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Studies on the Constituents of *Aster tataricus* L. f. I. Structures of Shionosides A and B, Monoterpene Glycosides Isolated from the Root

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Two new monoterpene glycosides named shionosides A and B were isolated from the root of *Aster tataricus* L. f. (Compositae), along with shionone, epifriedelinol and phytosterol glucosides.

The structures of the shionosides were elucidated based on chemical and spectral evidence as the β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (shionoside A) and the α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (shionoside B) of L-*endo*-camphanol [(1*R*,2*R*,4*S*)-3,3-dimethyl-bicyclo-[2.2.1]hept-2-yl-methanol].

Keywords——*Aster tataricus*; Asteris Radix; Compositae; monoterpene glycoside; shionoside; camphanol; (1*R*,2*R*,4*S*)-3,3-dimethyl-bicyclo[2.2.1]hept-2-yl-methanol; apiofuranosyl-glucopyranoside

The constituents of the root of *Aster tataricus* L. f. (Compositae) were investigated more than 20 years ago by several investigators. Nakaoki[1] reported the isolation of shionone, quercetin and a saponin named astersaponin, $C_{23}H_{44}O_{10}\cdot 1/2H_2O$ (an arabinoside of astersapogenin). Koyama *et al.*[2] isolated hederagenin monoglucoside from the defatted MeOH extract after HCl treatment. In 1959, Takahashi *et al.*[3] isolated shionone and a saponin which seemed to be so-called "astersaponin," along with friedelin and epifriedelinol from the same source. However, they were primarily interested in the structure of shionone, and "astersaponin" has been left uncharacterized.

Reinvestigation of the constituents of Asteris Radix was attempted in order to isolate and characterize "astersaponin", and in the course of the work, two monoterpene glycosides named shionosides A and B were isolated from the glycoside fraction (fr. 7 in Chart 1) less polar than the saponin fraction (Fr. I-Cb). This paper deals with their structures.

Procedures for fractionation and isolation of shionosides A and B are summarized in Chart 1 and described in the experimental section.

Thin-layer chromatography (TLC) of fraction 7 showed several faint dark brown spots on a brown background after spraying sulfuric acid and heating, and they were partly overlapped by spots of compounds which were flavonoid in nature. Two compounds showing dark brown spots, shionosides A and B, were isolated in a crystalline state by repeated chromatography on Sephadex LH-20, silica gel and LiChroprep RP-18.

Shionoside A (I) was obtained as colorless needles from EtOAc–MeOH, and the high-resolution fast atom bombardment mass spectrum (FAB-MS) showed an $[M+Na]^+$ ion peak at *m/z* 471.223, from which the molecular formula $C_{21}H_{36}O_{10}$ was deduced. On acid hydrolysis, I gave a progenin (II), $C_{16}H_{28}O_6$, and an aglycone (III), $C_{10}H_{18}O$. The gas-liquid chromatographic (GLC) analysis of the sugar fraction revealed the presence of two sugars, of which one was identified as D-glucose according to the method reported by Hara *et al.*[4]

The ^{13}C nuclear magnetic resonance (NMR) spectrum of I showed signals of four oxymethylene carbons (δ 65.7, 68.4, 68.8 and 75.0), five oxymethine carbons (δ 71.9, 75.1,

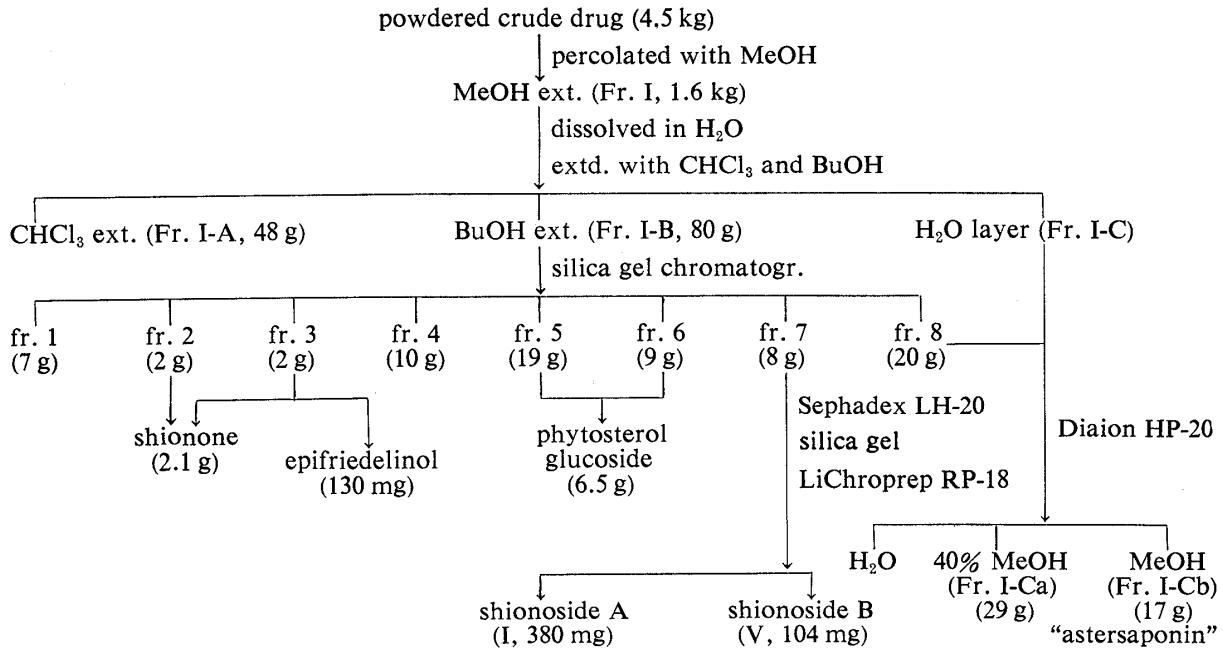

Chart 1

77.2, 77.8 and 78.6), one hydroxylated quaternary carbon (δ 80.4) and two anomeric carbons (δ 104.6 and 111.1). In a comparison of the ^{13}C-NMR spectra of I and II, signals of two oxymethylene carbons (δ 65.7 and 75.0), one oxymethine carbon (δ 77.8), one quaternary carbon (δ 80.4) and one anomeric carbon (δ 111.1) in I were no longer observed in II and the signal of one oxymethylene carbon (δ 68.8) shifted upfield to δ 62.9 on going from I to II. From the chemical shifts and the multiplicities of the lost signals, the terminal sugar linked to the C_6-hydroxyl group of D-glucopyranose was presumed to be apiofuranose. The presence of apiose was confirmed by a direct GLC comparison with an authentic sample of methyl apiofuranoside prepared from apiin. The β-glucoside linkage was determined based on the coupling constant (8 Hz) of the anomeric proton. The mode of the linkage of the apiofuranosyl group was determined as β by comparison of the molecular rotation difference ($\Delta[M]_D$ $-255°$) between I and II with the reported values of methyl tri-*O*-methyl-α-D-apiofuranoside ($+239°$) and its β anomer ($-163°$).[5] From these data, the structure of the sugar moiety of I was determined as β-D-apiofuranosyl-(1→6)-β-D-glucopyranose.

The aglycone (III) of I was obtained as a liquid having a camphor-like odor, and it was converted into a crystalline 3,5-dinitrobenzoate (IV). The ^{1}H-NMR spectrum (Fig. 1A) of IV showed the signals of two methyl groups (δ 0.96 and 1.09), each as a singlet, the signal of oxymethylene protons (δ 4.47, 2H, d-like) and a signal of the methine proton (δ 1.94, ddd-like), which collapsed to a doublet ($J=3$ Hz) on irradiation of the oxymethylene protons at δ 4.47. The ^{1}H–^{1}H NMR correlation (^{1}H-COSY) spectrum indicated that the oxymethylene protons couple with the methine proton (δ 1.94) and the latter couples further with a methine proton which appeared at δ 2.32 as a broad singlet. From these data, the connectivities of a hydroxymethylene carbon, a methine carbon and a quaternary carbon to a methine carbon became clear.

The ^{13}C-NMR spectrum of IV displayed the signals of two methyl carbons (δ 20.9 and 32.5), four methylene carbons (δ 20.5, 24.5, 37.3, and 66.2), three methine carbons (δ 40.4, 48.9, and 49.0) and one quaternary carbon (δ 37.3) in addition to the signals due to the dinitrobenzoyl group. Considering the degree of unsaturation apparent from the molecular formula as well as information from the NMR spectra, III was supposed to be a camphanol

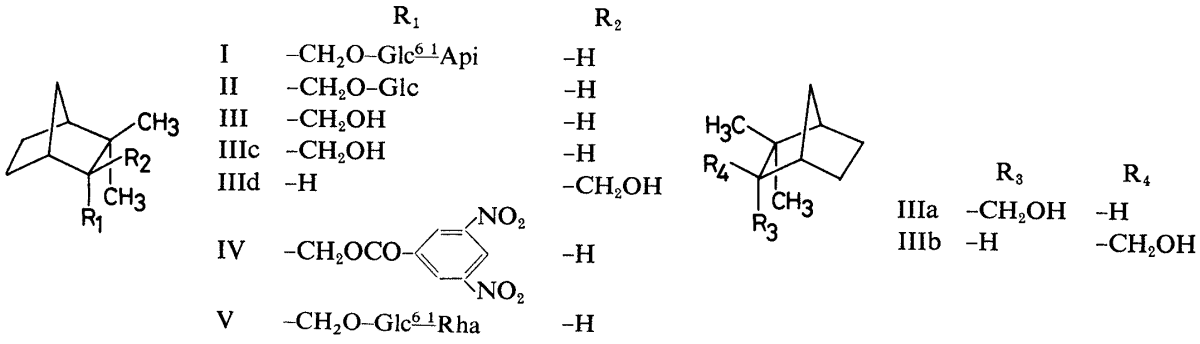

Chart 2

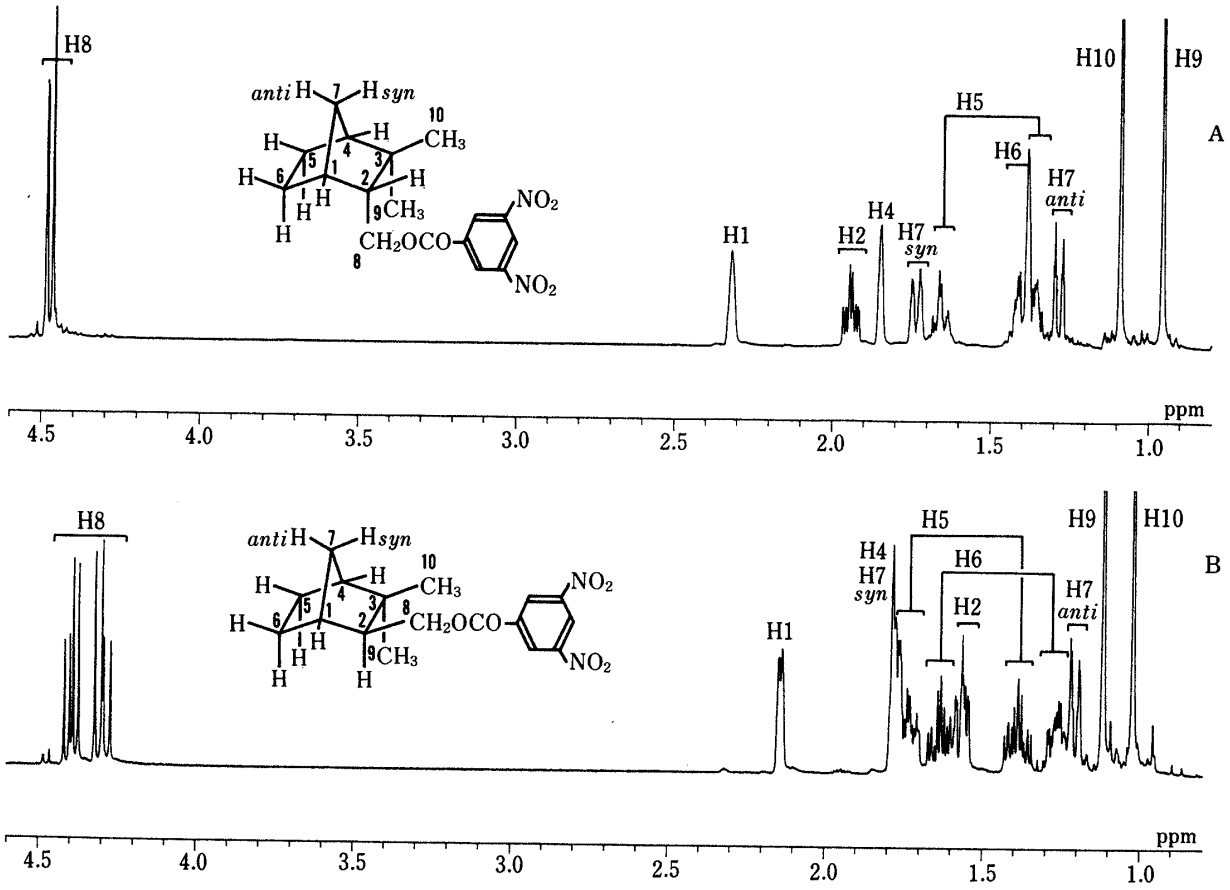

Fig. 1. 400 MHz ^{1}H-NMR Spectra of (A) IV and the 3,5-Dinitrobenzoate of IIIc, (B) the 3,5-Dinitrobenzoate of IIId (in $CDCl_3$)

(3,3-dimethyl-bicyclo[2.2.1]hept-2-yl-methanol). All the proton and carbon signals of IV were assigned as shown in Tables II and I by the COSY techniques and the nuclear Overhauser effect (NOE) difference spectra obtained by irradiation of specific protons. The NOEs were observed between the following sets of protons: C_8-H (δ 4.47)↔C_2-H (δ 1.94), CH_3 (δ 0.96), C_1-H (δ 2.32), C_6-H (δ 1.41); CH_3 (δ 0.96)↔C_4-H (δ 1.85), C_8-H (δ 4.47), C_5-H (δ 1.66); CH_3 (δ 1.09)↔C_4-H (δ 1.85), C_2-H (δ 1.94), C_7-H_{syn} (δ 1.74).

Based on the NOE analysis, relative steric relations were obtained among the two methyl groups, one of the bridged methylene protons, and a hydroxymethylene group. Compound III was therefore considered to be an *endo*-camphanol. In order to confirm the structure, four isomers [D-*endo*- (IIIa), D-*exo*- (IIIb), L-*endo*- (IIIc) and L-*exo*- (IIId) camphanols] were prepared from D- and L-camphenes by hydroboration according to the procedure of

TABLE I. ^{13}C-NMR Chemical Shifts of Shionosides and Related Compounds

	Pyridine-d_5			$CDCl_3$					
								3,5-DNBz of	
	I	V	II	III	IIIa, c	IIIb, d	IV	IIIa, c	IIIb, d
C-1	40.8	40.8	40.9	39.8	39.7	40.6	40.4	40.4	41.1
C-2	50.0	49.9	50.1	52.7	52.5	56.5	48.9	48.9	52.5
C-3	37.0	37.0	37.0	36.8	36.7	39.7	37.3	37.3	40.2
C-4	49.6	49.6	49.5	49.2	49.1	49.2	49.0	49.0	49.3
C-5	24.9	24.9	24.8	24.5	24.5	23.9	24.5	24.5	23.9
C-6	20.9	20.9	21.0	20.3	20.2	29.5	20.5	20.5	29.4
C-7	37.4	37.4	37.4	37.1	37.0	35.8	37.3	37.3	36.0
C-8	68.4	68.4	68.6	61.2	60.8	63.4	66.2	66.2	68.0
C-9 (*endo*)	20.7	20.7	20.7	20.5	20.4	28.0	20.9	20.9	28.0
C-10 (*exo*)	32.6	32.6	32.6	32.7	32.5	23.7	32.5	32.5	23.9
	Glc	Glc	Glc						
C-1	104.6	104.6	104.8						
C-2	75.1	75.1	75.2						
C-3	78.6	78.6	78.6						
C-4	71.9	71.9	71.8						
C-5	77.2	77.1	78.3						
C-6	68.8	68.5	62.9						
	Api	Rha							
C-1	111.1	102.6							
C-2	77.8	72.3							
C-3	80.4	72.7							
C-4	75.0	74.0							
C-5	65.7	69.7							
C-6		18.7							

3,5-Dinitrobenzoyl	
C-1	134.3
C-2,6	129.3
C-3,5	148.8
C-4	122.2
>C=O	162.5

Abbreviations: DNBz, dinitrobenzoate; Glc, β-D-glucopyranosyl; Api, β-D-apiofuranosyl; Rha, α-L-rhamnopyranosyl.

Biellmann and d'Orchymont.[6] The four camphanols were converted to the corresponding 3,5-dinitrobenzoates. The ^{1}H- and ^{13}C-NMR spectra of IV were superimposable on those of the 3,5-dinitrobenzoates of IIIa and IIIc.

The specific rotation of III at 350 nm is $+15°$, which is close to that of IIIc ($[\alpha]_{350}+7°$),[7] while $[\alpha]_{350}$ of IIIa is $-6°$.[7] Since IIIc-3,5-dinitrobenzoate afforded the same retention time as IV in high-performance liquid chromatography (HPLC) on Chiralpak OT,[8] III was concluded to be L-*endo*-camphanol [(1*R*,2*R*,4*S*)-3,3-dimethyl-bicyclo[2.2.1]hept-2-yl-methanol], and accordingly, shionoside A (I) is its β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Shionoside B (V), $C_{22}H_{38}O_{10}$, was obtained as colorless needles from EtOAc–MeOH. Compound V showed similar ^{1}H- and ^{13}C-NMR spectra to those of I at higher magnetic field, except for an additional proton signal (δ 1.63, 3H, d, $J=6$ Hz) and a carbon signal (δ 18.7), suggesting V to be a glycoside of III having a methylpentose as one of the component sugars. Compound V gave L-*endo*-camphanol (III), D-glucose and L-rhamnose on acid hydrolysis. The ^{13}C-NMR chemical shift (δ 68.5) of C_6 of the glucopyranosyl group showed the linkage of the rhamnopyranosyl group to the C_6-hydroxyl group of glucose, and the molecular rotation difference ($\Delta[M]_D-133°$) between V and II indicated the configuration of the rhamnosyl linkage to be α. Thus, shionoside B is the α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside of L-*endo*-camphanol.

The fraction having a foaming property (Fr. I-Cb), is presumed to be so-called

TABLE II. ^{1}H-NMR Chemical Shifts of Shionosides and Related Compounds

	I Pyridine-d_5	V Pyridine-d_5	II Pyridine-d_5	III $CDCl_3$	IV $CDCl_3$
1-H	2.32 br s	2.33 br s	2.28 br s	2.27 br s	2.32 br s
2-H	1.82 ddd (9, 7, 3)	1.83 ddd (9, 7, 3)	1.82 ddd (9, 7, 3)	*ca.* 1.58	1.94 ddd-like
4-H	1.63 br s	*ca.* 1.62	1.64 br s	1.75 br s	1.85 br s
5-H	1.16 br d	1.15 m	*ca.* 1.14	1.31 m	1.37 m
	ca. 1.54	1.55 m	1.48 br d	1.36 m	1.66 m
6-H	1.17 br d	1.17 m	*ca.* 1.14	1.28 m	1.41 (2H) m
	1.50 br d	*ca.* 1.53	1.35 br d	*ca.* 1.58	
7-H (*syn*)	1.54 br d	*ca.* 1.53	1.55 br d	1.65 br d	1.74 br d
7-H (*anti*)	1.04 br d	1.04 br d	1.07 br d	1.20 br d	1.29 br d
8-H	3.70 dd (10, 7)	3.73 dd (10, 7)	3.68 dd (10, 7)	3.60 dd (11, 9)	4.47 (2H) d-like
	4.22 dd (10, 9)	4.21 dd (10, 9)	4.14 dd (10, 9)	3.65 dd (11, 7)	
9-H (*endo*)	0.91 (3H) s	0.93 (3H) s	0.88 (3H) s	0.85 (3H) s	0.96 (3H) s
10-H (*exo*)	0.94 (3H) s	0.95 (3H) s	0.95 (3H) s	1.00 (3H) s	1.09 (3H) s
	Glc	Glc	Glc		3,5-Dinitrobenzoyl
1-H	4.79 d (8)	4.81 d (8)	4.81 d (8)		2,6-H 9.13 (2H) d (2)
2-H	3.98 dd (9, 8)	3.98 dd (9, 8)	3.97 dd (9, 8)		4-H 9.23 dd (2, 2)
3-H	4.19 dd (9, 9)	4.19 dd (9, 9)	4.21 dd (9, 9)		
4-H	4.01 dd (9, 9)	4.00 dd (9, 9)	4.18 dd (9, 9)		
5-H	4.09 ddd (9, 6, 2)	4.08 ddd (9, 6, 2)	3.95 ddd (9, 5, 2)		
6-H	4.21 dd (11, 6)	4.17 dd (11, 6)	4.36 dd (12, 5)		
	4.70 dd (11, 2)	4.65 dd (11, 2)	4.52 dd (12, 2)		
	Api	Rha			
1-H	5.80 d (2)	5.53 d (2)			
2-H	4.72 d (2)	4.57 dd (3, 2)			
3-H		4.50 dd (9, 3)			
4-H	4.33 d (9)	4.23 dd (9, 9)			
	4.55 d (9)				
5-H	4.14 (2H) s-like	4.36 dq (9, 6)			
6-H		1.63 (3H) d (6)			

Abbreviations: Glc, β-D-glucopyranosyl; Api, β-D-apiofuranosyl; Rha, α-L-rhamnopyranosyl. The numbers in parentheses are coupling constants in Hz.

"astersaponin." The TLC of the fraction showed it to be a mixture of several compounds, and the isolation and characterization of these compounds are in progress.

Experimental[9]

Plant Material——The crude drug used in this work was a product of the People's Republic of China and was purchased from Uchida Pharmacy for Oriental Medicine, Tokyo, Japan.

Extraction, Fractionation and Isolation of Shionone, Epifriedelinol and Shionosides A (I) and B (V)——A sticky powder (4.5 kg) of Asteris Radix was percolated with MeOH (40 l). The MeOH extract (Fr. I, 1.6 kg) was dissolved in H_2O (10 l) and extracted with $CHCl_3$ (3 l × 4) and then with BuOH (3 l × 4). The BuOH extract (Fr. I-B, 80 g) was mixed with silica gel (200 g), loaded on a column of silica gel (1 kg) and eluted with $CHCl_3$, $CHCl_3$–MeOH–H_2O (CMW) (15 : 3 : 0.2, 15 : 4 : 0.2) and then MeOH. Each fraction was checked by TLC. The eluate with $CHCl_3$ was divided into four fractions (fr. 1—4). Fraction 2 was almost pure shionone (1.5 g) and it was crystallized from EtOH. Fraction 3 was a mixture of shionone and epifriedelinol. The mixture was suspended in $CHCl_3$. The sparingly soluble powder was almost pure epifriedelinol. The soluble fraction was concentrated and crystallized from EtOH to give another crop (600 mg) of shionone. The eluates (frs. 5 and 6) with CMW (15 : 3 : 0.2) were combined and suspended in $CHCl_3$–MeOH (1 : 1). The precipitate (5 g) of phytosterol glucoside was filtered off. The filtrate was concentrated to dryness and again dissolved in MeOH. Another crop (1.5 g) of phytosterol glucoside was obtained as a white powdery precipitate.

Fraction 7 was repeatedly chromatographed on Sephadex LH-20 (MeOH), silica gel (CMW 15:3:0.3, 15:4:0.3) and LiChroprep RP-18 (E. Merck) (65% MeOH), and shionoside A (I, 380 mg) and shionoside B (V, 104 mg) were isolated.

Fraction 8 and the water layer (Fr. I-C) after BuOH extraction were combined and chromatographed on Diaion HP-20 (Mitsubishi Chemical Industries, Ltd.) (1000 ml). After being thoroughly washed with H_2O, the column was eluted with 40% MeOH (2 l) and then with MeOH (2 l). The eluate (Fr. I-Ca, 29 g) with 40% MeOH did not foam on shaking. The MeOH eluate (Fr. I-Cb, 17 g) has a foaming property.

Shionone——Colorless needles from EtOH, mp 155—156 °C (ref.[3] 158.5—159.5 °C), $[\alpha]_D^{22}$ −47.9° (c=1.05, $CHCl_3$) (ref.[3] −56.1°). FD-MS m/z: 426 ($[M]^+$). ^{1}H-NMR ($CDCl_3$): the chemical shifts were in good agreement with those reported for shionone.[10] ^{13}C-NMR ($CDCl_3$) δ: >C<, 31.7, 36.8, 38.5, 38.6, 42.1; >C-$\underline{C}H_3$, 14.6, 15.2, 19.5, 20.6, 32.9; >C=C'-$\underline{C}H_3$, 17.6, 25.7; >CH-$\underline{C}H_3$, 6.7; $-CH_2-$, 17.9, 22.2, 23.2, 29.3, 32.3, 34.6, 35.3, 41.1, 41.4, 43.6, 44.5; >CH–, 49.9, 58.2, 59.6; –CH=C<, 125.2 (d), 130.7 (s); >C=O, 212.7.

Epifriedelinol——Colorless plates from benzene, mp 278-280 °C (ref.[3] 279—283 °C). FD-MS m/z: 428 ($[M]^+$). Acetate: colorless plates from benzene, mp 299 °C (ref.[3] 298—299 °C), $[\alpha]_D^{23}$ +26.5° (c=1.50, $CHCl_3$) (ref.[3] +27.5°). The ^{1}H- and ^{13}C-NMR chemical shifts were in good agreement with those reported.[10,11]

Phytosterol Glucoside——The FD-MS showed $[M]^+$ ions at m/z 574 and 576. The aglycone fraction obtained by methanolysis was analyzed as the TMS ether by GLC (G-SCOT column, 50 m × 0.3 mm i.d.; liquid phase, OV-17; temp., 250 °C) to show the presence of stigmasterol (major) and β-sitosterol (minor). The methyl glycoside fraction was checked by GLC after trimethylsilylation to give peaks of methyl α- and β-D-glucopyranosides.

Shionoside A (I)——Colorless needles from EtOAc–MeOH, mp 163—164 °C, $[\alpha]_D^{22}$ −79.3° (c=1.05, MeOH). FAB-MS m/z: 471.223 ($[M+Na]^+$). $C_{21}H_{36}NaO_{10}$ requires m/z 471.220. The ^{13}C- and ^{1}H-NMR chemical shifts are given in Tables I and II.

Shionoside B (V)——Colorless needles from EtOAc–MeOH, mp 109—111 °C, $[\alpha]_D^{22}$ −50.5° (c=0.60, MeOH). FAB-MS m/z: 485.237 ($[M+Na]^+$). $C_{22}H_{38}NaO_{10}$ requires m/z 485.236. The ^{13}C- and ^{1}H-NMR chemical shifts are listed in Tables I and II.

Partial Acid Hydrolysis of I, Preparation of II——Compound I (100 mg) was heated in 1 N HCl at 70 °C for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-45 and passed through a column of Diaion CHP-20P. Water eluted a sugar fraction (30 mg). MeOH eluted a progenin (II, 65 mg), which was crystallized from EtOAc–MeOH to give colorless needles. mp 156—158 °C, $[\alpha]_D^{23}$ −31.7° (c=3.40, MeOH). FAB-MS m/z: 339.179 ($[M+Na]^+$). $C_{16}H_{28}NaO_6$ requires m/z 339.178. The ^{13}C- and ^{1}H-NMR chemical shifts are listed in Tables I and II.

Acid Hydrolysis of I and V——Compound I (100 mg) was heated in 1 N HCl at 95 °C for 3 h. After cooling, the solution was extracted with hexane. Evaporation of the hexane gave an aglycone (III) as a liquid (30 mg), $[\alpha]_D^{25}$ 0°, $[\alpha]_{350}^{25}$ +15° (c=0.75, n-hexane). EI-MS m/z: 154.136 ($[M]^+$), $C_{10}H_{18}O$ requires m/z 154.136. The ^{13}C- and ^{1}H-NMR chemical shifts are presented in Tables I and II. 3,5-Dinitrobenzoate of I (IV): colorless leaflets from EtOH, mp 91—92 °C. The ^{1}H-NMR spectrum is shown in Fig. 1A. The ^{13}C- and ^{1}H-NMR chemical shifts are given in Tables I and II.

The acidic water layer after hexane extraction was neutralized with Amberlite IRA-45 and the sugar fraction (70 mg) was obtaibed.

Compound V (30 mg) was also treated in the same manner to give an aglycone and the sugar moiety. The aglycone of V was identified as III by GLC, specific rotation, and by HPLC of its 3,5-dinitrobenzoate.

Identification of the Component Sugars of I and V——Each of I, V and apiin (2 mg) was heated in 1 N HCl–MeOH at 95 °C for 3 h. After cooling, the acidic MeOH solutions were neutralized with Ag_2CO_3, filtered and evaporated. The methanolysates were converted into the corresponding TMS ethers and checked by GLC. The results are shown in Table III.

The sugar fractions obtained by hydrolysis of I, V and apiin were converted to the corresponding TMS ethers of thiazolidine derivatives, and checked by GLC according to the method reported by Hara *et al.*[4] The results are shown in Table III.

Preparation of Camphanols (IIIa, IIIb, IIIc and IIId) from D- and L-Camphenes——Camphanols were prepared according to the method of Biellmann and d'Orchymont.[6] Thus, a 10 M solution (4 ml) of borane–dimethylsulfide complex was added dropwise to a hexane solution (40 ml) of D-camphene (14 g) at 0 °C with stirring. The mixture was stirred under an N_2 stream at room temperature for 3 h, then EtOH (40 ml), 3 N NaOH (13 ml) and 30% H_2O_2 (13 ml) were added. The reaction mixture was stirred for 1 h at 50 °C, then poured into H_2O (200 ml) and extracted with hexane (100 ml). The hexane solution was dried over Na_2SO_4 and the solvent was evaporated off to give an oily residue. The relative ratio of IIIa and IIIb roughly estimated from the GLC peak areas was 8/1. The residue was repeatedly chromatographed on silica gel using hexane–ether (9 : 1) as an eluant. Every fraction was checked by GLC, and gas chromatographically homogeneous IIIa and IIIb were obtained, both as oils. The same treatment of L-camphene gave IIIc and IIId as oils. The molecular weights of the four camphanols measured by high-resolution EI-MS were in good agreement with the theoretical value for $C_{10}H_{18}O$. The ^{13}C-NMR chemical shifts and assignments of 3,5-dinitrobenzoates are shown in Table I. The ^{1}H-NMR spectra of the 3,5-dinitrobenzoates of L-*endo*- and L-*exo*-camphanols are shown in Figures 1A and 1B, respectively. The corresponding D-enantiomers gave the same spectra.

TABLE III. Retention Times (min) of Sugar Moieties of I, II and Apiin[a]

TMS ethers of	Column oven temperature		
	130 °C	150 °C	210 °C
Methanolysate of I	10.3 10.9	6.0 6.4 6.8	
	11.5	19.5 19.8	
V	12.4 12.7	7.3	
		19.5 19.8	
apiin	10.3 10.9	6.0 6.4 6.8	
	11.5	19.5 19.8	
L-rhamnose	12.3 12.7	7.3	
D-glucose		19.5 19.8	
Thiazolidine derivatives of			
hydrolysate of I			10.4 16.5
V			12.0 16.5
apiin			10.4 16.5
D-rhamnose			12.4
L-rhamnose			12.0
D-glucose			16.5
L-glucose			17.5

a) GLC conditions: column, G-SCOT OV-17 on Silanox (0.3 mm i.d. × 50 m); injection port temp., 270 °C; carrier gas, He (0.75 ml/min).

IIIa (D-*endo*-camphanol): oil, $[\alpha]_{350}^{26}$ −5.7° (c=2.28, hexane), 3.5-dinitrobenzoate: colorless leaflets from EtOH, mp 94—95 °C. IIIb (D-*exo*-camphanol): oil, $[\alpha]_{350}^{26}$ 0° (c=2.00, hexane), 3,5-dinitrobenzoate: colorless leaflets from EtOH, mp 83—84 °C. IIIc (L-*endo*-camphanol): oil, $[\alpha]_{350}^{26}$ +7.1° (c=2.38, hexane), 3,5-dinitrobenzoate: colorless leaflets from EtOH, mp 86—88 °C. IIId (L-*exo*-camphanol): oil, $[\alpha]_{350}^{26}$ 0° (c=2.00, hexane), 3,5-dinitrobenzoate: colorless leaflets from EtOH, mp 77—78 °C.

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References and Notes

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