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Studies on the Constituents of *Boschniakia rossica* Fedtsch. *et* Flerov. I.[1] Isolation and Structures of New Phenylpropanoid Glycosides, Rossicasides B, C and D

Tenji Konishi[2] and Junzo Shoji*

School of Pharmaceutical Sciences, Showa University Hatanodai, Shinagawa-ku, Tokyo, 142, Japan

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Besides *p*-coumaric acid, methyl *p*-coumarate, β-sitosterol, oleanolic acid and 3-epi-oleanolic acid, three new phenylpropanoid glycosides, rossicasides B, C and D were isolated from fresh plants of *Boschniakia rossica* (Cham. *et* Schltdl.) Fedtsch. *et* Flerov (Orobanchaceae). The structures of rossicasides B, C and D were established as *p*-hydroxycinnamyl alcohol 1-O-β-D-glucopyranosyl(1→4)-α-L-rhamnopyranosyl(1→3)-β-D-(4-O-caffeyl)-glucopyranoside (1), *p*-hydroxycinnamyl alcohol 1-O-β-D-glucopyranosyl(1→2)-β-D-(6-O-*p*-coumaryl)-glucopyranoside (2), and *p*-hydroxycinnamyl alcohol 1-O-β-D-glucopyranosyl(1→2)-β-D-(4-O-*p*-coumaryl)-glucopyranoside (3), respectively.

Keywords——phenylpropanoid glycoside; rossicaside B; rossicaside C; rossicaside D; Orobanchaceae; *Boschniakia rossica*; parasitic plant; 3-epi-oleanolic acid; oleanolic acid

A dilleniaceous plant, *Actinidia polygama* Miq. and an orobanchaceous plant, *Boschniakia rossica* (Cham. *et* Schltdl.) Fedtsch. *et* Flerov (Japanese name: Oniku) were both found to have an interesting physiological action on Felidae. A number of cyclopentanoid monoterpenes were isolated from the former, while two active substances, boschniakine and boschnialactone, have been isolated by Sakan *et al.*[3] in addition to cyclopentanoid monoterpenes, onikulactone, *cis-cis*-isoiridomyrmecin and boschnaloside, from the latter.

B. rossica Fedtsch. *et* Flerov is a parasitic plant growing on the root of *Alnus maximowiczii* Callier (Betulaceae), and the dried herb or stem has been used from ancient times as a tonic in Japan. Although the tonic principle of this crude drug has not been elucidated, the isolation and the structure determination of *p*-coumaric acid, methyl *p*-coumarate, β-sitosterol, oleanolic acid, 3-epi-oleanolic acid and three kinds of new phenylpropanoid glycosides,[4] rossicasides B(1), C(2) and D(3), are reported in this paper.

The fresh plants collected at the foot of Mt. Fuji were extracted with methanol at room temperature and the methanolic extract was treated as shown in Chart 1 to provide an ether-soluble fraction (Fr. A) and a water-soluble fraction. The ether layer (Fr. A) was extracted successively with 5% $NaHCO_3$ (Fr. A-1) and 5% NaOH (Fr. A-2), and the ether layer (Fr. A-3) was dried over Na_2SO_4 and evaporated to dryness *in vacuo*. The residue was subjected to column chromatography on silica gel to afford β-sitosterol, oleanolic acid and 3-epioleanolic acid.[5]

After acidification, Fr. A-1 and Fr. A-2 were each extracted with ether, and *p*-coumaric acid and methyl *p*-coumarate were obtained from Fr. A-1 by column chromatography on Sephadex LH-20.

The water-soluble and ether-insoluble fraction described above was exteractd with butanol saturated with water. The butanol-soluble fraction (Fr. B in Chart 1) showed four spots on a thin-layer chromatography (TLC) plate, and these were named rossicasides A, B, C and D in order of decreasing polarity. The isolation procedure for three of the glycosides is described in the experimental section.

Rossicaside B(1), $C_{36}H_{46}O_{19}$, mp 177—178°C (dec.), rossicaside C(2), $C_{30}H_{36}O_{14}$, mp 236—237.5°C (dec.), and rossicaside D(3), $C_{30}H_{36}O_{14}$, mp 198—201°C (dec.), were inferred to have

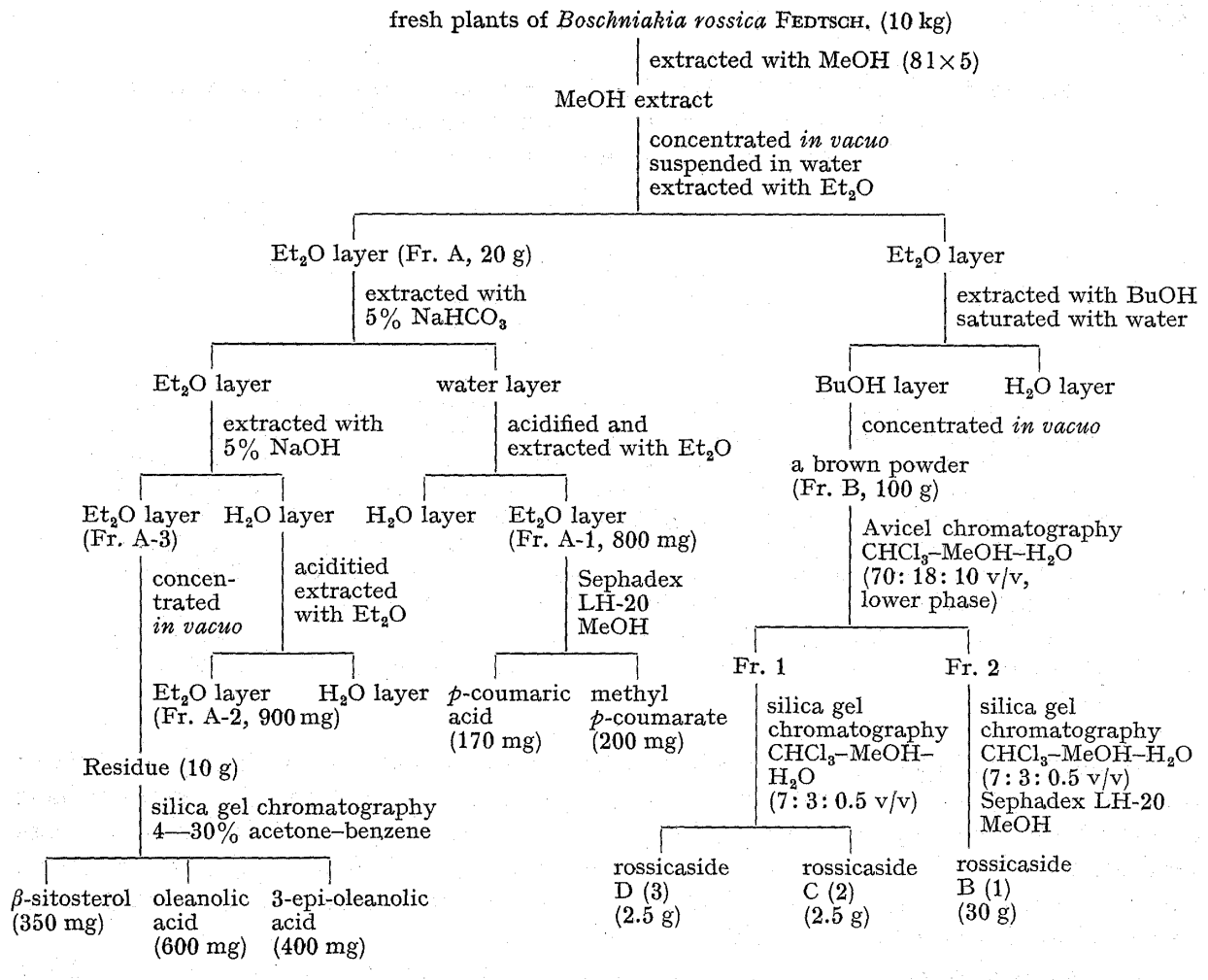

Chart 1

hydroxyl groups, an ester group, double bonds and aromatic rings on the basis of their ultraviolet (UV), infrared (IR) and proton magnetic resonance (PMR) spectra. These three rossicasides gave a positive ferric chloride test, and on acetylation in the usual way, yielded an undecaacetate (**1a**) from **1**, an octaacetate (**2a**) from **2** and an octaacetate (**3a**) from **3**.

When compounds **1**, **2**, and **3** were treated with 5% sodium methylate in methanol, a hydrolysis product (**4**), $C_{27}H_{40}O_{16}$, and methyl caffeate were formed from **1**, and a hydrolysis product (**5**), $C_{21}H_{30}O_{12}$ and methyl *p*-coumarate were obtained from **2** and **3**. The structures of **4** and **5** were established as follows. On enzymatic hydrolysis with crude hesperidinase, **4** gave *p*-coumaryl alcohol, D-glucose and L-rhamnose, while hydrolysis of **5** with β-glucosidase afforded *p*-coumaryl alcohol and D-glucose. On methylation of compounds **4** and **5** by Hakomori's method,[6] **4** gave a permethylate (**6**), $C_{37}H_{60}O_{16}$, and **5** afforded a permethylate (**7**), $C_{29}H_{46}O_{12}$. The PMR spectra of **6** and **7** each showed the signal of one aromatic methoxyl group at δ 3.81 ppm. On methanolysis with methanolic 3.7% hydrogen chloride, **6** afforded *p*-methoxycinnamyl alcohol, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, methyl 2,4,6-tri-O-methyl-D-glucopyranoside and methyl 2,3-di-O-methyl-L-rhamnopyranoside, while **7** gave *p*-methoxycinnamyl alcohol, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside and methyl 3,4,6-tri-O-methyl-D-glucopyranoside. The mass spectrum of **6** exhibited the molecular ion peak at *m/z* 760 and fragment ion peaks at *m/z* 219, 393 and 597 corresponding to O-methylated terminal glucose, glucosyl–rhamnose and glucosyl–rhamnosyl–glucose, respectively. Based on the foregoing results, the structures of **4** and **5** were deduced to be *p*-coumaryl alcohol 1-O-

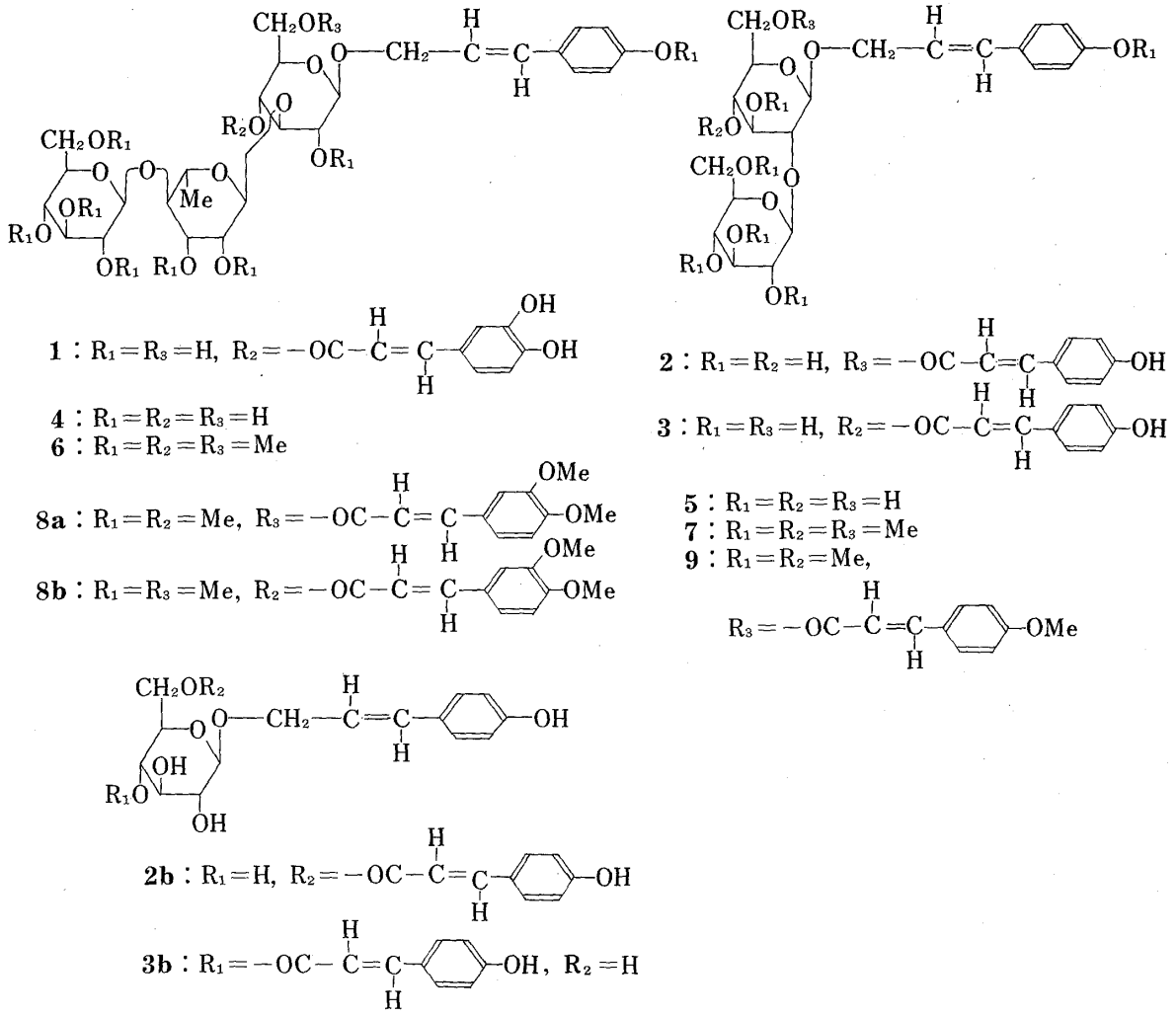

Chart 2

glucopyranosyl(1→4)-rhamnopyranosyl(1→3)-glucopyranoside and *p*-coumaryl alcohol 1-O-sophoroside, respectively.

On methylation by Hakomori's method, **1** afforded two products, (**8a**), $C_{47}H_{68}O_{19}$, mp 55—56°C, and (**8b**), $C_{47}H_{68}O_{19}$, mp 148—150°C, while compounds **2** and **3** gave two common products, **7** and **9**, $C_{38}H_{52}O_{14}$. Compounds **8a**, **8b** and **9** contain an ester linkage (IR peaks at 1705—1710 cm^{-1}), but **7** does not show any ester absorption band. On methanolysis, **8a** gave *p*-methoxycinnamyl alcohol, methyl 3,4-dimethoxycinnamate, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, methyl 2,3-di-O-methyl-L-rhamnopyranoside and methyl 2,4-di-O-methyl-D-glucopyranoside, while **8b** afforded *p*-methoxycinnamyl alcohol, methyl 3,4-dimethoxycinnamate, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, methyl 2,3-di-O-methyl-L-rhamnopyranoside and methyl 2,6-di-O-methyl-D-glucopyranoside. Consequently, it is clear that the caffeic acid in **8a** and **8b** is located at the C-6 and C-4 hydroxyl groups, respectively, of the glucose linked directly to the aglycone. On the other hand, methanolysis of compound **9** gave *p*-methoxycinnamyl alcohol, methyl *p*-methoxycinnamate, methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside and methyl 3,4-di-O-methyl-D-glucopyranoside. Therefore, *p*-coumaric acid in **9** is located at the C-6 hydroxyl group of the glucose bonded to the aglycone. The facts that, on methylation, **1** afforded two different products, **8a** and **8b**, while **2** and **3** gave the same product **9**, can be explained by migration of the acyl groups, as

Table I. ^{13}C Chemical Shifts of **1**, **2**, **3**, **4** and **5** in pyridine-d_5 at 37°C

Carbon No.	1	4	Carbon No.	2	3	5
Caffeic acid			*p*-Coumaric acid			
α′	146.7		α′	145.4	145.9	
β′	115.6		β′	130.7	130.7	
γ′	166.8		γ′	167.5	166.8	
1′	126.7		1′	126.0	126.0	
2′	114.5		2′	116.7	116.7	
3′	150.2		3′	130.7	130.7	
4′	147.3		4′	161.4	161.5	
5′	122.1		5′	130.7	130.7	
6′	128.3		6′	116.7	116.7	
p-Coumaryl alcohol			*p*-Coumaryl alcohol			
α	132.9	132.7	α	132.7	132.6	132.5
β	122.6	123.0	β	123.3	123.0	123.2
γ	70.1	70.1	γ	70.5	70.4	70.3
1	128.3	128.4	1	128.5	128.5	128.4
2	116.4	116.5	2	116.4	116.4	116.4
3	128.3	128.4	3	128.5	128.5	128.4
4	158.7	158.8	4	158.7	158.7	158.6
5	128.3	128.4	5	128.5	128.5	128.4
6	116.4	116.5	6	116.4	116.4	116.4
Glucose			Glucose			
1	103.0	103.3	1	101.9	101.8	101.8
2	72.2	72.4	2	83.8	83.7	83.8
3	84.8	85.5	3	77.8	75.4	77.8
4	75.6	69.5	4	71.1	72.1	71.1
5	76.1	78.5	5	75.2	76.3	77.8
6	62.0	62.5	6	64.3	62.1	62.5
Rhamnose			Glucose			
1	102.9	101.9	1	106.2	106.2	105.9
2	72.0	72.0	2	76.6	76.3	76.2
3	70.0	69.5	3	78.1	78.0	77.8
4	81.5	81.5	4	71.6	71.6	71.3
5	68.3	68.1	5	78.6	78.6	77.8
6	18.8	18.4	6	62.7	62.7	62.3
Glucose						
1	106.3	106.7				
2	75.6	75.8				
3	77.9	78.1				
4	71.3	71.3				
5	78.3	78.1				
6	62.5	62.5				

has been reported in the case of acteoside[4b] isolated from *Syringa vulgaris* L. (Oleaceae) and conandroside[4c] isolated from *Conandron ramoidides* (Gesneriaceae).

The location of the acyl group in **1** was determined as follows. It has been reported that the PMR spectra of the tetramethyl ethers of acteoside and conandroside reveal a triplet signal due to a methine proton bearing an ester group at δ 5.10 and 5.05 ppm (J=8.5 Hz each), respectively. Based on the PMR spectrum of **1**, which shows a triplet signal (J=9.0 Hz) corresponding to one proton at δ 5.02 ppm, it is suggested that caffeic acid of **1** is linked to the C-4 hydroxyl group of the glucose linked directly to the aglycone. Furthermore, C-13 nuclear magnetic resonance (CMR) spectra of **1** and **4** supported the proposed structure. In the CMR spectra of **1** and **4**, the C-4 signal of the glucose linked directly to the aglycone is shifted by 6.1 ppm downfield from that of **4**, while the C-3 and C-5 signals are shielded by 0.7 ppm and 2.4 ppm, respectively, and the other carbon signals of both compounds are almost

identical.[4d,7] The configurations of each monosaccharide of **1** were also assigned from the CMR spectra, and the coupling constants of the anomeric carbon with the anomeric proton (J_{H1-C1}) of the two glucoses (153.2, 159.0 Hz) and a rhamnose (169.7 Hz) revealed that the configurations of two glucoses are β-form and that of rhamnose is α-form.[8] In conculsion, the present results suggest that rossicaside B is *p*-hydroxycinnamyl alcohol 1-O-β-D-glucopyranosyl(1→4)-α-L-rhamnopyranosyl(1→3)-β-D-(4-O-caffeyl)-glucopyranoside (**1**).

The structures of **2** and **3** were established as follows. On enzymatic hydrolysis with almond emulsin, **2** gave a monoglucoside (**2b**), $C_{24}H_{26}O_9$, mp 114—120°C, and **3** afforded a monoglucoside (**3b**), $C_{24}H_{26}O_9$, mp 200—206°C (dec.). The PMR spectrum of **3b** showed a triplet signal due to a methine proton bearing an ester group at δ 4.86 ppm (J=9 Hz), but that of **2b** did not show any signal in the same region. Furthermore, CMR spectral analysis of **2** and **3** in comparison with **5** also suggested the location of *p*-coumaric acid. A downfield shift (+1.8 ppm) of C-6 and a high-field shift of C-5 (−2.6 ppm) of the glucose linked directly to the aglycone in **2** indicated that its C-6 hydroxyl group is combined with *p*-coumaric acid. Similarly, a downfield shift (+1.0 ppm) of C-4 and high-field shifts of C-3 (−2.4 ppm) and C-5 (−1.5 ppm) indicated that *p*-coumaric acid in **3** is linked to the C-4 hydroxyl group of the glucose linked directly to the aglycone. The β-configurations of the glucose moieties are proved by the coupling constants of the anomeric protons in the PMR spectra of **2** (δ 4.52, d, J=8 Hz; 4.64, d, J=8 Hz) and **3** (δ 4.58, d, J=8 Hz; 4.68, d, J=8 Hz). In conclusion, the structures of rossicasides C and D were thus elucidated to be *p*-hydroxycinnamyl alcohol 1-O-β-D-glucopyranosyl(1→2)-β-D-(6-O-*p*-coumaryl)-glucopyranoside(**2**) and *p*-hydroxycinnamyl alcohol 1-O-β-D-glucopyranosyl(1→2)-β-D-(4-O-*p*-coumaryl)-glucopyranoside(**3**), respectively. Further studies on rossicaside A and the other constituents of *Boschniakia rossica* are in progress.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus (hot-stage type) and are uncorrected. The optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter. The UV spectra were recorded with a Hitachi EPS-3 spectrometer, IR spectra with a Hitachi EPI-2 machine, PMR spectra with Hitachi R-22 (90 MHz) and JEOL FX-100 (100 MHz) spectrometers, and CMR spectra with a JEOL PFT-100 (22.15 MHz) spectrometer. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. GLC was run on a Shimadzu GC-6A unit with a flame ionization detector. Mass spectra (MS) were recorded on a Hitachi RMS-4 mass spectrometer. TLC was performed on pre-coated Kieselgel F_{254} plates (Merck) and detection was achieved by spraying ethanolic $FeCl_3$ solution or 10% H_2SO_4 followed by heating.

Extraction and Isolation——The fresh whole plants of *Boschniakia rossica* FEDTSCH. *et* FLEROV (10 kg) were chopped and extracted with MeOH (8*l*×5) at room temperature. The extract was concentrated under reduced pressure and the residue was suspended in water. This suspension was extracted with Et_2O (Fr. A, 40 g). The aqueous layer was further extracted with BuOH saturated with water and the BuOH soluble fraction was concentrated *in vacuo* to afford a brown powder (Fr. B, 600 g).

The ether solution (Fr. A, 20 g) was extracted successively with 5% $NaHCO_3$ (Fr. A-1) and 5% NaOH (Fr. A-2). The 5% $NaHCO_3$ solution containing Fr. A-1 was neutralized with 1 N HCl and extracted with Et_2O. The extract was washed with water, dried over Na_2SO_4 and evaporated to dryness (Fr. A-1). The residue (800 mg) was subjected to column chromatography on Sephadex LH-20. Elution with MeOH afforded two fractions, fr. 1 and 2. Fr. 1 was recrystallized from aq. MeOH to afford colorless needles, mp 206—208°C, IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 1690 (COOH), 1630 (olefine), 1600, 1510, 830 (aromatic ring), PMR (DMSO-d_6) δ: 6.27 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.79, 7.51 (each 2H, d, J=9 Hz, arom. H×4), 7.50 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–), 10.00 (1H, br, Ar–O<u>H</u>), 12.00 (1H, br, COO<u>H</u>). This compound was identified as *p*-coumaric acid by direct comparison with an authentic sample. Fr. 2 was recrystallized from MeOH to afford colorless needles, mp 143—145°C, IR ν_{max}^{KBr} cm^{-1}: 3390 (OH), 1690 (ester), 1630 (olefin), 1590, 1510, 830 (arom. ring), PMR (C_5D_5N) δ: 3.73 (3H, s, OCH_3), 6.44 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 7.05 (2H, d, J=8 Hz, arom. H), 7.47 (2H, d, J=8 Hz, arom. H), 7.80 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–). This compound was identified as methyl *p*-coumarate by comparison with an authentic sample (TLC, IR spectra and mixed fusion).

The ether layer (Fr. A-3) was dried over Na_2SO_4 and evaporated to dryness under reduced pressure.

The residue (10 g) was subjected to column chromatography on silica gel. Elution with benzene containing 4—30% acetone yielded three fractions (Fr. 1, 2 and 3). Fraction 1 was crystallized from MeOH to afford colorless needles (350 mg), mp 141—142°C, IR ν_{max}^{KBr} cm^{-1}: 3300—3500 (OH), which were identified as β-sitosterol by direct comparison with an authentic sample on GLC (3% SE-30 on Chromosorb W, 3 mm×2 m; column temp., 255°C; injection temp., 265°C; carrier gas, N_2 1.1 kg/cm^2; sample, TMS derivative; t_R(min) 7.9).

Fr. 2 was crystallized from MeOH to give colorless needles (600 mg), mp 295—298°C, $[\alpha]_D^{23}$ +60.8° (c=1.2, pyridine), which gave a monoacetate, mp 253—255°C, and a monomethyl ester, mp 204—209°C, in the usual way. These products were identified as oleanolic acid, oleanolic acid monoacetate and methyl oleanolate by direct comparisons with authentic samples.

Fr. 3 was purified by repeated crystallization from aqueous MeOH to give colorless needles (400 mg), mp 297—299°C, $[\alpha]_D^{15}$ +61° (c=0.39, $CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 3300—3500 (OH), 1680 (COOH), PMR (pyridine-d_5) δ: 0.83—1.22 (CH_3×7), 3.30 (1H, m), 3.56 (1H, br, C_3–H), 5.47 (1H, br, C_{12}–H). *Anal.* Calcd for $C_{30}H_{48}O_3\cdot H_2O$: C, 75.90; H, 10.62. Found: C, 75.61; H, 10.67. Acetylation of this compound with Ac_2O–pyridine and methylation with ethereal CH_2N_2 gave a monoacetate and a monomethyl ester, respectively. Monoacetate: colorless needles from MeOH, mp 275°C, $[\alpha]_D^{22}$ +34.5° (c=1.0, $CHCl_3$), IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1740 (ester), 1690 (COOH), PMR ($CDCl_3$) δ: 0.76—1.19 (CH_3×7), 2.07 (3H, s, $OCOCH_3$), 2.84 (1H, m), 4.62 (1H, br, C_3–H), 5.28 (1H, br, C_{12}–H), MS (m/z): 498 (M^+). *Anal.* Calcd for $C_{32}H_{50}O_4$: C, 77.22; H, 9.92. Found: C, 77.13; H, 9.75. Monomethyl ester: colorless needles from MeOH, mp 209—210°C, $[\alpha]_D^{22}$ +54.1° (c=1.4, $CHCl_3$), IR ν_{max}^{Nujol} cm^{-1}: 3530 (OH), 1710 ($COOCH_3$), PMR ($CDCl_3$) δ: 0.84—1.13 (CH_3×7), 2.84 (1H, dd, J=4, 13 Hz, C_{18}–H), 3.40 (1H, br, C_3–H), 3.60 (3H, s, OCH_3), 5.26 (1H, br, C_{12}–H).

The monomethyl ester described above was oxidized with 10% CrO_3 in AcOH for 10 h at room temperature to afford colorless needles in 90% yield, $C_{31}H_{48}O_3$, mp 180—183°C, $[\alpha]_D^{22}$ +87.1° (c=1.3, $CHCl_3$), IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1750 ($COOCH_3$), 1705 (>C=O), PMR ($CDCl_3$) δ: 0.84—1.20 (CH_3×7), 2.92 (1H, dd, J=4, 13 Hz, C_{18}–H), 3.66 (3H, s, OCH_3), 5.34 (1H, t, J=4 Hz, C_{12}–H). *Anal.* Calcd for $C_{31}H_{48}O_3$: C, 79.43; H, 10.32. Found: C, 79.00; H, 10.64. This compound was identified as methyl 3-oxo-oleanolate which was formed from methyl oleanolate in the same oxidation. Consequently, the compound isolated from Fr. 3 was proved to be 3-epi-oleanolic acid.

The BuOH extract (Fr. B, 100 g) was subjected to column chromatography on cellulose powder (Avicel) with $CHCl_3$–MeOH–H_2O (70: 18: 10 v/v, lower phase), and the eluate was separated into two fractions, Fr. 1 (15.0 g) and Fr. 2 (65 g). Fr. 1 was chromatographed on silica gel, using $CHCl_3$–MeOH–H_2O (7: 3: 0.5 v/v), to afford rossicaside C (**2**, 2.5 g) and rossicaside D (**3**, 2.5 g), while Fr. 2 was repeatedly chromatographed on silica gel, using $CHCl_3$–MeOH–H_2O (7: 3: 0.5 v/v), and on Sephadex LH-20 using MeOH to give rossicaside B (**1**, 30 g).

Properties of Rossicasides B(1), C(2) and D(3)——Rossicaside B (**1**): Colorless needles from aq. MeOH, mp 175—178.5°C (dec.), $[\alpha]_D^{17}$ −66.6° (c=1.1, MeOH), UV λ_{max}^{EtOH} nm (log ε): 263 (4.39), 281 (4.27), 299 (4.07), 340 (4.13), IR ν_{max}^{KBr} cm^{-1}: 3200—3500 (OH), 1705 (ester), 1630, 1610 (olefin), 1595, 1515, 810 (arom. ring), PMR (CD_3OD) δ: 4.15 (2H, d, J=7 Hz, anomeric H), 5.26 (1H, s, anomeric H), 5.02 (1H, t, J=9 Hz, methine H). *Anal.* Calcd for $C_{36}H_{46}O_{19}\cdot H_2O$: C, 53.99; H, 6.04. Found: C, 54.29; H, 6.16. Rossicaside C (**2**): colorless needles from MeOH, mp 236—237.5°C (dec.), $[\alpha]_D^{19}$ −18.3° (c=1.1, pyridine), UV λ_{max}^{EtOH} nm (log ε): 232 (4.45), 269 (4.78), 300 (4.69), 310 (4.73), IR ν_{max}^{KBr} cm^{-1}: 3200—3500 (OH), 1675 (ester), 1700 (shoulder), 1628, 1605 (olefin) 1580, 1510, 835 (arom. ring), PMR (CD_3OD) δ: 4.36 (2H, w 1/2 h, 3 Hz, $COOC\underline{H}_2$–), 4.52 (1H, d, J=8 Hz, anomeric H), 4.64 (1H, d, J=8 Hz, anomeric H). *Anal.* Calcd for $C_{30}H_{36}O_{14}\cdot 1/2H_2O$: C, 57.23; H, 5.92. Found: C, 57.34; H, 5.76. Rossicaside D (**3**): colorless needles from aq. MeOH, mp 198—201.5°C (dec.), $[\alpha]_D^{20}$ −58.3° (c=0.5, MeOH), UV λ_{max}^{EtOH} nm (log ε): 230 (4.43), 272 (4.51), 300 (4.53), 312 (4.56), IR ν_{max}^{KBr} cm^{-1}: 3200—3500 (OH), 1710 (ester), 1625 (olefin), 1600, 1510, 830 (arom. ring), PMR (CD_3OD) δ: 4.58 (1H, d, J=8 Hz, anomeric H), 4.68 (1H, d, J=8 Hz, anomeric H), 4.88 (1H, t, J=9 Hz, methine H). *Anal.* Calcd for $C_{30}H_{36}O_{14}\cdot 2/3H_2O$: C, 56.96; H, 5.95. Found: C, 56.89; H, 5.80.

Acetylation of 1, 2 and 3——Compounds **1** (200 mg), **2** (100 mg) and **3** (50 mg) were each dissolved in pyridine–acetic anhydride (1: 1 v/v) and the solution was allowed to stand overnight at room temperature. The reaction mixture was poured into ice-water and the precipitate was filtered off. Each crude acetate was purified by column chromatography on silica gel using benzene–acetone (5: 1 or 10: 1 v/v). Rossicaside B undecaacetate: a white powder from aq. MeOH, (mp 107—109°C), $[\alpha]_D^{26}$ −51.8° (c=1.0, MeOH), UV λ_{max}^{EtOH} nm (log ε): 212 (4.94), 255 (4.95), 285 (4.56), 295 (4.45). IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1750 (ester), 1635 (olefin), 1516, 1502, 835 (arom. ring), PMR ($CDCl_3$) δ: 1.08 (3H, d, J=6 Hz, CH_3), 1.98—2.14 (24H, OAc×8), 2.29—2.31 (9H, arom. OAc×3), 6.16 (1H, td, J=6, 16 Hz, Ar–CH=C$\underline{H}$–CH_2–), 6.35 (1H, d, J=16 Hz, Ar–C$\underline{H}$=CH–CO–), 6.61 (1H, d, J=16 Hz, Ar–C$\underline{H}$=CH–CH_1–), 7.03—7.38 (7H, arom. H×7), 7.64 (1H, d, J=16 Hz, Ar–CH=C$\underline{H}$–CO–). *Anal.* Calcd for $C_{58}H_{68}O_{30}$: C, 55.95; H, 5.50. Found: C, 56.07; H, 5.78. Rossicaside C octaacetate: colorless needles from MeOH, mp 110—111°C, $[\alpha]_D^{20}$ −2.2° (c=1.2, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 251 (4.40), 260 (4.61), 284 (4.50), 295 (4.43). IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1760, 1740, 1715 (ester), 1635 (olefin), 1600, 1580, 1505, 830 (arom. ring). PMR ($CDCl_3$) δ: 1.98—2.07 (18H, OAc×6), 2.27, 2.30 (each s, arom. OAc), 6.21 (1H, td, J=6, 16 Hz, Ar–CH=C$\underline{H}$–), 6.39 (1H, d, J=16 Hz, Ar–C$\underline{H}$=CH–), 6.65 (1H, d, J=16 Hz, Ar–C$\underline{H}$=CH–), 7.02—7.50 (8H, arom. H×8), 7.68 (1H, d, J=16 Hz, Ar–CH=C$\underline{H}$–), MS (m/z): 782 (M^+—

(·CH–CH=CH-ϕ-OAc)), 766 (M^+–(·CH–CH=CH-ϕ-OAc)), 765 (M^+–(·O–CH_2–CH=CH-ϕ-OAt)), 331 (terminal peracetylated hexose). *Anal.* Calcd for $C_{46}H_{52}O_{22}$: C, 57.74; H, 5.47. Found: C, 57.48; H, 5.09. Rossicaside D octatacetate: colorless needles from MeOH, mp 190—191°C, $[\alpha]_D^{20}$ −31.6° (c=1.3, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 257 (4.58), 263 (4.59), 285 (4.55), 295 (4.50). IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1760—1730, 1700 (ester), 1620 olefin), 1590, 1505, 840 (arom. ring). PMR ($CDCl_3$) δ: 1.97—2.04 (18H, OAc×6), 2.31 (6H, arom. OAc×2), 6.23 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.29 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.67 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 7.05—7.52 (8H, arom. H×8), 7.64 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–), MS (m/z): 782 (M^+–(·CH–CH=CH-ϕ-OAc)), 766 (M^+–(·CH–CH=CH-ϕ-OAc)), 765 (M^+–(·OCH_2–CH=CH-ϕ-OAc)), 331 (terminal peracetylated hexose). *Anal.* Calcd for $C_{46}H_{52}O_{22}$: C, 57.74; H, 5.47. Found: C, 57.30; H, 5.47.

Deacylation of 1, 2 and 3 with 5% NaOMe——A solution of **2** (100 mg) or **3** (150 mg) in methanolic 5% NaOMe (10 ml) was allowed to stand for 5 h at room temperature. After dilution with water, the reaction mixture was acidified with 1 N HCl and extracted with ether. The ether layer was washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on silica gel. Elution with benzene–acetone (5: 1 v/v) afforded the same product in each case (25 mg from **2** and 15 mg from **3**), as colorless needles from aq. MeOH. The material was identified as methyl p-coumarate by direct comparison.

The aqueous layer was neutralized with Amberlite IRA-410 and evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel. Elution with $CHCl_3$–MeOH–H_2O (7: 3: 0.2 v/v) afforded the same product in each case (**5**, 40 mg from **2** and 70 mg from **3**), colorless needles from MeOH, mp 198—201°C (dec.), $[\alpha]_D^{20}$ −15.4° (c=2.9, MeOH), UV λ_{max}^{EtOH} (log ε): 264 (4.95), 296 (3.89), 307 (3.12), IR ν_{max}^{Nujol} cm^{-1}: 3300—3500 (OH), 1610 (olefin), 1590, 1510, 835 (arom. ring). PMR (DMSO-d_6) δ: 4.36 (2H, d, J=6 Hz, anomeric H×2), 6.09 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.51 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.66 (2H, d, J=9 Hz, arom. H×2), 7.20 (2H, d, J=9 Hz, arom. H×2), 9.53 (1H, s, Ar–O<u>H</u>). *Anal.* Calcd for $C_{21}H_{30}O_{12}\cdot 1/2H_2O$: C, 52.17; H, 6.46. Found: C, 52.26; H, 6.50.

Compound **1** (1.0 g) was treated with 5% NaOMe by the procedure described above to give methyl caffeate (100 mg) and **4** (300 mg). Methyl caffeate: Colorless needles from aq. MeOH, mp 167—168°C. This product was identified as methyl caffeate by direct comparison with an authentic sample. **4**: a white powder from aq. MeOH, (mp 153—156°C (dec.)), $[\alpha]_D^{20}$ −36.5° (c=1.0, MeOH), UV λ_{max}^{EtOH} nm (log ε): 264 (4.75), 295 (3.90), 307 (3.60). IR ν_{max}^{Nujol} cm^{-1}: 3300—3500 (OH), 1610 (olefin), 1590, 1510, 845 (arom. ring), PMR (DMSO-d_6) δ: 1.24 (3H, d, J=7 Hz, sec. CH_3), 4.28 (1H, d, J=7 Hz, anomeric H), 4.43 (1H, d, J=6 Hz, anomeric H), 5.42 (1H, s, anomeric H), 6.11 (1H, td, J=6, 16 Hz, Ar-CH=C<u>H</u>–), 6.55 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.75 (2H, d, J=8 Hz, arom. H×2), 7.24 (2H, d, J=8 Hz, arom. H×2), 9.67 (1H, br, Ar–O<u>H</u>). *Anal.* Calcd for $C_{27}H_{40}O_{16}\cdot 1/3H_2O$: C, 51.75; H, 6.54. Found: C, 51.75; H, 6.89.

Enzymatic Hydrolysis of 4 and 5——Compound **4** (400 mg) was incubated with crude hesperidinase (100 mg) for 48 h at 32°C, and the resulting precipitate was filtered off. The filtrate was evaporated to dryness *in vacuo* and the residue was chromatographed on Sephadex LH-20, using MeOH, to give a mixture of monosaccharides and an aglycone, which was recrystallized from water to give colorless needles (25 mg), mp 103—104°C. This compound was identified as p-coumaryl alcohol by direct comparison with an authentic sample. A mixture of monosaccharides was examined by TLC and GLC. TLC (solvent: $CHCl_3$–MeOH–H_2O (7: 3: 0.5 v/v), Rf 0.10 (glucose), 0.40 (rhamnose). GLC (5% SE-52 on Chromosorb W, 3 mm×2 m; column temp., 175°C; injection temp., 240°C; carrier gas, N_2 1.0 kg/cm^2; sample TMS derivative): t_R (min) 16.8, 24.2 (glucose), 5.5, 7.3 (rhamnose). The mixture of glucose and rhamnose (100 mg) was separated by column chromatography on silica gel, using $CHCl_3$–MeOH–H_2O (7: 3: 0.4 v/v), into D-glucose (28.6 mg), $[\alpha]_D^{15}$ +47.0° (c=1.9, H_2O), lit.[9] $[\alpha]_D$ +52.7°, and L-rhamnose (16 mg), $[\alpha]_D^{18}$ +7.9° (c=1.9, H_2O), lit.[9] $[\alpha]_D$ +8.9°.

Compound **5** (50 mg) was hydrolyzed with β-glucosidase by the procedure described above to afford D-glucose and p-coumaryl alcohol.

Permethylation of 4 and 5 by Hakomori's Method——According to Hakomori's method, NaH (500 mg) defatted with benzene and petroleum ether was stirred with dimethylsulfoxide (DMSO, 25 ml) at 70°C for 1 h under an N_2 gas flow. A solution of **4** (400 mg) in DMSO (5 ml) was then added to this reagent and the mixture was stirred for 1 h at room temperature under an N_2 gas flow. CH_3I (5 ml) was added to the solution and the reaction mixture was stirred at room temperature for 3 h. After dilution with water, the mixture was extracted with Et_2O and the Et_2O layer was washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a column of silica gel with benzene–acetone (5: 1 v/v) to afford a permethylate of **4** (**6**). Compound **5** (250 mg) was methylated in a similar manner to afford a permethylate of **5** (**7**). **6**: a colorless syrup, $[\alpha]_D^{17}$ −25.0° (c=2.8, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 260 (4.48), 292 (3.76), 304 (3.56), IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1608 (olefin), 1575, 1510, 840 (arom. ring), PMR ($CDCl_3$) δ: 1.30 (3H, d, J=6 Hz, sec. CH_3), 3.38—3.64 (27H, OCH_3×9), 3.81 (3H, s, arom. OCH_3), 4.37 (1H, d, J=8 Hz, anomeric H), 4.66 (1H, d, J=7 Hz, anomeric H), 5.40 (1H, s, anomeric H), 6.16 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.57 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.86, 7.32 (each 2H, d, J=9 Hz, arom. H). MS (m/z): 760 (M^+), 613 [M–(·CH_2–CH=CH-ϕ-OCH_3)]$^+$, 597 [M–(OCH_2–CH=CH-ϕ-OCH_3)]$^+$ and [(glucose-rhamnose-

glucose)$(OMe)_9]^+$, 541 [M−glucose $(OMe)_4]^+$, 393 [(glucose-rhamnose) $(OMe)_6]^+$, 367 (M−(glucose-rhamnose) $(OMe)_6]^+$, 219 [glucose $(OMe)_4]^+$. *Anal.* Calcd for $C_{37}H_{60}O_{16}$: C, 58.40; H, 7.95. Found: C, 58.38; H, 8.17. **7**: a colorless syrup, $[\alpha]_D^{17}$ −6.8° (c=0.7, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 264 (4.39), 290 (3.30), 302 (3.17), IR $\nu_{max}^{CCl_4}$: OH (nil), 1605 (olefin), 1570, 1505, 830 (arom. ring). PMR ($CDCl_3$) δ: 3.35, 3.41, 3.52, 3.54, 3.62 (each 3H, s, OCH_3), 3.64 (6H, s, $OCH_3\times2$), 3.81 (3H, s, arom. OCH_3), 4.48 (1H, d, J=7 Hz, anomeric H), 4.55 (1H, d, J=7 Hz, anomeric H), 6.15 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.61 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.85, 7.32 (each 2H, d, J=9 Hz, arom. H). *Anal.* Calcd for $C_{29}H_{46}O_{12}$: C, 59.37; H, 7.92. Found: C, 59.31; H, 7.72.

Methanolysis of 6 and 7 with Methanolic HCl——A solution of **6** or **7** (5 mg) in methanolic 3.7% HCl (2 ml) was refluxed for 3 h. The reaction mixture was neutralized with Ag_2CO_3 and filtered. The filtrate was evaporated to dryness *in vacuo*, and the residue was dissolved in MeOH and subjected to column chromatography on Sephadex LH-20 to yield an aglycone and methylated monosaccharides. The aglycone was identified as *p*-methoxycinnamyl alcohol by TLC (hexane–AcOEt (6: 1 v/v), *Rf* 0.23). The methylated monosaccharides were examined by TLC (benzene–acetone (1: 1 v/v)) and GLC (5% NPGS on Chromosorb W, 3 mm×2 m; column temp., 155°; injection temp., 180°; carrier gas, N_2 1 kg/cm²). **6**: *Rf* 0.35, 0.49; t_R (min) 17.0, 26.0 (methyl 2,4,6-tri-O-methyl-D-glucopyranoside), *Rf* 0.50, 0.61; t_R (min) 7.9, 11.2 (methyl 2,3-di-O-methyl-L-rhamnopyranoside), *Rf* 0.73, 0.80; t_R (min) 6.0, 8.5 (methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside). **7**: *Rf* 0.51, 0.58; t_R (min) 11.6, 17.3 (methyl 3,4,6-tri-O-methyl-D-glucopyranoside), *Rf* 0.73, 0.80; t_R (min) 6.0, 8.5 (methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside).

Permethylation of 1, 2 and 3 by Hakomori's Method——**1** (1.0 g), **2** (100 mg) and **3** (100 mg) were each methylated by Hakomori's method as described above and the products were purified by column chromatography on silica gel using benzene–acetone (5: 1 or 10: 1 v/v). Compound **1** gave **8a** (190 mg) and **8b** (350 mg), while **2** and **3** gave **7** (25 mg) and **9** (15 mg), respectively. **8a**: a white powder from aq. MeOH, (mp 55—65°C), $[\alpha]_D^{23}$ −48.3° (c=1.4, MeOH), UV λ_{max}^{EtOH} nm (log ε): 263 (4.83), 293 (4.65), 305 (4.36), 324 (4.32). IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1705 (ester), 1625, 1605 (olefin), 1570, 1505, 840 (arom. ring), PMR ($CDCl_3$) δ: 1.31 (3H, d, J=6 Hz, sec. CH_3), 3.43—3.67 (24H, $OCH_3\times8$), 3.84, 3.85, 3.96 (3H each, s, arom. OCH_3), 4.42 (1H, d, J=7 Hz, anomeric H), 4.51 (2H, d, J=4 Hz, $COOC\underline{H}_2$–), 4.71 (1H, d, J=7 Hz, anomeric H), 5.45 (1H, s, anomeric H), 6.20 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.43 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.65 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.88—7.36 (7H, arom. H×7), 7.75 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–). *Anal.* Calcd for $C_{47}H_{68}O_{19}$: C, 60.24; H, 7.32. Found: C, 60.03; H, 7.60. **8b**: colorless needles from aq. MeOH, mp 148—150°C, $[\alpha]_D^{23}$ −103.36° (c=1.2, MeOH), UV λ_{max}^{EtOH} nm (log ε): 260 (4.49), 296 (4.29), 305 (4.27), 328 (4.35). IR ν_{max}^{Nujol} cm^{-1}: OH (nil), 1710 (ester), 1625, 1605 (olefin), 1595, 1575, 1510, 840 (arom. ring). PMR ($CDCl_3$) δ: 1.22 (3H, d, J=5 Hz, sec. CH_3), 3.49—3.71 (24H, $OCH_3\times8$), 3.88—4.00 (9H, arom. $OCH_3\times3$), 4.57 (1H, d, J=8 Hz, anomeric H), 4.61 (1H, d, J=7 Hz, anomeric H), 5.10 (1H, t, J=9 Hz, –O–C<u>H</u>–), 5.41 (1H, s, anomeric H), 6.27 (1H, td, J=6, 16 Hz, Ar–CH=CH–), 6.32 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.71 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.96—7.49 (7H, arom. H×7), 7.72 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–). *Anal.* Calcd for $C_{47}H_{68}O_{19}$: C, 60.24; H, 7.32. Found: C, 60.09; H, 7.46. **9**: a colorless syrup, $[\alpha]_D^{17}$ −18.0° (c=1.8, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 260 (4.56), 295 (4.18), 305 (4.13), IR $\nu_{max}^{CCl_4}$ cm^{-1}: OH (nil), 1710 (ester), 1630, 1605 (olefin), 1570, 1508, 835 (arom. ring). PMR ($CDCl_3$) δ: 3.36, 3.52, 3.55, 3.63 (3H each, s, OCH_3), 3.62 (6H, $OCH_3\times2$), 3.79, 3.85 (3H each, s, arom. OCH_3), 4.56 (1H, d, J=8 Hz, anomeric H), 4.64 (1H, d, J=7 Hz, anomeric H), 6.16 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.36 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.57 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.82—7.46 (8H, arom. H×8), 7.68 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–). *Anal.* Calcd for $C_{38}H_{52}O_{14}$: C, 62.28; H, 7.15. Found: C, 62.09; H, 6.96.

Methanolysis of 8a, 8b and 9——Compounds **8a** (10 mg), **8b** (15 mg) and **9** (5 mg) were each refluxed with methanolic 3.7% HCl for 3 h and methanolysate was treated in a manner similar to that described above. Each residue was dissolved in MeOH and subjected to column chromatography on Sephadex LH-20 to separate aromatic compounds and O-methylated monosaccharides. The aromatic compounds were purified by silica gel column chromatography, using hexane–acetone (7: 1 v/v). *p*-Methoxycinnamyl alcohol was detected by TLC (solvent: hexane–AcOEt (6: 1 v/v) *Rf* 0.23) in each methanolysate (**8a**, **8b**, **9**). Methyl 3,4-dimethoxycinnamate was isolated from the methanolysates of **8a** and **8b**, colorless needles from MeOH, mp 70.5—71.5°C. This product was identified by TLC and mixed fusion with an authentic sample. Methyl *p*-methoxycinnamate was obtained from the methanolysate of **9**, colorless needles from EtOH, mp 90.5—91.5°C; it was identified by TLC and mixed fusion with an authentic sample.

The methylated monosaccharides were examined by TLC (benzene–acetone (1: 1 v/v)) and GLC (5% NPGS on Chromosorb W, 3 mm×2 m; column temp., 150°; injection temp., 180°C for **8a** and **8b**, 170° for **9**; carrier gas, N_2 1.2 kg/cm²). **8a**: *Rf* 0.22, 0.33, t_R (min) 47.5, 71.5 (methyl 2,4-di-O-methyl-D-glucopyranoside); *Rf* 0.50, 0.61, t_R (min) 8.3, 12.6 (methyl 2,3-di-O-methyl-L-rhamnopyranoside), *Rf* 0.73, 0.80, t_R (min) 6.3, 9.1 (methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside). **8b**: 0.19, 0.27, t_R (min) 40.0, 73.5 (methyl 2,6-di-O-methyl-D-glucopyranoside); *Rf* 0.50, 0.61, t_R (min) 8.3, 12.6 (methyl 2,3-di-O-methyl-L-rhamnopyranoside); *Rf* 0.73, 0.80, t_R (min) 6.3, 9.1 (methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside). **9**: *Rf* 0.35, t_R (min) 42.8 (methyl 3,4-di-O-methyl-D-glucopyranoside); *Rf* 0.73, 0.80, t_R (min) 11.6, 17.3 (methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside).

Enzymatic Partial Hydrolysis of 2 and 3——A solution of **2** (500 mg) or **3** (500 mg) in H_2O (20 ml) was

incubated with almond emulsin (50 mg) for 30 h at 37°C. The reaction mixture was filtered and the filtrate was evaporated to dryness *in vacuo*. Each residue was subjected to column chromatography on silica gel, using $CHCl_3$–MeOH (10: 1 v/v), to give a white powder, **2b** (30 mg) or **3b** (80 mg). **2b**: a white powder from aq. MeOH, (mp 114—120°C), $[\alpha]_D^{24}$ −36.5° (c=0.85, MeOH), UV λ_{max}^{EtOH} nm (log ε): 270 (4.35), 300 (4.38), 310 (4.40). IR ν_{max}^{KBr} cm^{-1}: 3100—3500 (OH), 1680 (ester), 1625, 1600 (olefin), 1585, 1508, 830 (arom. ring). PMR (acetone-d_6) δ: 4.38 (2H, d, J=3 Hz, –COOC<u>H</u>$_2$–), 4.44 (1H, d, J=7 Hz, anomeric H), 6.14 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.40 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.72 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.77, 6.88, 7.27, 7.55 (2H each, d, J=9 Hz, arom. H), 7.65 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–). *Anal.* Calcd for $C_{24}H_{26}O_9 \cdot 1/2H_2O$: C, 61.66; H, 5.86. Found: C, 61.72; H, 5.88. **3b**: a white powder from aq. MeOH, (mp 200—206°C), $[\alpha]_D^{24}$ −12.0° (c=0.4, MeOH), UV λ_{max}^{EtOH} nm (log ε): 270 (4.24), 300 (4.25), 310 (4.27). IR ν_{max}^{KBr} cm^{-1}: 3200—3500 (OH), 1680 (ester), 1630, 1600 (olefin), 1585, 1508, 830 (arom. ring). PMR (CD_3OD) δ: 4.49 (1H, d, J=7 Hz, anomeric H), 4.86 (1H, t, J=8 Hz, –COO–C<u>H</u>–), 6.12 (1H, td, J=6, 16 Hz, Ar–CH=C<u>H</u>–), 6.33 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.56 (1H, d, J=16 Hz, Ar–C<u>H</u>=CH–), 6.72, 6.75, 7.24, 7.65 (2H each, d, J=8 Hz, arom. H), 7.65 (1H, d, J=16 Hz, Ar–CH=C<u>H</u>–). *Anal.* Calcd for $C_{24}H_{26}O_9 \cdot 2/3H_2O$: C, 61.27; H, 5.86. Found: C, 61.19; H, 5.72.

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References and Notes

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2) Present address: *Kyoto College of Pharmacy, Yamashina-ku, Kyoto, 607, Japan.*
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