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Studies on the Acyl Glycosides from *Leucoseptrum japonicum* (Miq.) Kitamura *et* Murata

Toshio Miyase,*,[a] Akira Koizumi,[a] Akira Ueno,[a] Tadataka Noro,[a] Masanori Kuroyanagi,[a] Seigo Fukushima,[a] Yoshihiko Akiyama,[b] and Tsunematsu Takemoto[c]

Shizuoka College of Pharmacy,[a] 2-2-1, Oshika, Shizuoka, 422, Japan, Tsumura Juntendo Co., Ltd.,[b] 392, Tsuiji, Fujieda, Shizuoka-ken, 426, Japan and Institute of Pharmacognosy, Tokushima-Bunri University,[c] Yamashiro-cho, Tokushima, 770, Japan

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Two new acyl glycosides, leucosceptosides A (IV) and B (V), have been isolated from *Leucosceptrum japonicum* (Miq.) Kitamura *et* Murata, together with martynoside (III), acteoside (I) and an acteoside isomer (II). The structures of IV and V were determined to be 2-(3,4-dihydroxyphenylethyl) 1-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-(4-*O*-caffeyl)-glucopyranoside and 2-(3-hydroxy-4-methoxyphenylethyl) 1-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[β-D-apiofuranosyl (1→6)]-β-D-glucopyranoside, respectively, on the basis of chemical and spectral data.

Keywords——*Leucosceptrum japonicum*; Labiatae; martynoside; acteoside; acteoside isomer; leucosceptoside A; leucosceptoside B

From the fresh leaves of *Leucosesptrum japonicum* (Miq.) Kitamura *et* Murata (Japanese name: Tenninso) five flavonoids, pectolinarigenin, comanthoside A, comanthoside B, pectolinarigenin-7-*O*-β-D-glucuronic acid methyl ester and pectolinarigenin-7-*O*-β-D-glucuronide, have been isolated by Arisawa *et al.*[1]

We wish to report the isolation and structure elucidation of two new acyl glycoside, leucosceptosides A and B, from the roots of *L. japonicum*.

The fresh roots of *L. japonicum* were extracted with hot methanol and the methanolic extract was treated with *n*-butanol. The *n*-butanol-soluble fraction was chromatographed on a silica gel column to give six fractions (Fr. 1—6). After repeated chromatography (silica gel, polyamide, cellulose, Amberlite XAD-2) of these fractions, five acyl glycosides, acteoside (I), an acteoside isomer (II), martynoside (III), and leucosceptosides A (IV) and B (V), have been isolated. The ultraviolet (UV) spectra of these five compounds were similar to each other showing absorption maxima at near 330, 290 and 245 nm (Table I).

Acteoside (I)

The infrared (IR) spectrum suggested the presence of hydroxyl groups (3380 cm^{-1}), a conjugated ester (1695 cm^{-1}), a double bond (1628 cm^{-1}) and aromatic rings (1602, 1515 cm^{-1}). The proton magnetic resonance (PMR) spectrum showed the presence of a secondary methyl group [δ 1.10 (3H, d, J=6 Hz)], methylene protons [δ 2.78 (2H, t, J=7 Hz)], two anomeric protons [δ 4.36 (1H, d, J=8 Hz) and 5.17 (1H, s)], two *trans* olefinic protons as AB type signals [δ 6.28 and 7.64 (1H, each, J=15 Hz)] and aromatic protons [δ 6.4—7.1 (6H)].

Acetylation of I with acetic anhydride in pyridine afforded the nonaacetate (Ia), $C_{47}H_{54}O_{24}$. Acid hydrolysis of I afforded glucose and rhamnose in a ratio of 1 to 1. From these results, I was assumed to be acteoside, which has previously been isolated from some species of Tubiflorale.[2-5] Thus, the structure of I was established by direct comparison [thin layer chromatography (TLC), IR] of the nonaacetate (Ia) with an authentic sample.

An Acteoside Isomer (II)

The IR and PMR spectra were very similar to those of I. Acetylation of II with acetic

anhydride in pyridine afforded the nonaacetate (IIa), $C_{47}H_{54}O_{24}$. Acid hydrolysis of II afforded glucose and rhamnose in a ratio of 1 to 1. The ^{13}C-nuclear magnetic resonance (CMR) spectrum of II was similar to that of I, except that two carbons were shifted down-field. One of the two, assigned to the C-3 of glucose, shifted to δ 84.2 (Δ +2.7 ppm) and the other, assigned to the C-6 of glucose, shifted to δ 64.7 (Δ +2.6 ppm). Thus, the structure of II was established as an acteoside isomer,[5] in which the rhamnosyl and caffeoyl groups are attached to C-3 and C-6 of the glucose moiety, respectively.

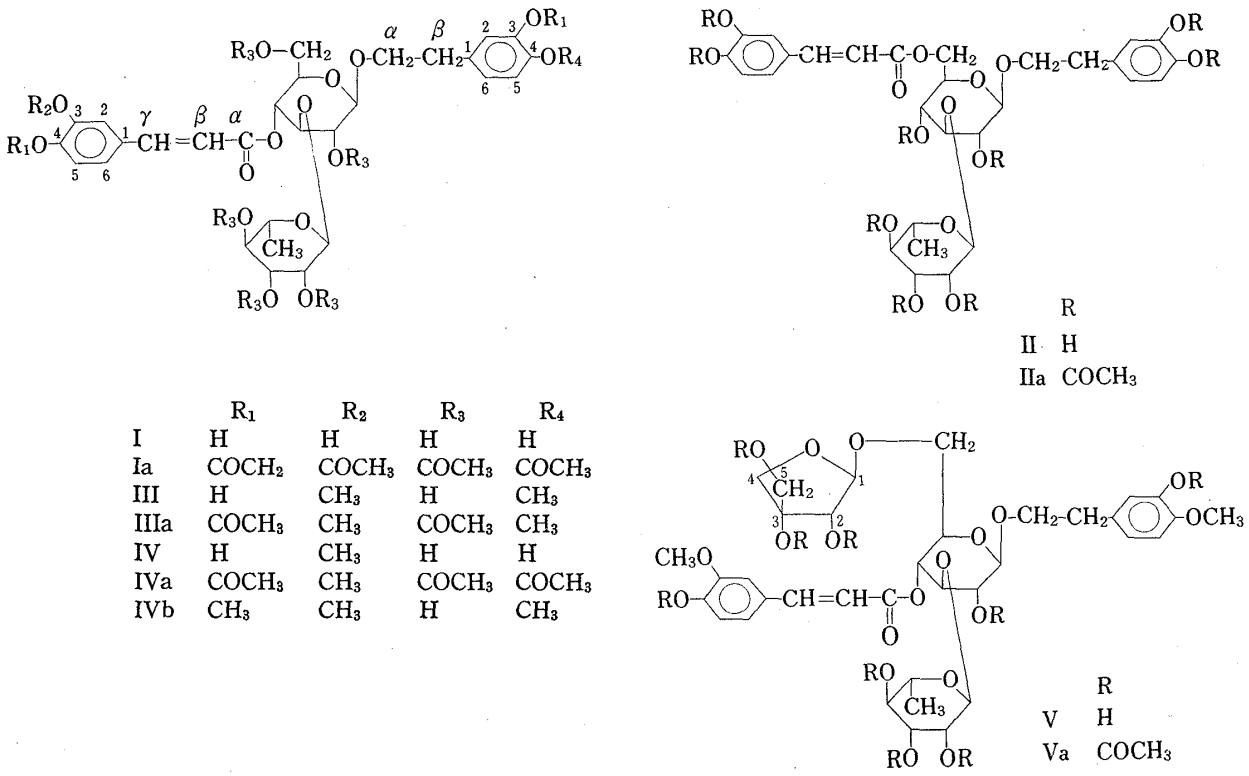
Table I. The UV Spectra of I, II, III, IV, and V in Methanol

	λ nm (log ε)		
I	330(4.27)	290(4.11)	246(sh 3.98)
II	328(4.24)	289(4.14)	246(sh 4.05)
III	327(4.33)	287(4.16)	246(sh 4.11)
IV	327(4.31)	289(4.14)	246(sh 4.00)
V	327(4.31)	287(4.13)	246(sh 4.05)

Table II. ^{13}C Chemical Shifts of I, II, III, IV, and V in Methanol-d_4

Carbon No.		I	II	III	IV	V
Aglycone moiety	1	131.4	131.4	132.7	131.5	132.9
	2	116.3	116.6	117.0	116.5	117.1
	3	144.0	144.5	147.1	144.4	147.2
	4	145.5	145.9	147.2	145.9	147.4
	5	117.0	117.1	112.8	117.1	113.0
	6	121.2	121.3	121.1	121.3	121.2
	α	71.9	72.3	72.2	72.1	72.2
	β	36.1	36.6	36.4	36.4	36.5
Caffeic (ferulic) acid moiety	1	127.4	127.7	127.5	127.6	127.6
	2	114.5	115.0	111.9	111.9	112.0
	3	149.1	149.4	150.4	150.6	150.7
	4	146.2	146.5	149.1	149.2	149.3
	5	116.3	116.4	116.6	116.3	116.6
	6	123.1	123.1	124.2	124.2	124.3
	α	168.2	169.1	168.1	168.2	168.0
	β	115.3	115.1	115.1	115.0	115.2
	γ	147.8	147.2	147.8	147.8	147.8
Glucose moiety	1	103.7	104.2	104.0	104.0	104.2
	2	75.4	75.3	75.9	75.8	74.6[d]
	3	81.5	84.2	81.5	81.4	81.4
	4	70.1	70.0[a]	70.3[b]	70.3[c]	70.3[e]
	5	75.7	75.5	75.9	76.0	76.1
	6	62.1	64.7	62.4	62.3	68.4
Rhamnose moiety	1	102.6	102.6	102.8	102.8	102.9
	2	71.9	72.3	72.2	72.1	72.1
	3	71.9	72.3	72.2	72.1	72.1
	4	73.6	74.0	73.7	73.7	73.8
	5	70.1	70.4[a]	70.6[b]	70.6[c]	70.9[e]
	6	18.2	17.9	18.4	18.4	18.4
Apiose moiety	1					111.0
	2					78.1
	3					80.5
	4					75.1[d]
	5					65.7
	OCH_3			56.5	56.5	56.6
				56.5		56.6

a, b, c, d, e) Assignments may be interchanged in each column.



	R_1	R_2	R_3	R_4
I	H	H	H	H
Ia	$COCH_2$	$COCH_3$	$COCH_3$	$COCH_3$
III	H	CH_3	H	CH_3
IIIa	$COCH_3$	CH_3	$COCH_3$	CH_3
IV	H	CH_3	H	H
IVa	$COCH_3$	CH_3	$COCH_3$	$COCH_3$
IVb	CH_3	CH_3	H	CH_3

	R
II	H
IIa	$COCH_3$

	R
V	H
Va	$COCH_3$

Chart 1

Martynoside (III)

The PMR spectrum was similar to that of I, except that the signals of two methoxyl groups were found at δ 3.80 and 3.88. Acetylation of III with acetic anhydride in pyridine afforded the heptaacetate (IIIa), $C_{45}H_{54}O_{22}$. On methanolysis of III, methyl ferulate was detected. Acid hydrolysis of III afforded glucose and rhamnose in a ratio of 1 to 1. From these results, III was assumed to be martynoside which has previously been isolated from *Martynia louisiana* Mill.[3] Thus, the structure of III was established by direct comparison (IR, PMR) of the acetate (IIIa) with an authentic sample.

Leucosceptoside A (IV)

The IR spectrum suggested the presence of hydroxyl groups (3400 cm^{-1}), a conjugated ester (1700 cm^{-1}), a double bond (1625 cm^{-1}) and aromatic rings (1600, 1590, 1515 cm^{-1}). The PMR spectrum showed signals of a secondary methyl group [δ 1.11 (3H, d, J=6 Hz)], methylene protons [δ 2.78 (2H, t, J=7 Hz)], a methoxyl group [δ 3.89 (3H, s)], two anomeric protons [δ 4.38 (1H, d, J=8 Hz) and 5.23 (1H, s)], two *trans* olefinic protons as AB type signals [δ 6.36 and 7.67 (1H, each J=15 Hz)] and aromatic protons [δ 6.5—7.3 (6H)].

Acetylation of IV with acetic anhydride in pyridine afforded the octaacetate (IVa), $C_{46}H_{54}O_{23}$. The PMR spectrum of IVa showed the signals of five alcoholic acetoxyl groups [δ 1.87, 1.94, 2.02 (3H each) and 2.10 (6H)] and three phenolic acetoxyl groups [δ 2.28 (6H) and 2.31 (3H)]. Acid hydrolysis of IV afforded glucose and rhamnose in a ratio of 1 to 1. On methanolysis of IV, methyl ferulate and 3,4-dihydroxyphenethyl alcohol were detected.

The CMR spectrum of IV was almost identical with that of I, especially in the sugar carbon region, so rhamnose was attached to the C-3 of glucose and ferulic acid was attached to the C-4 of glucose. Methylation of IV with dimethyl sulfate and potassium carbonate in acetone afforded the methyl ether (IVb), which was identical with the tetramethyl ether of acteoside (I). These results led us to conclude that the structure of leucosceptside A is IV.

Leucosceptoside B (V)

The IR spectrum suggested the presence of hydroxyl groups (3400 cm^{-1}), a conjugated ester (1702 cm^{-1}), a double bond (1628 cm^{-1}) and aromatic rings (1600, 1590, 1512 cm^{-1}). The PMR spectrum showed the signals of a secondary methyl group [δ 1.08 (3H, d, J=6 Hz)], methylene protons [δ 2.82 (2H, t, J=7 Hz)], two methoxyl groups [δ 3.82 and 3.89 (3H, each)], two anomeric protons [δ 4.35 (1H, d, J=8 Hz) and 5.16 (1H, s)], two *trans* olefinic protons as AB type signals [δ 6.35 and 7.64 (1H, each, J=16 Hz)] and aromatic protons [δ 6.6—7.2 (6H)].

In the CMR spectrum, sp^2-carbon signals were almost identical with those of III, but five more carbon signals (C×1, CH×2, CH_2×2) were found in the sugar carbon region. The partial acid hydrolysis of V afforded apiose and martynoside (III). Acetylation of V with acetic anhydride in pyridine afforded the nonaacetate (Va), $C_{54}H_{66}O_{28}$. In the PMR spectrum of Va, the signals of seven alcoholic acetoxyl groups [δ 1.88, 1.94, 2.01, 2.05, 2.10 (3H, each) and 2.03 (6H)] and two phenolic acetoxyl groups [δ 2.31 and 2.33 (3H, each)] and the signal of H-2 of apiose [δ 5.33 (1H, s)][5] were observed.

In the CMR spectrum of V, the signal of C-6 of glucose was shifted by 6.0 ppm downfield from that of III, while the chemical shifts of other carbons were almost identical. Thus, apiose was attached to the C-6 of glucose, and rhamnose to the C-4. The stereochemistry of the apiose moiety was decided to be D-β-form from the difference (−220.1°) between the molecular rotation of V (−641.3°) and that of III (−421.2°),[6] and the coupling constant (J=0 Hz) of the signal due to H-2 of apiose.[5]

These results led us to conclude that the structure of leucosceptoside B is V.

Experimental

Melting points were determined on a Yanaco MP-500 micromelting point apparatus and are uncorrected. Optical rotations were determined with a Yanaco automatic polarimeter. IR spectra were run on a JASCO IRA-2 grating infrared spectrophotometer and UV spectra on a Hitachi 124 spectrometer. PMR and CMR spectra were recorded on a JEOL FX-90Q machine (90 MHz and 22.5 MHz, respectively). Chemical shifts are given on a δ (ppm) scale with tetramethyl silane as an internal standard (s, singlet; d, doublet; t, triplet). Gas chromatography (GC) was run on a Hitachi K53 gas chromatograph.

Isolation——Fresh roots of *L. japonicum* (29 kg) were extracted with methanol (50 l×2) under reflux. The extract was concentrated under reduced pressure and the residue was suspended in water. This suspension was extracted with *n*-butanol and then the *n*-butanol-soluble fraction was concentrated *in vacuo* to afford the residue (250 g). This residue was chromatographed on a silica gel (2 kg) column using ethyl acetate and ethyl acetate–methanol as eluents. Six fractions were obtained from ethyl acetate eluate (Fr. 1—3), ethyl acetate–methanol (95: 5) eluate (Fr. 4) and ethyl acetate–methanol (90: 10) eluate (Fr. 5—6). Fr. 2 was rechromatographed on a silica gel column using chloroform–methanol (92: 8) to give martynoside (III) (1.5 g), Fr. 2-1 and Fr. 2-2. After repeated chromatography (silica gel) of Fr. 2-1, leucosceptoside A (IV) (280 mg) was isolated. Fr. 2-2 was rechromatographed on a cellulose column using water as an eluent to give acteoside (I) (12 g) and an acetoside isomer (II) (10 g). Fr. 4 was chromatographed on a silica gel column [chloroform–methanol (89: 11)], a silanized silica gel column [water–acetonitrile (95: 5)] and an Amberlite XAD-2 (water) column repeatedly to give leucosceptoside B (V) (500 mg).

Acteoside (I)——Amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 3380, 1695, 1628, 1602, 1515. UV: Table I. PMR (methanol-d_4) δ: 1.10 (3H, d, J=6 Hz, CH_3), 2.78 (2H, t, J=7 Hz, Ar–CH_2), 4.36 (1H, d, J=8 Hz, H-1 of glucose), 5.17 (1H, s, H-1 of rhamnose), 6.28 (1H, d, J=15 Hz, Ar–C=CH), 6.4—7.1 (6H, aromatic H), 7.57 (1H, d, J=15 Hz, Ar–CH=C). CMR: Table II.

Acteoside Isomer (II)——Amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 3280, 1686, 1624, 1602, 1512. UV: Table I. PMR (methanol-d_4) δ: 1.26 (3H, d, J=6 Hz, CH_3), 2.77 (2H, t, J=7 Hz, Ar–CH_2), 4.33 (3H, d, J=8 Hz, H-1 of glucose), 5.18 (1H, s, H-1 of rhamnose), 6.28 (1H, d, J=16 Hz, Ar–C=CH), 6.4—7.1 (6H, aromatic H), 7.54 (1H, d, J=16 Hz, Ar–CH=C). CMR: Table II.

Martynoside (III)——Amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 3400, 1704, 1626, 1590, 1510. UV: Table I. PMR (methanol-d_4) δ: 1.09 (3H, d, J=6 Hz, CH_3), 2.81 (2H, t, J=7 Hz, Ar–CH_2), 3.80, 3.88 (3H each, OCH_3), 4.35 (1H, d, J=8 Hz, H-1 of glucose), 5.17 (1H, s, H-1 of rhamnose), 6.34 (1H, d, J=15 Hz, Ar–C=CH), 6.5—7.2 (6H, aromatic H), 7.64 (1H, d, J=15 Hz, Ar–CH=C). CMR: Table II.

Leucosceptoside A (IV)——Amorphous powder. $[\alpha]_D^{19}$ −42.5° (c=1.59, methanol). IR ν_{max}^{KBr} cm^{-1}: 3400, 1700, 1625, 1600, 1590, 1515. UV: Table I. PMR (methanol-d_4) δ: 1.10 (3H, d, J=6 Hz, CH_3), 2.78 (2H,

t, J=7 Hz, Ar-CH_2), 3.89 (3H, s, OCH_3), 4.38 (1H, d, J=8 Hz, H-1 of glucose), 5.23 (1H, s, H-1 of rhamnose), 6.36 (1H, d, J=15 Hz, Ar-C=CH), 6.5—7.3 (6H, aromatic H), 7.67 (1H, d, J=15 Hz, Ar-CH=C). CMR: Table II.

Leucosceptoside B (V)——Amorphous powder. $[\alpha]_D^{19}$ −81.8° (c=3.43, methanol). IR ν_{max}^{KBr} cm^{-1}: 3400, 1702, 1628, 1600, 1595, 1512. UV: Table I. PMR (methanol-d_4) δ: 1.08 (3H, d, J=6 Hz, CH_3), 2.82 (2H, t, J=7 Hz, Ar-CH_2), 3.82, 3.89 (3H each, OCH_3), 4.35 (1H, d, J=8 Hz, H-1 of glucose), 5.16 (1H, s, H-1 of rhamnose), 6.35 (1H, d, J=16 Hz, Ar-C=CH), 6.6—7.2 (6H, aromatic H), 7.64 (1H, d, J=16 Hz, Ar-CH=C). CMR: Table II.

Acetylation of Acteoside (I)——Acteoside (I) (30 mg) was dissolved in pyridine (1 ml) and acetic anhydride (1 ml) and left at room temperature overnight. The reagents were evaporated off *in vacuo* and the residue was chromatographed on a silica gel column using benzene–acetone (9: 1) to give the nonaacetate (Ia) (210 mg), $C_{47}H_{54}O_{24}$, as an amorphous powder. *Anal.* Calcd for $C_{47}H_{54}O_{24}$: C, 56.43; H, 5.43. Found: C, 56.39; H, 5.51. IR ν_{max}^{KBr} cm^{-1}: 2925, 1746, 1634, 1498, 1424. PMR ($CDCl_3$) δ: 1.04 (3H, d, J=7 Hz, CH_3), 1.88, 1.94, 2.03, 2.09, 2.10, 2.28, 2.29 (3H each, s, $OCOCH_3$), 2.31 (6H, s, 2×$OCOCH_3$), 2.88 (2H, t, J=7 Hz, Ar-CH_2), 6.35 (1H, d, J=16 Hz, Ar-C=CH), 7.0—7.5 (6H, aromatic H), 7.66 (1H, d, J=16 Hz, Ar-CH=C). This was identified by direct comparison (TLC, IR) with an authentic sample.

Acid Hydrolysis of Acteoside (I), Acteoside Isomer (II), Martynoside (III) and Leucosceptoside A (IV)——A solution of a glycoside (*ca.* 2 mg) in 10% sulfuric acid (1 ml) was heated in a boiling water bath for 30 min. The solution was passed through an Amberlite IRA-45 column and concentrated to give a residue, which was reduced with sodium borohydride (*ca.* 3 mg) for 1 h. The reaction mixture was passed through an Amberlite IR-120 column and concentrated to dryness. Boric acid was removed by distillation with methanol and the residue was acetylated with acetic anhydride (1 drop) and pyridine (1 drop) at 100°C for 1 h. The reagents was evaporated off *in vacuo*. From each glycoside, glucitol acetate and rhamnitol acetate were detected in a ratio of 1 to 1 by GC. Conditions: column, 1.5% OV-17, 3 mm×1 m; column temperature, 230°C, carrier gas, N_2, t_R 1.3 min. (rhamnitol acetate), 3.8 min. (glucitol acetate).

Acetylation of Acteoside Isomer (II)——An acteoside isomer (II) (100 mg) was acetylated in the same manner as for I to give the nonaacetate (IIa) (90 mg), $C_{47}H_{54}O_{24}$, as an amorphous powder. *Anal.* Calcd for $C_{47}H_{54}O_{24}$: C, 56.43; H, 5.43. Found: C, 56.57; H, 5.87. IR ν_{max}^{KBr} cm^{-1}: 2930, 1742, 1630, 1498. PMR ($CDCl_3$) δ: 1.14 (3H, d, J=7 Hz, CH_3), 1.95, 2.03, 2.05, 2.09, 2.13 (3H each, s, $OCOCH_3$), 2.27, 2.31 (6H each, s, 2×$OCOCH_3$), 2.87 (2H, t, J=7 Hz, Ar-CH_2), 6.42 (1H, d, J=16 Hz, Ar-C=CH), 6.9—7.5 (6H, aromatic H), 7.64 (1H, d, J=16 Hz, Ar-CH=C).

Acetylation of Martynoside (III)——Martynoside (III) (200 mg) was acetylated in the same manner as for I to give the heptaacetate (IIIa) (130 mg), $C_{45}H_{54}O_{22}$, as an amorphous powder. *Anal.* Calcd for $C_{45}H_{54}O_{22}$: C, 57.08; H, 5.75. Found: C, 57.19; H, 5.73. IR ν_{max}^{KBr} cm^{-1}: 2940, 1746, 1632, 1602, 1515. PMR ($CDCl_3$) δ: 1.05 (3H, d, J=6 Hz, CH_3), 1.89, 1.95, 2.05, 2.10, 2.11, 2.32, 2.33 (3H each, s, $OCOCH_3$), 2.83 (2H, t, J=7 Hz, Ar-CH_2), 3.81, 3.86 (3H each, s, OCH_3), 6.36 (1H, d, J=16 Hz, Ar-C=CH), 6.8—7.3 (6H, aromatic H), 7.68 (1H, d, J=16 Hz, Ar-CH=C). This was identified by direct comparison (IR, PMR) with an authentic sample.

Methanolysis of Martynoside (III)——Martynoside (III) (*ca.* 1 mg) was refluxed with acetyl chloride–methanol (1: 20) (2 ml) for 20 min. The reagents were evaporated off and methyl ferulate was detected in the residue by TLC [Kiesel gel GF_{254}, benzene–acetone (8: 2) *Rf* 0.67].

Methanolysis of Leucosceptoside A (IV)——Leucosceptoside A (IV) (*ca.* 1 mg) was refluxed with acetyl chloride–methanol (1: 20) (2 ml) for 20 min. The reagents were evaporated off and methyl ferulate and 3,4-dihydroxyphenethyl alcohol were detected in the residue by TLC [Kiesel gel GF_{254}, benzene–acetone (8: 2), *Rf* 0.67 and 0.37, respectively].

Acetylation of Leucosceptoside A (IV)——Leucosceptoside A (IV) (100 mg) was acetylated in the same manner as for I to give the octaacetate (IVa) (76 mg), $C_{46}H_{54}O_{23}$, as an amorphous powder. *Anal.* Calcd for $C_{46}H_{54}O_{23}$: C, 56.67; H, 5.58. Found: C, 56.44; H, 5.63. IR ν_{max}^{KBr} cm^{-1}: 1750, 1635, 1600, 1505, 1372, 1260, 1220, 1045. PMR ($CDCl_3$) δ: 1.04 (3H, d, J=6 Hz, CH_3), 1.87, 1.94, 2.02, 2.31 (3H each, s, $OCOCH_3$), 2.10, 2.28 (3H each, s, 2×$OCOCH_3$), 2.86 (2H, t, J=7 Hz, Ar-CH_2), 3.86 (3H, s, OCH_3), 6.34 (1H, d, J=6 Hz, Ar-C=CH), 6.9—7.4 (6H, aromatic H), 7.67 (1H, d, J=16 Hz, Ar-CH=C).

Methylation of Leucosceptoside A (IV)——Dimethyl sulfate (0.2 ml) was added to a solution of leucosceptoside A (IV) (100 mg) in dry acetone (20 ml) containing anhydrous potassium carbonate (300 mg). The reaction mixture was refluxed for 1.2 h, then filtered and concentrated. The residue was purified by silica gel column chromatography using chloroform–methanol (96.5: 3.5) to give the methyl ether (IVb) (27 mg) as an amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 3480, 1710, 1630, 1600, 1515, 1465, 1420, 1265, 1160, 1140, 1025. PMR (acetone-d_6) δ: 1.13 (3H, d, J=6 Hz, CH_3), 2.85 (2H, t, J=7 Hz, Ar-CH_2), 3.78, 3.81, 3.87, 3.90 (3H each, s, OCH_3), 4.45 (1H, d, J=8 Hz, H-1 of glucose), 5.31 (1H, s, H-1 of rhamnose), 6.46 (1H, d, J=16 Hz, Ar-C=CH), 6.7—7.4 (6H, aromatic H), 7.66 (1H, d, J=16 Hz, Ar-CH=C). This was found to be identical with the tetramethyl ether of acteoside by direct comparison (TLC, IR).

Partial Acid Hydrolysis of Leucosceptoside B (V)——Leucosceptoside B (V) (200 mg) was dissolved in 1% aqueous sulfuric acid solution (20 ml) and heated for 5 min in a boiling water bath. The reaction mixture was passed through an Amberlite IRA-45 column and eluted with water (1 l) and methanol (1 l) successively.

The methanol eluate was concentrated *in vacuo* to give the residue, which was chromatographed on a silica gel column using chloroform–methanol (89: 11) to give an amorphous powder (45 mg). $[\alpha]_D^{19}$ −73.9° (c = 4.49, methanol). IR ν_{max}^{KBr} cm^{-1}: 3400, 1704, 1626, 1590, 1510. PMR (methanol-d_4) δ: 1.09 (3H, d, J=6 Hz, CH_3), 2.81 (2H, t, J=7 Hz, Ar–CH_2), 3.80, 3.88 (3H each, s, OCH_3), 4.35 (1H, d, J=8 Hz, H-1 of glucose), 5.17 (1H, s, H-1 of rhamnose), 6.34 (1H, d, J=15 Hz, Ar–C=CH), 6.5—7.2 (6H, aromatic H), 7.64 (1H, d, J=15 Hz, Ar–CH=C). This was found to be identical with martynoside (III) by direct comparison (TLC, IR, PMR). From the water eluate, apiose was detected as an alditol acetate by the same procedure as described previously. GC conditions: column, 1.5% OV-17, 3 mm×1 m, column temperature, 215°C, carrier gas, N_2, t_R, 2.0 min.

Acetylation of Leucosceptoside B (V)——Leucosceptoside B (V) (200 mg) was acetylated in the same manner as for I to give the nonaacetate (Va) (64 mg), $C_{54}H_{66}O_{28}$, as an amorphous powder. *Anal* calcd for $C_{54}H_{66}O_{28}$: C, 55.76; H, 5.72. Found: C, 55.63; H, 5.81. IR ν_{max}^{KBr} cm^{-1}: 2930, 1746, 1616, 1592, 1508. PMR ($CDCl_3$) δ: 1.05 (3H, d, J=6 Hz, CH_3), 1.88, 1.94, 2.01, 2.05, 2.10, 2.31, 2.33 (3H each, s, $OCOCH_3$), 2.03 (6H, s, 2×$OCOCH_3$), 2.80 (2H, t, J=7 Hz, Ar–CH_2), 3.81, 3.87 (3H each, s, OCH_3), 5.33 (1H, s, H-2 of apiose), 6.37 (1H, d, J=16 Hz, Ar–C=CH), 6.8—7.3 (6H, aromatic H), 7.68 (1H, d, J=16 Hz, Ar–CH=C).

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