The Resin Glycosides from the Sweet Potato (*Ipomoea batatas* L. Lam.)

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Four new and two known ether-soluble resin glycosides were isolated from popular sweet potato (the roots of *Ipomoea batatas* L. Lam., Kokei 14 go, Convolvulaceae) in Japan. Unlike ester-type dimers, batatins I and II, obtained from other sweet potato (*Ipomoea batabas* var. *batatas*), the glycosides were tetra or pentasaccharide monomers in which the sugar moieties are partially acylated by organic acids and combine with the aglycone, jalapinolic acid, to form a macrocyclic ester.

Key words resin glycoside; sweet potato; *Ipomoea batatas*; Convolvulaceae; macrocyclic ester

The sweet potato (*Ipomoea batatas*) is called "camote" in Mexico, and this tuber is a common vegetable throughout the Orient, and is also an important raw material for making starch or alcohol. This plant belongs to the Convolvulaceae family, which is known to contain characteristic constituent, resin glycoside. In our previous study, we found that a sweet potato, locally grown Brazilian cultivar (cv. Simon), contained small amounts of resin glycoside, and isolated five compounds, simonins I—V.[1] Recently, Mexican researchers isolated two ester-type dimers, batatins I and II, together with a monomer, batatinoside, from the resin glycoside fraction of common sweet potato (*Ipomoea batatas* var. *batatas*).[2] Concerning the ester-type dimers, we first isolated merremin from the roots of *Merremia hungaiensis* (Convolvulaceae).[3] Almost all resin glycosides so far isolated from *Ipomoea* species were monomers, and, including the above merremin and batatins, only three examples of isolation of the ester-type dimers have been reported.[4]

This study was undertaken to survey whether these ester-type dimers are present in popular sweet potato (*Ipomoea batatas* L. Lam., Kokei 14 go), which is widely cultivated in Japan.

The $CHCl_3$–acetone extract of the fresh roots was shaken with $CHCl_3$–MeOH–H_2O (1 : 1 : 1) and the lower layer gave, on evaporation, a fraction, which was chromatographed on Sephadex LH-20 (MeOH) to give a crude resin glycoside. This fraction was subjected successively to silica gel and Cosmosil 75C18-OPN column chromatographies. The final separation was achieved by HPLC to give four novel resin glycosides (**1**—**4**) together with simonin IV[1] and operculin VII.[5]

Results and Discussion

A part of the crude resin glycoside fraction was saponified with 10% KOH and then fractionated into an organic and glycosidic acid fractions. The former was examined by GC, which revealed the presence of five acids, isobutyric (Iba), 2-methylbutyric (Mba), *n*-decanoic (Deca), *n*-dodecanoic (Dodeca), and *trans*-cinnamic (Cna) acids. The absolute configuration of Mba was confirmed to be *S* according to the method reported by Gaspar *et al.*[6] The latter glycosidic acid fraction was treated with 10% H_2SO_4 to give a hydroxyfatty acid together with a sugar fraction.

Methylation of the hydroxyfatty acid with diazomethane followed by application of the modified Mosher's method[7] revealed that it was methyl 11(*S*)-jalapinolate. The sugar fraction was treated with *N*-(trimethylsilyl)-imidazole and the products were examined by GC and found identical to trimethylsilylethers of glucose (Glc), fucose (Fuc), and rhamnose (Rha). The absolute configurations of these sugars, Glc, Fuc, and Rha, were determined to be D, D, and L forms, respectively, by the method of Hara *et al.*[8] All parts of the resin glycosides of this plant were thus identified.

The molecular formula of **1** was determined to be $C_{62}H_{110}O_{20}$ by high-resolution electron spray ionization mass spectrometry (HR-ESI-MS). The ^{1}H-NMR spectrum of **1** exhibited four anomeric proton signals at δ 4.69, 5.49, 6.03, and 6.22 and signals at δ 2.25 and 2.41 due to the nonequivalent CH_2 in addition to two triplet signals assignable to the equivalent CH_2 of organic acids (Org). The ^{13}C-NMR spectrum showed three carbonyl (δ 173.1, 173.3, 173.5) and four anomeric carbons (δ 98.6, 100.2, 103.5, 104.4). The negative ion FAB-MS exhibited, besides an $[M-H]^-$ ion peak at *m*/*z* 1173, fragment ion peaks at *m*/*z* 1019 [1173−Deca]$^-$, 837 [1019−Dodeca]$^-$, and 691 [837−146 (deoxyhexose unit)]$^-$ in addition to characteristic fragment ion peaks at *m*/*z* 545 [691−146 (deoxyhexose unit)]$^-$, 417 [545−146 (deoxyhexose unit)+18]$^-$, and 271 [417−146 (deoxyhexose unit), jalapinolic acid−H]$^-$, implying that the carboxy group of jalapinolic acid (Jla) combines with the second deoxyhexose counted from the aglycone.[9]

Assignments of proton and carbon signals arising from **1** by the ^{1}H–^{1}H, ^{1}H–^{13}C COSY, and NOESY spectra revealed that **1** consisted of the glycosidic acid, operculinic acid C,[10] and that H-2 of Rha, H-2 of Rha′, and H-4 of Rha″ were remarkably shifted downfield due to acylation (Table 1). This information together with the significant correlations, H-1(Fuc)/C-11(Jla), H-2(Fuc)/C-1(Rha), H-2(Rha)/C-1(Jla), H-4(Rha)/C-1(Rha′), H-2(Rha′)/C-1(Org), H-4(Rha′)/C-1(Rha″), and H-4(Rha″)/C-1(Org) in the HMBC spectrum, demonstrated that the carboxyl group of Jla combined with HO-2 of Rha to form a macrocyclic ring, and that Deca and Dodeca are attached at HO-2 of Rha′ and HO-4 of Rha″ (Fig. 1).

Final discrimination of the two organic acids (Deca or Dodeca) was achieved by MS spectrometric analysis. Acetylation of **1** gave a hexaacetate (**1a**), whose EI-MS showed diagnostic fragment ion peak at *m*/*z* 413 assignable to Dodeca attached at HO-4 of Rha″, but no fragment ion peak at *m*/*z* 385, expected if the location of Deca at this position was observed

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Table 1. ^{1}H-NMR Data for **1**, **2**, **3** and **4** in C_5D_5N (600 MHz)

		1	**2**	**3**	**4**
Fuc	1	4.69 (d, 7.6)	4.75 (d, 7.3)	4.76 (d, 7.6)	4.72[a)]
	2	4.14 (dd, 7.6, 9.6)	4.17 (dd, 7.3, 9.6)	4.19 (dd, 7.6, 9.6)	4.13 (dd, 7.4, 9.4)
	3	4.02 (dd, 9.6, 3.6)	4.09 (dd, 9.6, 3.5)	4.10 (dd, 9.6, 3.6)	4.06 (dd, 9.4, 3.6)
	4	3.97 (dd, 3.6, 0.5)	4.00 (dd, 3.5, 0.5)	4.00 (dd, 3.6, 0.9)	3.97 (dd, 3.6, 0.5)
	5	3.74 (dq, 0.5, 6.3)	3.78 (dq, 0.5, 6.6)	3.78 (dq, 0.9, 6.6)	3.76 (dq, 0.5, 6.3)
	6	1.50 (d, 6.3)	1.52 (d, 6.6)	1.52 (d, 6.6)	1.50 (d, 6.3)
Rha	1	5.49 (d, 1.3)	5.49 (d, 1.8)	5.51 (d, 1.8)	5.48 (d, 1.8)
	2	5.93 (dd, 1.3, 3.3)	5.97 (dd, 1.8, 3.3)	5.98 (dd, 1.8, 3.2)	5.93 (dd, 1.8, 3.3)
	3	5.00 (dd, 3.3, 9.3)	5.03 (dd, 3.3, 9.4)	5.05 (dd, 3.2, 9.4)	5.00 (br s)
	4	4.19 (dd, 9.3, 9.6)	4.23 (dd, 9.4, 9.4)	4.23 (dd, 9.4, 9.6)	4.20 (dd, 9.6, 9.3)
	5	4.44 (dq, 9.6, 6.0)	4.47 (dq, 9.4, 6.3)	4.48 (dq, 9.6, 6.3)	4.44 (dq, 9.3, 6.3)
	6	1.65 (d, 6.0)	1.64 (d, 6.3)	1.65 (d, 6.3)	1.63 (d, 6.3)
Rha′	1	6.03 (d, 1.5)	6.13 (d, 1.8)	6.18 (d, 1.8)	6.09 (d, 1.8)
	2	5.99 (dd, 1.5, 3.0)	6.01 (dd, 1.8, 3.0)	6.05 (dd, 1.8, 3.0)	5.99 (dd, 2.0, 3.0)
	3	4.67 (dd, 3.0, 9.4)	4.67 (dd, 3.0, 9.3)	4.64 (dd, 3.0, 8.7)	4.65 (dd, 3.0, 9.1)
	4	4.30 (dd, 9.4, 9.4)	4.32 (dd, 9.3, 9.3)	4.37 (dd, 8.7, 8.7)	4.31 (dd, 9.1, 9.6)
	5	4.38 (dq, 9.4, 6.1)	4.38 (dq, 9.3, 6.0)	4.38[a)]	4.36 (dq, 9.6, 6.0)
	6	1.71 (d, 6.1)	1.69 (d, 6.0)	1.68 (d, 5.5)	1.68 (d, 6.0)
Rha″	1	6.22 (d, 1.2)	5.83 (d, 2.0)	5.85 (d, 2.0)	5.82 (d, 2.0)
	2	4.82 (dd, 1.2, 3.3)	6.02 (dd, 2.0, 3.3)	6.04 (dd, 2.0, 3.3)	6.01 (dd, 2.0, 2.8)
	3	4.58 (dd, 3.3, 9.6)	4.74 (dd, 3.3, 9.3)	4.74 (dd, 3.3, 9.3)	4.75[a)]
	4	5.86 (dd, 9.6, 9.8)	5.74 (dd, 9.3, 9.3)	5.75 (dd, 9.3, 9.6)	5.77 (dd, 9.3, 9.3)
	5	4.43[a)]	4.47 (dq, 9.3, 6.3)	4.44 (dq, 9.6, 6.0)	4.44 (dq, 9.3, 6.3)
	6	1.48 (d, 6.3)	1.50 (d, 6.3)	1.50 (d, 6.0)	1.54 (d, 6.3)
Rha‴	1		5.67 (d, 1.3)	5.63 (d, 1.3)	5.64 (d, 1.2)
	2		4.93 (br s)	4.92[a)]	4.88 (br s)
	3		4.43 (dd, 3.3, 8.4)	4.46 (dd, 3.3, 9.0)	4.39 (dd, 3.1, 8.9)
	4		4.27 (dd, 8.4, 8.4)	4.26 (dd, 9.0, 9.3)	4.21 (dd, 8.9, 9.6)
	5		4.29[a)]	4.32 (dq, 9.3, 6.0)	4.25 (dq, 9.6, 6.0)
	6		1.59 (d, 5.7)	1.62 (d, 6.0)	1.57 (d, 6.0)
Jla	2	2.25 (ddd, 4.2, 8.1, 14.7)	2.24 (ddd, 4.0, 8.4, 14.7)	2.26 (ddd, 3.8, 8.3, 14.7)	2.23 (ddd, 4.2, 7.8, 14.7)
		2.41 (ddd, 4.2, 8.1, 14.7)	2.39[a)]	2.42 (ddd, 3.8, 8.3, 14.7)	2.41 (ddd, 4.2, 7.8, 14.7)
	11	3.84 (br s)	3.87 (br s)	3.87 (br s)	3.86 (br s)
	16	0.86 (t, 7.2)	0.87 (t, 7.4)	0.84 (t, 7.2)	0.87 (t, 6.6)
Cna	2		6.56 (d, 16.1)	6.53 (d, 16.1)	6.55 (d, 16.1)
	3		7.75 (d, 16.1)	7.77 (d, 16.1)	7.76 (d, 16.1)
Mba	2		2.39 (tq, 6.5, 6.5)		2.38 (tq, 6.6, 6.6)
	4		0.88 (t, 7.1)		
	5		1.10 (d, 6.8)		1.11 (d, 6.8)
Iba	3		1.18 (d, 7.1)	1.18 (d, 6.8)	
	4		1.21 (d, 7.1)	1.21 (d, 7.1)	
Oga	2	2.29 (m)	2.66 (m)	2.26 (m)	2.47 (ddd, 1.2, 6.6, 6.6)
		2.46 (m)		2.66 (m)	
	16	0.87 (t, 7.2)		0.88 (t, 6.9)	0.89 (t, 7.2)
		0.88 (t, 6.9)			

δ in ppm from TMS. Org: Deca and Dodeca. *a*) Signals are overlapping.

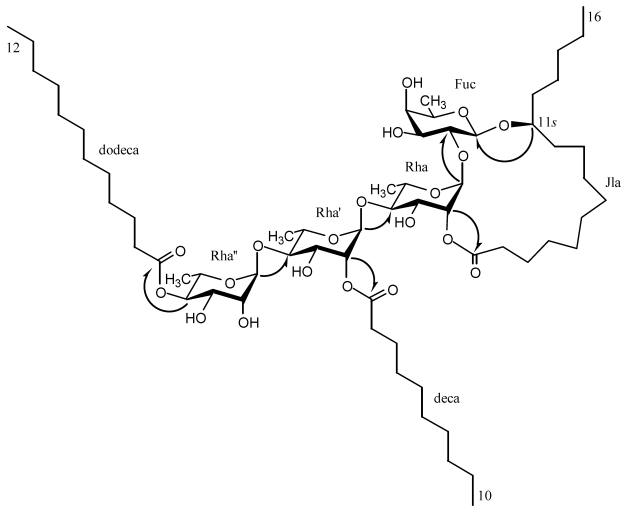

Fig. 1. Selected HMBC Correlations of **1**

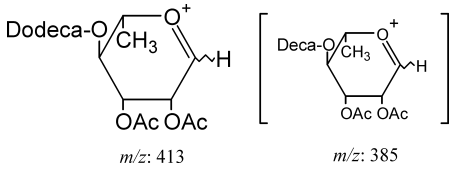

Fig. 2. MS Fragment Ion of **1**

(Fig. 2). Consequently, it was confirmed that the Deca and Dodeca are linked with HO-2 of Rha′ and HO-4 of Rha″, respectively.

On the basis of the above results, the structure of **1** is determined to be (11*S*)-[[*O*-4-*O*-*n*-dodecanoyl-α-L-rhamnopyranosyl-(1→4)-*O*-2-*O*-*n*-decanoyl-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranosyl]oxy]-jalapinolic acid, intramolecular 1,2″-ester (**1**).

The HR-ESI-MS of **2** exhibited an $[M-H]^-$ ion peak at *m*/*z* 1267.6483 consistent with the molecular formula,

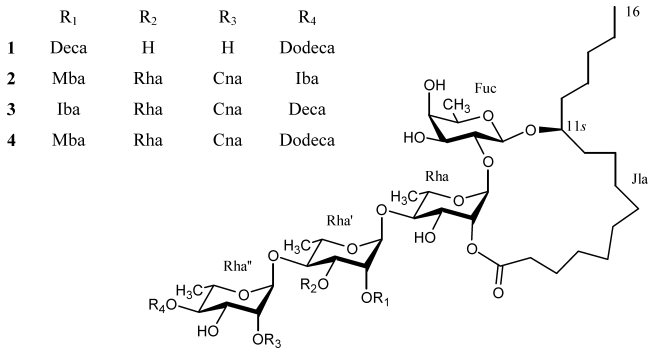

Fig. 3. Structures of **1**—**4**

$C_{64}H_{100}O_{25}$. The ^{1}H-NMR spectrum showed five anomeric (δ 4.75, 5.49, 5.67, 5.83, 6.13) and methyl signals (δ 1.50, 1.52, 1.59, 1.64, 1.69) and signals attributable to one unit each of Iba, Mba, and Cna. The ^{13}C-NMR spectrum gave five anomeric (98.8, 99.1, 100.4, 104.3, 104.8), four ester carbonyl (166.8, 173.1, 175.4, 176.7) and eight olefinic signals (118.4, 128.7×2, 129.1×2, 130.6, 134.7, 145.6). The negative ion FAB-MS exhibited an $[M-H]^-$ ion peak at *m*/*z* 1267 and fragment ion peaks at *m*/*z* 1137 $[1267-Cna]^-$, 921 $[991-Iba]^-$, and 837 $[921-Mba]^-$, in addition to the same characteristic fragment ion peaks at *m*/*z* 545, 417 and 271 as observed in **1**. From these findings, together with the ^{1}H–^{1}H, ^{1}H–^{13}C COSY and NOESY spectroscopic data, it was found that **2** consisted of the glycosidic acid, simonic acid B,[1] and one unit each of Iba, Mba, and Cna, and that four ester linkage positions were HO-2 of Rha, HO-2 of Rha′, HO-2 of Rha″, and HO-4 of Rha″. The HMBC spectrum of **2** exhibited diagnostic correlations, H-1(Fuc)/C-11(Jla), H-2(Rha′)/C-1(Mba), H-2(Rha″)/C-1(Cna), H-4(Rha″)/C-1(Iba), and H-1(Rha)/C-1(Jla). Therefore, three organic acids, Mba, Can, and Iba, were attached respectively at HO-2 of Rha′, HO-2 of Rha″, and HO-4 of Rha″, and the carboxy group of Jla also combined with HO-2 of Rha to form an intramolecular macrocyclic ester structure. Accordingly, the structure of compound **2** was characterized as (11*S*)-[[*O*-α-L-rhamnopyranosyl-(1→3)-*O*-[(2-*O*-*trans*-cinnamoyl)-(4-*O*-isobutanoyl)-α-L-rhamnopyranosyl-(1→4)]-*O*-2-*O*-(2*S*)-methylbutanoyl-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranosyl]oxy]-jalapinolic acid, intramolecular 1,2″-ester (**2**) (Fig. 3).

The ^{1}H-NMR spectroscopic and FAB-MS data of compounds **3** and **4** showed that they consisted of the same glycosidic acid, simonic acid B, and differed only in the organic acid residues: compound **3** has Iba, Cna, and Deca, while compound **4** has Mba, Cna, and Dodeca. The HMBC spectrum of **3** showed correlations, H-1(Fuc)/C-11(Jla), H-2(Rha′)/C-1(Iba), H-2(Rha″)/C-1(Cna), H-4(Rha″)/C-1(Deca), and H-1(Rha)/C-1(Jla). Compound **4** also gave correlations H-1(Fuc)/C-11(Jla), H-2(Rha′)/C-1(Mba), H-2(Rha″)/C-1(Cna), H-4(Rha″)/C-1(Dodeca), and H-1(Rha)/C-1(Jla) in its HMBC spectrum. These findings showed that the Mba and Iba in **2** are replaced respectively by Iba and Deca in **3**, and the Iba in **2** is replaced by Dodeca in **4**. Figure 3 shows the structures of **3** and **4**.

In conclusion, four new and two known resin glycosides were obtained. They are monomers consisting of quite similar glycosidic and organic acids to those of simonins[1] and batatinoside,[2] and differed in the ester-linkage positions of organic acid. Unlike the resin glycosides of the sweet potato (*Ipomoea batatas* var. *batatas*),[2] we could not obtain ester-type dimers from the sweet potatoes.

Table 2. ^{13}C-NMR Data for **1**, **2**, **3** and **4** in C_5D_5N (150 MHz)

		1	**2**	**3**	**4**
Fuc	1	104.4	104.3	104.3	104.4
	2	80.0	80.3	80.3	80.4
	3	73.5	73.4	73.4	73.4
	4	72.9	73.1	73.2	73.2
	5	70.9	70.8	70.9	70.8
	6	17.3	17.4	17.4	17.3
Rha	1	98.6	98.8	98.8	98.8
	2	73.7	73.9	73.9	73.9
	3	69.8	69.9	69.8	69.9
	4	81.0	80.3	80.2	80.3
	5	68.7	68.6	68.7	68.6
	6	19.3	19.5	19.5	19.5
Rha′	1	100.2	99.1	99.1	99.1
	2	74.2	73.5	73.7	73.6
	3	70.9	79.8	79.6	79.7
	4	80.5	80.3	79.8	80.2
	5	68.6	68.6	68.5	68.6
	6	18.9	18.9	19.0	18.9
Rha″	1	103.5	100.4	100.3	100.3
	2	72.4	74.2	74.1	74.2
	3	70.3	68.1	68.1	68.2
	4	75.4	75.0	75.0	75.2
	5	68.1	68.4	68.4	68.5
	6	18.1	18.0	18.0	18.0
Rha‴	1		104.8	104.5	105.8
	2		72.3	72.2	72.3
	3		72.6	72.7	72.6
	4		73.0	73.0	73.0
	5		70.7	70.9	70.7
	6		18.6	18.7	18.6
Jla	1	173.1	173.1	173.1	173.1
	11	82.4	82.3	82.4	82.4
	16	14.3	14.3	14.3	14.3
Mba	1		175.4		175.4
	4		11.8		11.8
	5		16.8		16.8
Iba	1		176.7	176.8	
	2		19.2	19.3	
	2′		19.2	19.1	
Org	1	173.3		172.9	173.5
	1	173.5			
Cna	1		166.8	166.8	166.9
	2		118.4	118.4	118.5
	3		145.6	145.7	145.7
	4		130.6	130.6	130.6
	5, 9		128.7×2	128.6×2	128.7×2
	6, 8		129.1×2	129.1×2	129.1×2
	7		134.7	134.7	134.8

δ in ppm from TMS. Org: Deca and Dodeca.

Experimental

General Experimental Procedures Optical rotations were measured at 25 °C with a JASCO P-1020 polarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-GX400 or ECA-600SN spectrometer, using tetramethylsilane as an internal reference. Samples were measured at a probe temperature of 25 °C. The NOESY spectrum was obtained using a mixing time of 500 ms. The HMBC spectrum was recorded at 600 MHz with 64 scans ($^{2,3}J_{CH}$=7 Hz). EI-MS and FAB-MS including high-resolution MS were recorded on a JEOL JMS-700T spectrometer. (EI-MS: ionization voltage, 30 eV; accelerating voltage, 10 kV; FAB-MS: accelerating voltage, 10 kV; matrix, triethanolamine; collision gas, He). TLC was carried out on silica gel precoated Al sheets (Merck, Art 5556 for HPTLC). The solvent

systems were $CHCl_3$–MeOH–H_2O (8 : 1.5 : 0.1). Spots were visualized with 5% H_2SO_4 in MeOH (by heating). Column chromatography was carried out on Sephadex LH-20 (Amersham Pharmacia Biotech AB), silica gel (Kieselgel 60, Merck), and Cosmosil 75C_{18}-OPN (Nacalai Tesque Inc.) columns. Preparative HPLC was conducted over Inertsil ODS-3 (4 μm, 10 mm i.d.×250 mm, GL Sciences Inc.) and Unison UK-C18 (3 μm, 10 mm i.d.×100 mm, Imtakt Co.) columns with a JASCO PU-2080 Plus. The elution profile was monitored with a refractive index detector, JASCO RI-2031 Plus.

Plant Material The sweet potato (Kokei 14 go) was supplied by Nishitomi Shouten (cultivated in Yawata, Kyoto), and a voucher specimen was deposited at the Faculty of Pharmaceutical Sciences, Setsunan University.

Isolation of Compounds, 1—4 The sliced sweet potato (7.3 kg) was percolated with $CHCl_3$–acetone (1 : 1) at room temperature and the solution was concentrated to give an extract (156.9 g). The extract was partitioned between $CHCl_3$–MeOH–H_2O (1 : 1 : 1). The lower layer was concentrated to give a brown residue (10.0 g). The residue was subjected to column chromatography on Sephadex LH-20 (MeOH) to give a crude resin glycoside fraction (3.6 g). A part of this fraction (3.1 g) was column chromatographed on silica gel to provide three fractions, fr-1 (337 mg), fr-2 (1.79 g), and fr-3 (185 mg). Fr-2 (1.26 g) was subjected to column chromatography on Cosmosil 75C18-OPN to give two fractions, fr-4 (650 mg) and fr-5 (607 mg). The former was further separated by column chromatography on silica gel to give four fractions, fr-6—9. Preparative HPLC of fr-6 with Inertsil ODS-3 and Unison UK-C18 columns using 95% MeOH gave **2** (11 mg). Preparative HPLC of fr-7 with Inertsil ODS-3 and Unison UK-C18 columns using 98% MeOH gave **3** (13 mg), and of fr-8 (MeOH) gave **1** (13 mg) and **4** (113 mg). The latter was subjected to column chromatography on Cosmosil 75C_{18}-OPN (90% MeOH) to give three fractions, fr-10—12. HPLC separation of fr-10 in the same condition as described for fr-7 gave **5** (81 mg) and **6** (36 mg). **1**: White powder; mp 86—89 °C; $[\alpha]_D$ −29.2 (c=1.1, MeOH). HR-ESI-MS m/z: 1173.7518 $[M-H]^-$ (Calcd for $C_{62}H_{109}O_{20}$: 1173.7512). **2**: White powder; mp 133—137 °C; $[\alpha]_D$ −20.7 (c=1.1, MeOH). HR-ESI-MS m/z: 1267.6483 $[M-H]^-$ (Calcd for $C_{64}H_{99}O_{25}$: 1267.6476). **3**: White powder; mp 105—109 °C; $[\alpha]_D$ −12.5 (c=0.1, MeOH). HR-ESI-MS m/z: 1337.7262 $[M-H]^-$ (Calcd for $C_{69}H_{109}O_{25}$: 1337.7258). **4**: White powder; mp 118—121 °C; $[\alpha]_D$ −10.8 (c=2.3, MeOH). HR-ESI-MS m/z: 1379.7729 $[M-H]^-$ (Calcd for $C_{72}H_{115}O_{25}$: 1379.7728). ^{1}H- and ^{13}C-NMR of **1**—**4**: see Tables 1 and 2.

Compounds **5** and **6** were identified as simonin IV[1] and operculin VII,[5] respectively, by comparison of their ^{1}H- and ^{13}C-NMR spectroscopic data with those of corresponding authentic samples.

Characterization of the Component of Resin Glycosides A part of the crude resin glycoside fraction (53 mg) was treated with 10% KOH at 90 °C for 2 h. The reaction mixture was acidified to pH 3.0 and shaken with ether. The ether layer was analyzed by GC (fused silica capillary column bonded MPS-50 (Quadrex), 0.25 mm i.d.×50 m; column temp.; 80 °C, carrier gas; He 33.4 ml/min), t_R (min): 4.32 (isobutyric acid), 6.42 (2-methylbutyric acid). The above ether layer was methylated with diazomethane and the mixture was analyzed by GC (column temp.; 150 °C); t_R (min): 7.23 (methyl *n*-decanate), 12.81 (methyl *trans*-cinnamate), 13.59 (methyl *n*-dodecanate).

The H_2O layer was passed through Diaion HP-20 (H_2O→MeOH) and the MeOH eluate was concentrated to give a glycosidic acid fraction (45 mg). This fraction was treated with 10% H_2SO_4 at 95 °C for 2 h, and the reaction mixture was extracted with ether. The ether layer was concentrated to give a hydroxyfatty acid (9 mg). This product was methylated with diazomethane to give a methylate, which was identified as methyl jalapinolate by comparison with an authentic sample.

The aqueous layer was neutralized with $Ba(OH)_2$ and the precipitate filtered off. The filtrate was concentrated to give a sugar fraction (36 mg). This fraction (1 mg) was treated with *N*-trimethylsilylimidazole (Acros Organics) and the product was examined by GC (fused silica capillary column bonded MPS-50 (Quadrex), 0.25 mm×50 m; column temp.; 180 °C, carrier gas; He 33.4 ml/min), t_R (min): 6.81 (rhamnose), 7.48 (fucose), 13.7 (glucose).

Determination of Absolute Configurations of 2-Methylbutyric Acid, Methyl Jalapinolate, and Sugars 2-Methylbutyric acid formed by the procedure described above was analyzed by GC using a capillary chiral column according to the method reported by Gaspar *et al.*[6] (CP Chirasil-Dex CB, GL Sciences Inc., 0.25 mm i.d.×30 m; column temp.; 50 °C (hold 10 min)→180 °C at 3 °C/min, carrier gas; He 1.2 ml/min), t_R (min): 16.64 (2*R*-methylbutyric acid), 17.13 (2*S*-methylbutyric acid). The former peak was not detected.

(+)-α-Methoxy-a-(trifluoromethyl)phenylacetyl chloride ((+)-MTPA-Cl, 30 mg, Tokyo Chemical Industry Co., Ltd.) was added to the methyl jalapinolate in pyridine (1 ml) and stirred at room temperature overnight. After removal of the solvent under a stream of N_2, the residue was chromatographed on silica gel to give an MTPA ester (4 mg). ^{1}H-NMR ($CDCl_3$) δ: 0.876 (3H, t, J=6.7 Hz, H_3-16), 2.302 (2H, t, J=7.5 Hz, H_2-2), 3.560 (3H, q, J=1.1 Hz, $OC\underline{H}_3$), 3.668 (3H, s, $COOC\underline{H}_3$), 5.084 (1H, tt, J=6.7, 6.8 Hz, H-11). Its ^{1}H-NMR spectrum was superimposable on that of corresponding (+)-MTPA ester of methyl (*S*)-jalapinolate.

According to the method reported by Hara *et al.*[8] after neutralization, the sugar mixture (5 mg) was subjected to GC analysis. The trimethylsilyl ethers of the methyl thiazolidine (*R*)-2-carboxylate derivatives (fused silica capillary column bonded MPS-50 (Quadrex), 0.25 mm×50 m; column temp.; 230 °C, carrier gas; He 33.4 ml/min), t_R (min): 13.78 (L-rhamnose), 14.49 (D-fucose), 17.95 (D-glucose).

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