) I. Kitagawa and M. Yoshikawa, *Kagaku to Seibutsu*, **21**, 224 (1983).
3) *a*) I. Kitagawa, H. K. Wang, M. Saito, and M. Yoshikawa, *Chem. Pharm. Bull.*, **31**, 664 (1983); *b*) *Idem, ibid.*, **31**, 674 (1983); *c*) *Idem, ibid.*, **31**, 683 (1983).
4) *a*) I. Kitagawa, H. K. Wang, A. Takagi, M. Fuchida, I. Miura, and M. Yoshikawa, *Chem. Pharm. Bull.*, **31**, 689 (1983); *b*) I. Kitagawa, H. K. Wang, M. Saito, A. Takagi, and M. Yoshikawa, *ibid.*, **31**, 698 (1983); *c*) I. Kitagawa, H. K. Wang, M. Saito, and M. Yoshikawa, *ibid.*, **31**, 709 (1983).
5) *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, *ibid.*, **30**, 2294 (1982).
6) I. Kitagawa, M. Yoshikawa, K. Kobayashi, Y. Imakura, K. S. Im, and Y. Ikenishi, *Chem. Pharm. Bull.*, **28**, 296 (1980).
7) I. Kitagawa, "Chemistry of Natural Products, '80A," Kagaku No Ryoiki Zokan No. 125, ed. by S. Ito, T. Goto, and S. Nozoe, Nankodo, Tokyo, 1980, p. 45.
8) *a*) I. Kitagawa, M. Yoshikawa, Y. Imakura, and I. Yosioka, *Chem. Pharm. Bull.*, **22**, 1339 (1974); *b*) M. Yoshikawa, H. Kayakiri, and I. Kitagawa, presented at the 103rd Annual Meeting of the Pharmaceutical Society of Japan, Abstract p. 182 (April 1983, Tokyo).
9) *a*) I. Kitagawa, M. Yoshikawa, K. S. Im, and Y. Ikenishi, *Chem. Pharm. Bull.*, **25**, 657 (1977); *b*) I. Kitagawa, M. Yoshikawa, and A. Kadota, *ibid.*, **26**, 484 (1978).
10) I. Kitagawa, Y. Ikenishi, M. Yoshikawa, and K. S. Im, *Chem. Pharm. Bull.*, **25**, 1408 (1977).
11) I. Kitagawa, T. Kamigauchi, H. Ohmori, and M. Yoshikawa, *Chem. Pharm. Bull.*, **28**, 3078 (1980).
12) I. Kitagawa, M. Saito, and M. Yoshikawa, presented at the 100th Annual Meeting of the Pharmaceutical Society of Japan, Abstract p. 182 (April 1980, Tokyo). The structure elucidation of soyasaponin A_1 will be reported in our forthcoming paper.
13) In soybeans from the U.S.A., Canada, and China, soyasaponins I, II, III, A_1, and A_2 are contained as partially acetylated derivatives. Soyasaponin contents in those imported soybeans were reported in our recent papers: *a*) I. Kitagawa, M. Yoshikawa, T. Hayashi, and T. Taniyama, *Yakugaku Zasshi*, **104**, 162 (1984); *b*) *Idem, ibid.*, **104**, 275 (1984).
14) *a*) S. Seo, Y. Tomita, K. Tori, and Y. Yoshimura, *J. Am. Chem. Soc.*, **100**, 3331 (1978); *b*) S. Takabe, T. Takeda, and Y. Ogihara, *Shoyakugaku Zasshi*, **34**, 69 (1980).
15) S. Hakomori, *J. Biochem.* (Tokyo), **55**, 205 (1964).
16) *a*) I. Yosioka, T. Nishimura, A. Matsuda, and I. Kitagawa, *Chem. Pharm. Bull.*, **18**, 1610 (1970); *b*) *Idem, ibid.*, **18**, 1621 (1970); *c*) *Idem, ibid.*, **19**, 1186 (1971).
17) *a*) G. Holfe, W. Steglich, and H. Vorbruggen, *Angew. Chem. Int. Ed. Engl.*, **17**, 569 (1978); *b*) M. Yoshikawa, Y. Ikeda, H. Kayakiri, K. Takenaka, and I. Kitagawa, *Tetrahedron Lett.*, **23**, 4717 (1982).
18) *a*) H. Deshayes, J. P. Pete, C. Portella, and D. Scholler, *J. Chem. Soc., Chem. Commun.*, **1975**, 439; *b*) I. Kitagawa, H. Shibuya, and H. Fujioka, *Chem. Pharm. Bull.*, **25**, 2718 (1977).
19) *a*) R. Kasai, M. Suzuo, J. Asakawa, and O. Tanaka, *Tetrahedron Lett.*, **1977**, 175; *b*) K. Tori, S. Seo, Y. Yoshimura, H. Arita, and Y. Tomita, *ibid.*, **1977**, 179.

20) The one remaining anomeric proton signal was overlapped by other signals.
21) *a*) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **1975**, 2647; *b*) I. Kitagawa, H. Shibuya, H. Fujioka, A. Kajiwara, Y. Yamamoto, S. Tsujii, A. Takagi, and M. Hori, *Chem. Pharm. Bull.*, **29**, 2540 (1981).
22) All attempts at for crystallization failed. These compounds are described as they were obtained.