Resin Glycosides. XIX.[1] Woodrosins I and II, Ether-Insoluble Resin Glycosides from the Stems of *Ipomoea tuberosa*

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Two new ether-insoluble resin glycosides named woodrosins I and II were isolated from the stems of *Ipomoea tuberosa* L., and their structures were determined on the basis of chemical and spectral data. Contrary to anticipation, they had an intramolecular cyclic ester structure similar to that of ether-soluble resin glycosides (Mayer's jalapin) hitherto isolated.

It is proposed to use the terms, "jalapin" and "convolvulin," not according to the solubilily in ether (Mayer's classification), but according to the structure, *i.e.*, intramolecular esters and others, respectively.

Keywords *Ipomoea tuberosa*; resin glycoside; ether-insoluble jalapin; Mayer's classification; jalapin; convolvulin

Ipomoea tuberosa L. (*Merremia tuberosa* (L.) RENDLE), Convolvulaceae, is called "woodrose" after the shape of its dried calyx, which resembles a rose, and its tubers are used for food.[2] Other than a study on the nutritive value of the leaves and seeds,[3] there has been no report on the chemical constituents of this plant. In the course of our studies on the resin glycosides, characteristic ingredient of the Convolvulaceae plants, we have examined the stems of this plant and isolated two ether-insoluble resin glycosides named woodrosins I and II. This paper deals with the isolation and structure elucidation of these compounds.

The MeOH extractive (25.5 g) obtained from the air-dried stems (1.06 kg) was partitioned between *n*-BuOH and H_2O. A mixture of compounds (9.0 g) obtained from the *n*-BuOH layer was subjected successively to a series of column chromatographies on Sephadex LH-20, silica gel and preparative high performance liquid chromatograhy (HPLC) to give woodrosins I (**1**) (315 mg) and II (**2**) (290 mg).

Woodrosin I (**1**), an amorphous solid analyzed as $C_{66}H_{112}O_{30}$, gave on alkaline hydrolysis with 1 N KOH an organic acid and a new glycosidic acid named woodrosinic acid A (**3**). The former was identified as 2-methylbutyric acid by gas chromatography (GC) and determined to be of *S* configuration by Helmchen's method.[4]

Acidic hydrolysis of **3** yielded a hydroxyfatty acid and a monosaccharide mixture. The methyl ester (**4**) of the acid was identified as methyl jalapinolate[4,5] (methyl 11-hydroxy-*n*-hexadecanoate) by comparison of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum with that of an authentic specimen. The configuration at 11-C of **4** was established to be *S* by Mosher's method.[1] Thin layer chromatography (TLC) of the monosaccharide mixture revealed the presence of glucose and rhamnose. Their absolute configurations were determined to be D- and L-form, respectively, according to the procedure developed by Hara *et al.*[6]

Compound **3** showed the quasi-molecular ion peak, $[M-H]^-$, at *m/z* 1065 and the fragment ion peaks at *m/z* 919 $[1065-146$ (deoxyhexose unit)$]^-$, 903 $[1065-162$ (hexose unit)$]^-$, 741 $[903-162]^-$, 595 $[741-146]^-$, 433 $[595-162]^-$ and 271 $[433-162$, jalapinolic acid $-H]^-$ in the negative ion fast atom bombardment mass spectrum (negative FAB-MS), suggesting that **3** is a pentaglycoside composed of 1 mol each of jalapinolic acid and L-rhamnose and 4 mol of D-glucose, and that the sugar moiety forms a branched chain having rhamnose and glucosyl-glucose at the terminals.

The ^{1}H-NMR spectrum of **3** exhibited signals ascribable to the terminal methyl and an equivalent 2-H_2 of the jalapinolic acid residue, together with five anomeric proton signals. The coupling patterns of C-H and C-H_2 signals of the sugar moiety were ambiguous because of overlapping of those due to the four glucosyl groups, but their chemical shifts and connectivities were differentiated on the basis of COSY and ^{1}H–^{13}C heteronuclear shift-correlated 2D-NMR (HETCOR) spectra (Table I). Then, **3** was derived to the peracetate (**5**), of which the ^{1}H-signals were assigned successfully on the basis of the COSY and NOESY spectra (Fig. 2, Table I). The coupling constants of the anomeric and the adjacent methine proton signals of **3** and **5** as well as the chemical shifts of the ^{13}C-signals in **3** (Table II) indicated that all the monosaccharide units are pyranose type, and that the glycosidic linkages of the four glucose residues adopt β^4C_1 conformation while that of the rhamnose residue takes α^1C_4 conformation.

When compared with those of methyl pyranosides in the literature,[7] the ^{13}C-signals of **3** showed glycosylation shifts at 2-C of the first glucose unit (Glc) (+4.5 ppm) counted from the aglycone, 2-C of the second glucose (Glc′) (+2.7 ppm), 3-C of Glc′ (+12.3 ppm), 6-C of the third glucose (Glc″) (+7.3 ppm) and 11-C of jalapinolic acid (+9.9 ppm). In order to determine the arrangement of the sugar moiety, the NOESY spectra of **3** and **5** were recorded. Three of the cross peaks observed in the spectrum of **3** were assigned as those between 1-H of Glc′/2-H of Glc, 1-H of Rha/2-H of Glc′, and 1-H of Glc″/3-H of Glc′, whereas that of **5** revealed relations between 1-H of Glc/11-H of jalapinolic acid, 1-H of Glc′/2-H of Glc, and 1-H of Glc″/3-H of Glc′ (Fig. 2).

Consequently, the structure of **3** was concluded to be (*S*)-jalapinolic acid 11-*O*-*β*-D-glucopyranosyl-(1→6)-*O*-*β*-D-glucopyanosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→2)]-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopyranoside (Fig. 1).

Woodrosin I (**1**) showed, in the ^{1}H-NMR spectrum, the signals due to nonequivalent 2-H_2 of the jalapinolic acid group at δ 2.57 and 2.40 (each 1H), as well as the signals due to four 2-methylbutyric acid residues. The negative FAB-MS of **1** exhibited the $[M-H]^-$ ion peak at *m/z* 1383

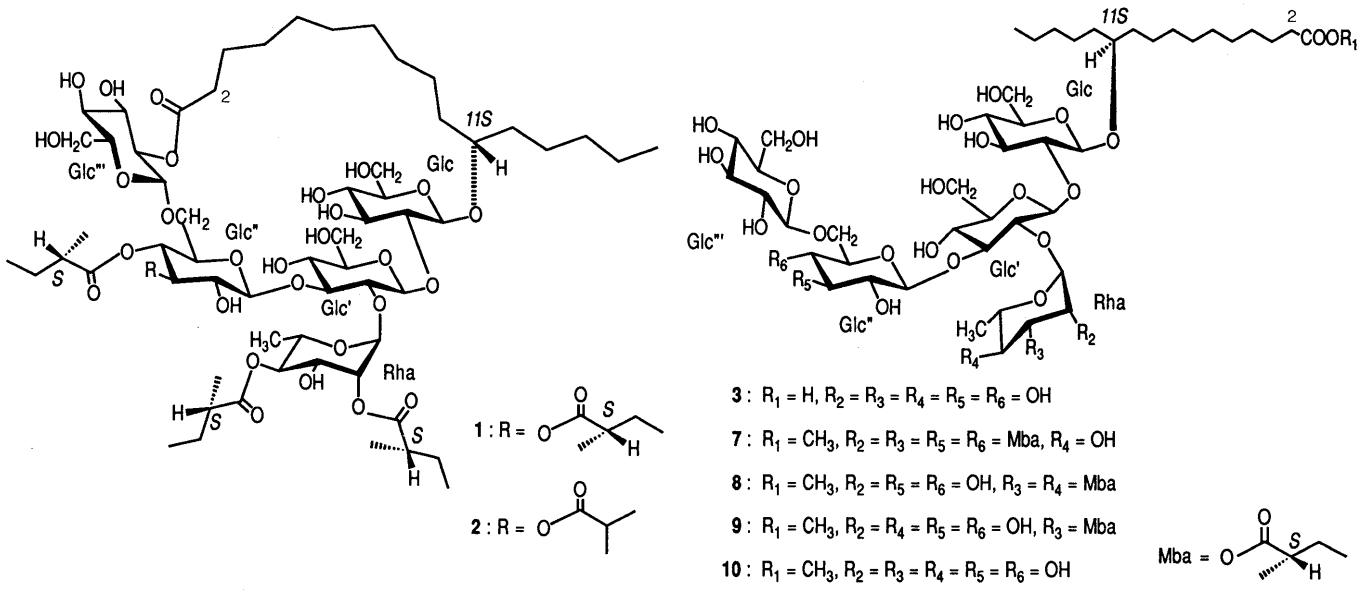

Fig. 1

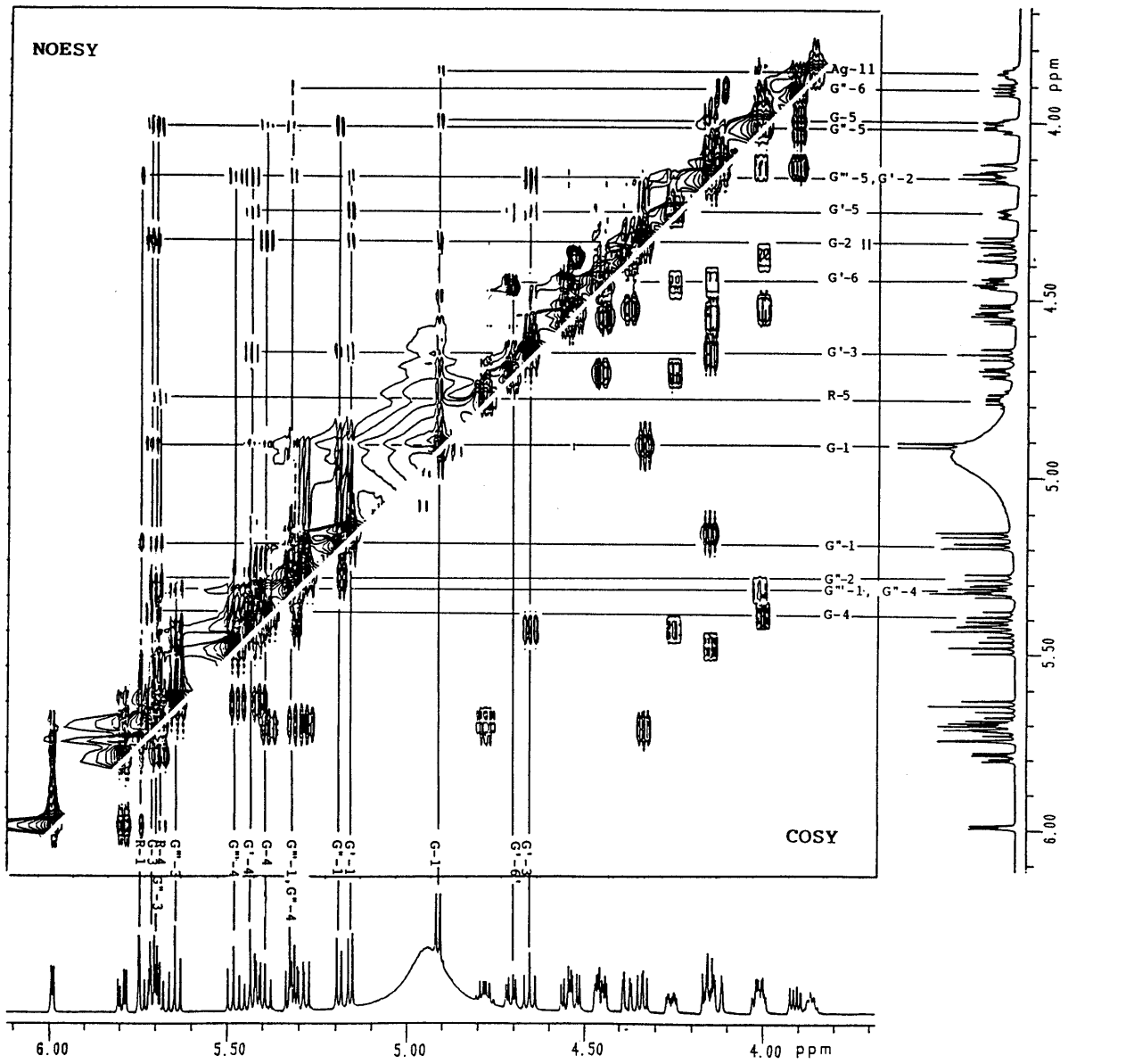

Fig. 2. COSY and NOESY Spectra of **5** (in Pyridine-d_5, 600 MHz)

TABLE I. ^{1}H-NMR Data for **1**, **2**, **3** and **5** (in Pyridine-d_5, 600 MHz)

	3	5	1	2
Glc -1	4.98, d (7.7)	4.91, d (7.0)	4.89, d (7.5)	4.89, d (7.7)
-2	*ca.* 4.35	4.34, dd (7.0, 9.0)	4.39, dd (7.5, 9.1)	4.39, dd (7.7, 8.6)
-3	4.52, dd (9.2, 9.2)	5.71, dd (9.0, 9.0)	4.45, dd (9.1, 9.1)	4.45, dd (8.6, 8.6)
-4	4.12, dd (9.2, 9.2)	5.39, dd (9.0, 9.0)	4.11, dd (9.1, 9.1)	4.11, dd (8.6, 8.6)
-5	*ca.* 3.87	4.00, ddd (2.2, 4.9, 9.0)	*ca.* 3.88	*ca.* 3.88
-6	*ca.* 4.32	4.38, dd (2.2, 12.3)	4.34, dd (5.1, 11.7)	4.34, dd (5.1, 11.7)
	ca. 4.45	4.53, dd (4.9, 12.3)	4.50, dd (2.2, 11.7)	4.50, dd (2.2, 11.7)
Glc′ -1	5.75, d (7.7)	5.16, d (7.7)	5.84, d (8.1)	5.84, d (7.7)
-2	*ca.* 4.19	4.16, dd (7.7, 9.0)	4.16, dd (8.1, 8.6)	*ca.* 4.17
-3	*ca.* 3.88	4.66, dd (9.0, 9.0)	*ca.* 3.92	*ca.* 3.92
-4	3.99, dd (8.8, 8.8)	5.43, dd (9.0, 9.0)	*ca.* 3.92	*ca.* 3.92
-5	3.73, ddd (2.2, 5.5, 8.8)	4.26, ddd (2.6, 4.4, 9.0)	3.71, ddd (2.9, 5.8, 9.3)	3.71, ddd (2.9, 6.2, 9.1)
-6	*ca.* 4.20	4.46, dd (2.6, 12.1)	4.20, dd (5.8, 11.7)	4.20, dd (6.2, 12.1)
	4.37, dd (2.2, 11.4)	4.71, dd (4.4, 12.1)	4.46, dd (2.9, 11.7)	*ca.* 4.45
Glc″ -1	4.85, d (7.7)	5.19, d (7.7)	4.90, d (7.7)	4.90, d (7.7)
-2	*ca.* 3.98	5.28, dd (7.7, 9.5)	*ca.* 3.91	*ca.* 3.91
-3	4.10, dd (9.3, 9.3)	5.70, dd (9.5, 9.5)	5.59, dd (9.4, 9.4)	5.57, dd (9.3, 9.3)
-4	*ca.* 3.93	5.32, dd (9.5, 9.5)	5.49, dd (9.4, 9.4)	5.49, dd (9.3, 9.3)
-5	*ca.* 4.14	4.01, ddd (2.0, 6.0, 9.5)	*ca.* 3.88	*ca.* 3.88
-6	*ca.* 3.87	3.91, dd (6.0, 12.3)	4.01, dd (4.0, 12.6)	4.01, dd (4.0, 12.5)
	ca. 4.97	4.12, dd (2.0, 12.3)	4.10, dd (2.6, 12.6)	*ca.* 4.10
Glc‴ -1	4.78, d (7.7)	5.32, d (8.1)	4.97, d (8.1)	4.95, d (8.1)
-2	4.01, dd (7.7, 9.2)	5.42, dd (8.1, 9.3)	5.49, dd (8.1, 9.4)	5.49, dd (8.1, 9.5)
-3	4.20, dd (9.2, 9.2)	5.64, dd (9.3, 9.3)	4.30, dd (9.4, 9.4)	4.30, dd (9.5, 9.5)
-4	4.24, dd (9.2, 9.2)	5.48, dd (9.3, 9.3)	4.19, dd (9.4, 9.4)	4.19, dd (9.5, 9.5)
-5	*ca.* 3.86	4.15, ddd (2.6, 4.9, 9.3)	*ca.* 3.86	*ca.* 3.86
-6	*ca.* 4.32	4.45, dd (2.6, 12.3)	4.31, dd (4.7, 11.7)	4.31, dd (5.1, 12.1)
	ca. 4.45	4.55, dd (4.9, 12.3)	4.44, dd (2.9, 11.7)	*ca.* 4.44
Rha -1	6.27, s	5.74, d (1.1)	6.24, d (1.5)	6.26, d (1.5)
-2	4.80, br d (3.3)	5.99, dd (1.1, 4.0)	5.86, dd (1.5, 3.7)	5.88, dd (1.5, 3.3)
-3	4.62, dd (3.3, 9.2)	5.79, dd (4.0, 10.1)	4.93, dd (3.7, 9.9)	4.92, dd (3.3, 9.9)
-4	4.28, dd (9.2, 9.2)	5.69, dd (10.1, 10.1)	5.70, dd (9.9, 9.9)	5.69, dd (9.9, 9.9)
-5	*ca.* 4.98	4.78, dq (10.1, 6.2)	5.19, dq (9.9, 6.2)	5.19, dq (9.9, 6.2)
-6	1.78, d (5.9)	1.64, d (6.2)	1.67, d (6.2)	1.67, d (6.2)
Ag -16	0.82, t (7.0)	0.90, t (7.0)	0.82, t (7.0)	0.82, t (7.0)
-11	*ca.* 3.95	3.87, sep (5.5)	*ca.* 3.88	*ca.* 3.88
-2	2.51, t (7.5)	2.58, t (7.5)	2.57, ddd (7.0, 7.0, 15.8)	2.57, ddd (7.0, 7.0, 16.1)
			ca. 2.43	*ca.* 2.43
Mba -2			2.51, ddq (7.0, 7.0, 7.0)	2.51, ddq (7.0, 7.0, 7.0)
			2.51, ddq (7.0, 7.0, 7.0)	2.41, ddq (7.0, 7.0, 7.0)
			2.42, ddq (7.0, 7.0, 7.0)	2.39, ddq (7.0, 7.0, 7.0)
			2.40, ddq (7.0, 7.0, 7.0)	
Mba -4			0.95, dd (7.3, 7.3)	0.92, dd (7.0, 7.0)
			0.93, dd (7.3, 7.3)	0.87, dd (7.0, 7.0)
			0.87, dd (7.1, 7.1)	0.86, dd (7.0, 7.0)
			0.86, dd (7.1, 7.1)	
Mba -5			1.30, d (7.0)	1.29, d (7.0)
			1.23, d (7.0)	1.22, d (7.0)
			1.22, d (7.0)	1.15, d (7.0)
			1.16, d (7.0)	
Iba -2				2.67, qq (7.0, 7.0)
-3				1.25, d (7.0)
-3′				1.23, d (7.0)
$OCOCH_3$		1.95, 1.97, 2.03, 2.04		
		2.05, 2.06, 2.07, 2.14		
		2.00, 2.21, 2.29, 2.33		
		2.33, 2.47, 2.57		

δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses); Glc, glucopyranosyl; Rha, rhamnopyranosyl; Ag, aglycone ((*S*)-jalapinolic acid); Mba, 2(*S*)-methylbutyryl; Iba, isobutyryl.

and diagnostic fragment peaks as shown in Fig. 3, demonstrating that **1** consists of 4 mol of 2-methylbutyric acid and 1 mol of **3**, and that the aglycone is combined with the terminal glucose residue (Glc‴) to form an intramolecular ester structure.

In order to clarify the sites of the ester linkages, the ^{1}H- and ^{13}C-signals of the sugar moiety in **1** were assigned with the aid of COSY and HETCOR spectra (Tables I and II). In comparison with those of **3**, the signals due to 3-H and 4-H of Glc″, 2-H of Glc‴, and 2- and 4-H of Rha were shifted downfield by 1.49, 1.56, 1.48, 1.06 and 1.42 ppm, respectively. The electron impact-mass spectrum (EI-MS) of the peracetate of **1** (**6**) showed the strong fragment ion peak at m/z 357, assignable to the terminal deoxyhexose

TABLE II. ^{13}C-NMR Spectral Data for **1**, **2** and **3** (in Pyridine-d_5, 150 MHz)

	3	Methyl glycoside[7] α-	Methyl glycoside[7] β-	1	2		3	Methyl glycoside[7] α-	Methyl glycoside[7] β-	1	2
Glc -1	102.6	101.3	105.5	104.0	104.0	Rha -4	74.3	73.8	73.7	75.4	75.4
-2	79.4	74.0	74.9	79.1	79.1	-5	69.5	69.5	73.4	66.9	66.9
-3	79.3	75.3	78.3	79.9	79.9	-6	19.0	18.6	18.5	18.7	18.8
-4	72.0	72.1	71.6	71.8	71.8	Ag -16	14.3			14.3	14.3
-5	77.9[a]	73.8	78.3	78.3	78.3	-11	80.9			83.0	83.0
-6	62.8[b]	62.8	62.7	62.7	62.7	-2	35.4			34.4	34.4
Glc′ -1	101.7			100.9	100.9	-1	176.5			173.2	173.2
-2	77.6			75.5	75.6	Mba-1				176.7	175.8
-3	90.6			89.8	90.0					176.4	176.4
-4	70.4			70.6	70.6					175.8	176.7
-5	76.8			77.5	77.5					175.8	
-6	62.6			63.0	63.0	Mba-2				41.1	41.2
Glc″ -1	105.1			104.0	104.1					41.3	41.3
-2	74.5			72.6	72.6					41.3	41.6
-3	78.4			75.8	76.0					41.6	
-4	71.8			69.0	68.9	Mba-4				11.7	11.8
-5	76.4			73.3	73.4					11.8	11.8
-6	70.0			66.2	66.3					11.8	12.0
Glc‴-1	104.4			102.1	102.1					11.9	
-2	75.6			75.0	75.1	Mba-5				16.4	16.5
-3	77.8			76.1	76.1					16.7	16.8
-4	71.3			71.6	71.6					16.8	17.4
-5	78.5[a]			78.9	78.9					17.4	
-6	62.5[b]			62.3	62.3	Iba -1					176.1
Rha -1	102.2	102.6	102.6	97.8	97.9	-2					34.4
-2	72.2	72.7	72.1	73.4	73.4	-3					19.1
-3	72.6	72.1	75.3	67.6	67.6	-3′					19.3

δ in ppm from TMS. Glc, glucopyranosyl; Rha, rhamnopyranosyl; Ag, aglycone ((*S*)-jalapinolic acid); Mba, 2(*S*)-methylbutyryl; Iba, isobutyryl. *a, b*) Assignments may be interchanged.

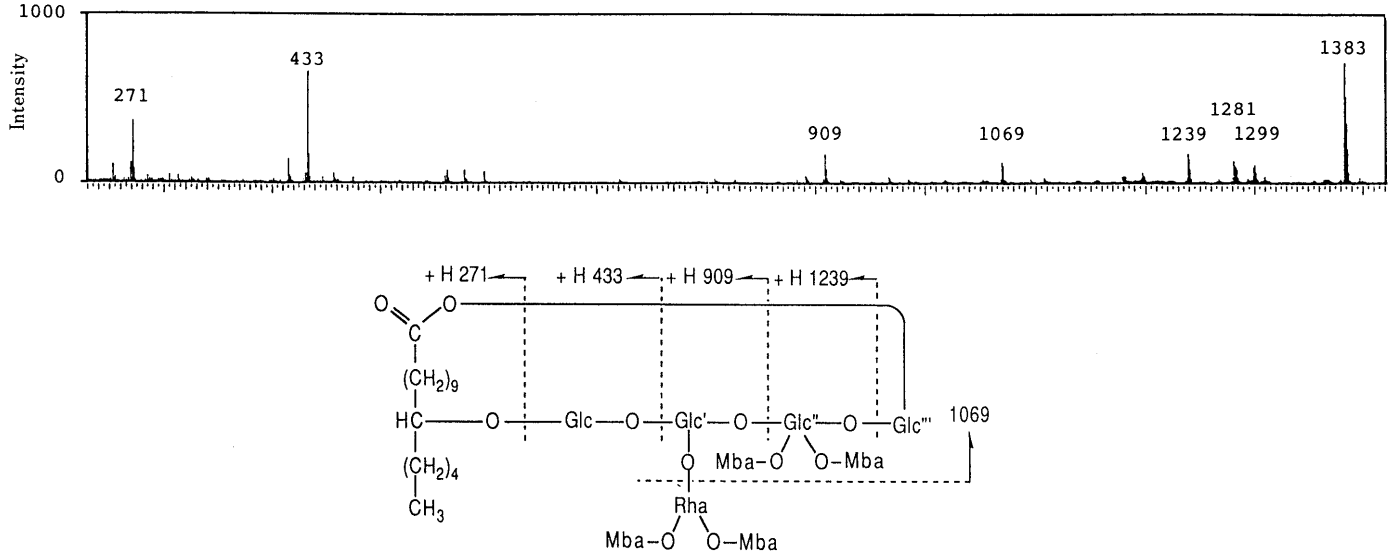

Fig. 3. Negative FAB-MS of **1**

residue (Rha) bearing two 2-methylbutyric acid groups, whereas no fragment peak due to either the terminal glucose residue (*m/z* 331) or those carrying one or two 2-methylbutyric acids (*m/z* 373 or 415) was detected. These data suggest that 2 mol of 2-methylbutyric acid are attached to 2- and 4-OH of Rha and the other two are at 3- and 4-OH of the third glucose (Glc″), so that the macrocyclic ester linkage is at 2-OH of the terminal glucose (Glc‴).

The site of the macrocyclic ester group was further confirmed by partial solvolysis of **1** as follows. Compound **1** was treated with 3% triethylamine in MeOH to give four products, **7**, **8**, **9** and methyl ester of **3** (**10**). Among them, **7** exhibited the $[M-H]^-$ ion peak at *m/z* 1415, 32 mass units (CH_3OH) more than that of **1**, suggesting **7** to be the product which was solvolyzed only at the cyclic ester group. The ^{1}H-NMR spectrum of **7** revealed the presence of an ester methyl and an equivalent methylene (2-H_2) of the methyl jalapinolate group and four 2-methylbutyric acid residues. Comparing the signals due to the sugar moieties between **1** and **7**, the acylation shifts were seen at 3- and 4-H

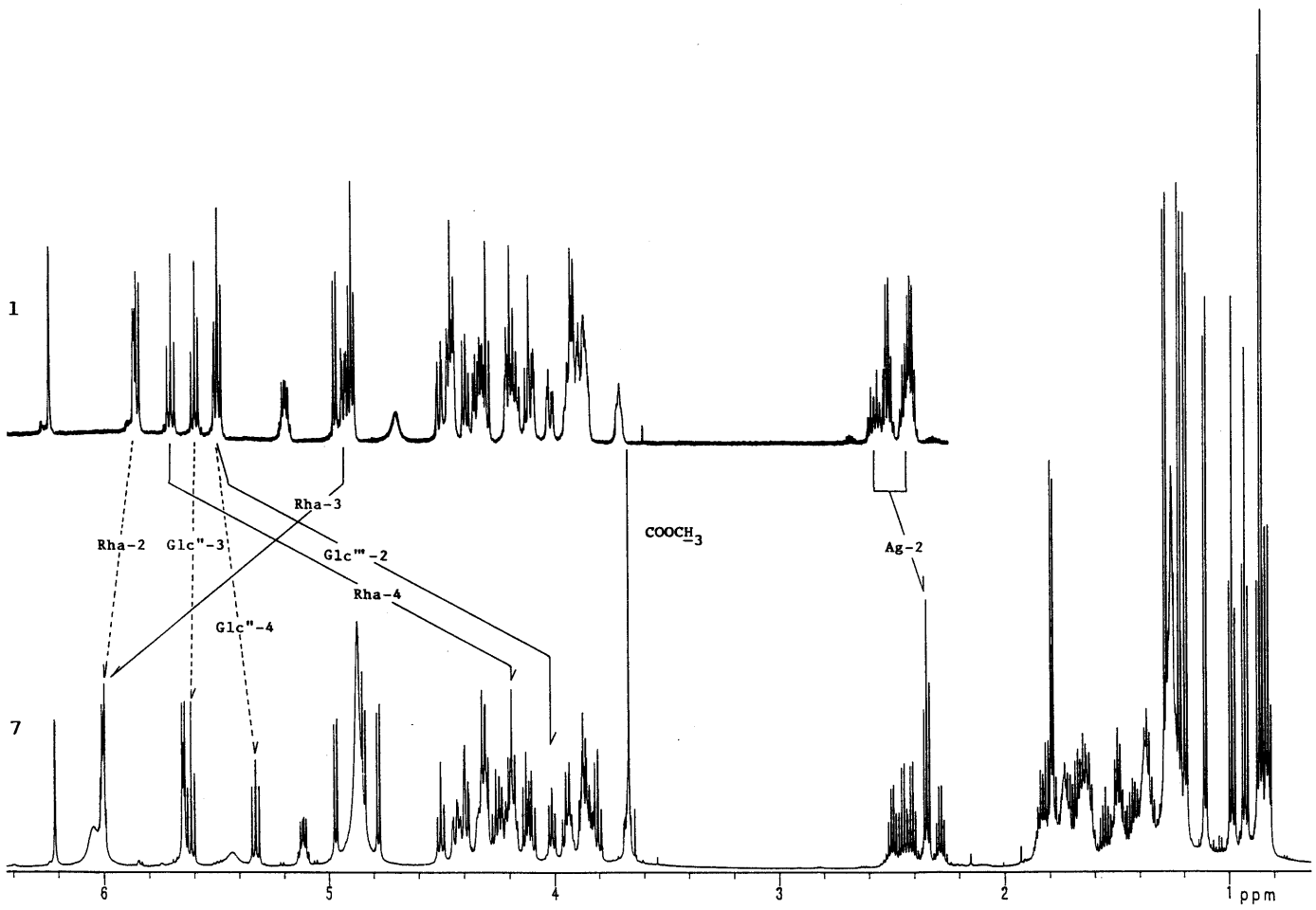

Fig. 4. ^{1}H-NMR Spectra of **1** and **7** (in Pyridine-d_5, 600 MHz)

of Glc″, and 2- and 3-H of Rha (1.52, 1.40, 1.20 and 1.38 ppm, respectively; Fig. 4, Tables I and II), indicating that the 2-methylbutyric acid group at 4-OH in Rha had migrated to 3-OH in the same sugar unit and the other three remained at the original positions. On the other hand, the signal of 2-H of Glc‴ at 5.49 in **1** was shifted to highfield by 1.48 ppm in **7** due to solvolysis of the cyclic ester bond at 2-OH of Glc‴. The jalapinolic acid group in **1**, therefore, is linked with 2-OH of Glc‴ to form a 26-membered ring ester structure.

Compounds **8**, **9** and **10** were characterized by comparing their ^{1}H-NMR spectra with that of **7** as shown in Fig. 1.

Consequently, the full structure of **1** is concluded to be (*S*)-jalapinolic acid 11-*O*-*β*-D-glucopyranosyl-(1→6)-*O*-(3,4-di-*O*-2(*S*)-methylbutyryl)-*β*-D-glucopyranosyl-(1→3)-*O*-[(2,4-di-*O*-2(*S*)-methylbutyryl)-α-L-rhamnopyranosyl-(1→2)]-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopyranoside, intramolecular, 1, 2⁗-ester (Fig. 1).

Woodrosin II (**2**), $C_{65}H_{110}O_{30}$, afforded, on alkaline hydrolysis, 2(*S*)-methylbutyric acid, isobutyric acid and **3**, and exhibited the $[M-H]^-$ ion peak at *m/z* 1369 and the fragment ion peaks at *m/z* 1225 and 1055 which were, respectively, 14 mass units (CH_2) less than those of **1**, suggesting **2** to be an analog in which one of four 2(*S*)-methylbutyric acids in **1** was replaced by isobutyric acid. This was supported by the ^{1}H- and ^{13}C-NMR spectra, which were quite similar to those of **1**, in particular, concerning the chemical shifts of the signals due to 3- and 4-H of Glc″, 2-H of Glc‴, and 2- and 4-H of Rha, except for the appearance of signals due to one isobutyric acid residue and the loss of those due to one of four 2-methylbutyric acid residues.

The fragment ion peaks at *m/z* 909, 433 and 271 in the negative FAB-MS of **2** as well as that at *m/z* 357 in the EI-MS of its peracetate (**11**) were, respectively, the same as those of **1** and **8**. Therefore, the isobutyric acid group should be attached to either 3- or 4-OH of Glc″. It was verified that the former is the case by the cross peaks observed between 3-H of Glc″, and 1-C and 2-H of the isobutyric acid group in the ^{1}H-detected heteronuclear multiple-bond multiple-quantum coherence (HMBC) spectrum of **2** measured at J_{C-H} 150 Hz (Fig. 5).

Consequently, the structure of **2** was concluded to be (*S*)-jalapinolic acid 11-*O*-*β*-D-glucopyranosyl-(1→6)-*O*-(3-*O*-isobutyryl, 4-*O*-2(*S*)-methylbutyryl)-*β*-D-glucopyranosyl-(1→3)-*O*-[(2,4-di-*O*-2(*S*)-methylbutyryl)-α-L-rhamnopyranosyl(1→2)]-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopyranoside, intramolecular 1, 2⁗-ester, as shown in Fig. 1.

In 1855 Mayer classified the so-called resin glycosides, according to their solubility in ether, into two groups, jalapin (soluble) and convolvulin (insoluble).[8] This classification has since been conventionally used. All the resin glycosides *hitherto* isolated and characterized, that is, oriza-

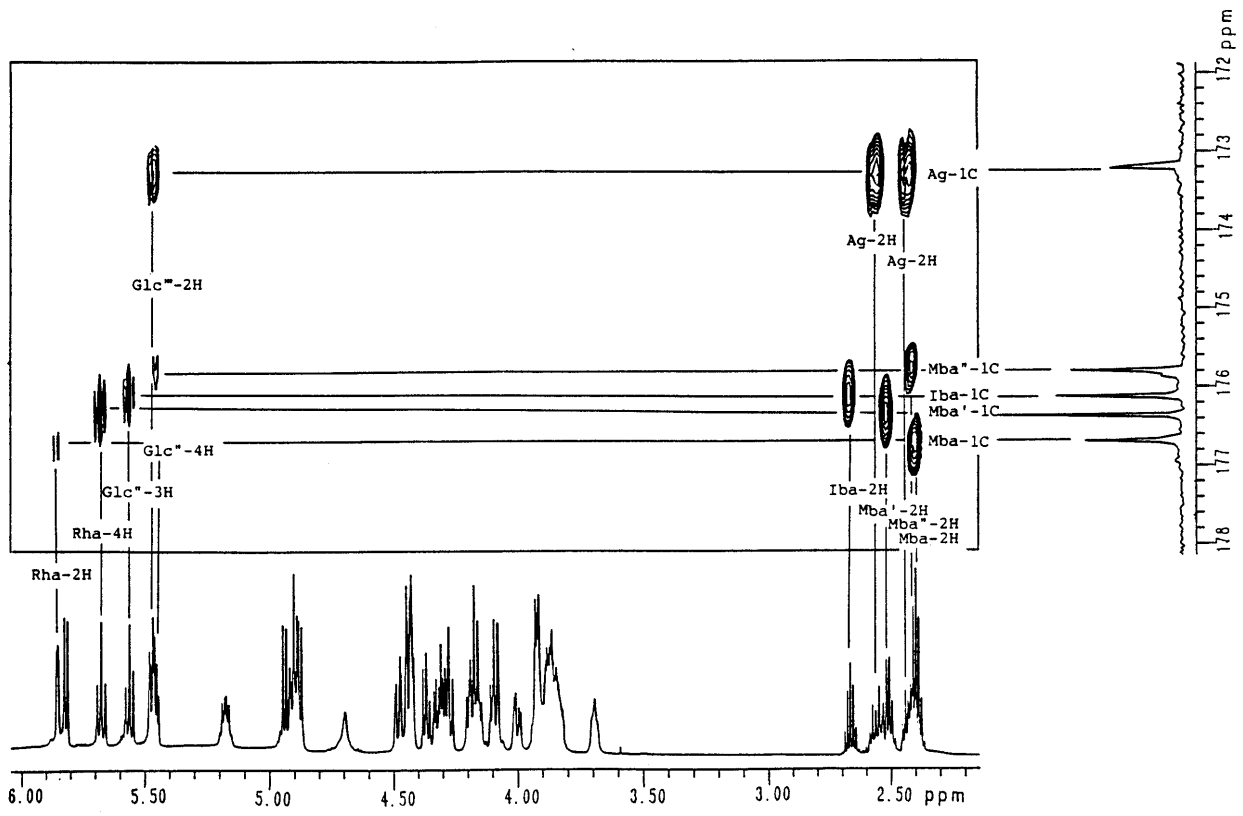

Fig. 5. HMBC Spectrum of **2** (in Pyridine-d_5, 600 MHz)
J_{C-H} = 150 Hz.

bins,[9a] muricatins,[9b] merremosides,[9c] mammosides,[9d] operculins,[9e] scammonins,[9f] quamoclins,[9g] simonins[9h] and marubajalapins,[9i] are soluble in ether, belonging to Mayer's jalapin category, and they all had, without exception, common intramolecular macrocyclic ester structures composed of 1 mol of a variety of acylated glycosidic acids. On the other hand, Mayer's convolvulin category includes the ether-insoluble resin glycosides obtained from Mexican Jalap (convolvulin),[10] Brazilian Jalap (rhamnoconvolvulin)[11] and Pharbitidis Semen (pharbitin),[12] which have large molecular weights (*ca.* 6000—20000 by titration and/or TOF-MS)[13] and show tailing or broad peaks on TLC and HPLC, suggesting that they are quite different from jalapin in chemical structure, probably being oligomer of acylated glycosidic acids with free carboxylic acid(s), as postulated by Mannich and Schumann.[11] Woodrosins I and II in this study are the first examples of ether-insoluble resin glycosides having an intramolecular cyclic ester structure similar to jalapin.

Taking the above findings into account, we propose that the terms, "jalapin" and "convolvulin," should be used not on the basis of the solubility in ether, but rather to describe structural groups, namely, the resin glycosides having intramolecular cyclic ester structures and the others, respectively. Thus, woodrosins I and II represent ether-insoluble jalapins.

Experimental

All instruments and materials used were as cited in the preceding report[9g] unless otherwise specified.

Isolation of Woodrosins I and II The cut, air-dried stems (1064 g) of *Ipomoea tuberosa* L. collected at the botanical garden in Fukuoka University were extracted with MeOH (15 l) at room temperature and the extract was evaporated under reduced pressure to give a brown syrup (89.8 g). The syrup (25.49 g) was partitioned between H_2O (170 ml) and *n*-BuOH (170 ml). Concentration of the *n*-BuOH layer furnished a brown syrup (9.02 g). Chromatography of the syrup on a Sephadex LH-20 column using MeOH afforded fr. 1 (2.91 g), fr. 2 (0.49 g), fr. 3 (1.81 g), fr. 4 (0.33 g) and fr. 5 (3.25 g). Fraction 1 was chromatographed over silica gel [($CHCl_3$–MeOH–H_2O, 10:2:0.1→8:2:0.2)→MeOH] to furnish fr. 6 (44 mg), fr. 7 (1.88 g), fr. 8 (136 mg) and fr. 9 (371 mg). Preparative HPLC on an Inertsil ODS column (GL Sciences, 2.0 cm i.d. × 25 cm, 96% MeOH) of fr. 7 yielded fr. 10 (36 mg), fr. 11 (71 mg), **1** (315 mg), **2** (290 mg) and fr. 12 (35 mg).

1: White powder, mp 142—148 °C, $[\alpha]_D^{25}$ −25.4° (c = 2.9, MeOH). Negative FAB-MS m/z (%): 1383 (100) $[M-H]^-$, 1299 (15) [1383 − 84 (2-methylbutyric acid $-H_2O$)]$^-$, 1281 (18) [1383 − 102 (2-methylbutyric acid)]$^-$, 1239 (24) [1383 − 144 (hexose unit $-H_2O$)]$^-$, 1069 (16) [1383 − 84 × 2 − 146]$^-$, 909 (24) [1239 − 162 (hexose unit) − 84 × 2]$^-$, 433 (93) [909 − 84 × 2 − 146 (deoxyhexose unit) − 162]$^-$, 271 (51) [433 − 162, jalapinolic acid $-H]^-$. ^{1}H-NMR δ: see Table I. ^{13}C-NMR δ: see Table II. *Anal.* Calcd for $C_{66}H_{112}O_{30}$: C, 57.21; H, 8.14. Found: C, 57.18; H, 8.33.

2: White powder, mp 148—152 °C, $[\alpha]_D^{25}$ −29.1° (c = 3.8, MeOH). Negative FAB-MS m/z (%): 1369 (100) $[M-H]^-$, 1285 (17) [1369 − 84]$^-$, 1267 (11) [1369 − 102]$^-$, 1225 (23) [1369 − 144]$^-$, 1055 (18) [1369 − 84 × 2 − 146]$^-$, 909 (19) [1225 − 162 − 84 − 70 (isobutyric acid unit)]$^-$, 433 (76) [909 − 84 × 2 − 146 − 162]$^-$, 271 (47) [433 − 162]$^-$. ^{1}H-NMR δ: see Table I. ^{13}C-NMR δ: see Table II. *Anal.* Calcd for $C_{65}H_{110}O_{30}$: C, 56.92; H, 8.08. Found: C, 56.82; H, 8.29.

Alkaline Hydrolysis of 1 and 2 Suspensions of **1** (36 mg) and **2** (25 mg) in 1 N KOH were each heated at 95 °C for 1 h. The mixture was adjusted to pH 3 with 1 N HCl and diluted with H_2O (10 ml) then extracted with Et_2O (5 × 10 ml). The Et_2O layer was washed with H_2O (10 ml), and evaporated to give an organic acid fraction (8 mg from **1**; 5 mg from **2**), which was subjected to GC [column, Unisole 30T (5%), 3.2 mm i.d. × 2 m glass column; column temperature, 110 °C; carrier gas, N_2 (1.0 kg/cm^2)], t_R (min): 5.78 (2-methylbutyric acid) for **1**, 3.47 (isobutyric acid), and 5.84 (2-methylbutyric acid) for **2**].

The aqueous layer was chromatographed over MCI-gel CHP 20P to give a glycosidic acid (**3**) (23 mg from **1**; 14 mg from **2**), white powder, mp

143—150 °C, $[\alpha]_D^{17}$ −36.5° (c=4.0, MeOH). Negative FAB-MS m/z (%): 1065 (100) $[M-H]^-$, 919 (10) [1065−146 (6-deoxyhexose unit)]$^-$, 903 (22) [1065−162 (hexose unit)]$^-$, 741 (31) [903−162]$^-$, 595 (10) [741−146]$^-$, 433 (55) [595−162]$^-$ and 271 (45) [433−162, jalapinolic acid−H]$^-$. ^{1}H-NMR δ: see Table I. ^{13}C-NMR δ: see Table II. *Anal.* Calcd for $C_{46}H_{82}O_{27}\cdot 2H_2O$: C, 50.08; H, 7.86. Found: C, 50.38; H, 7.74. Each organic acid fractions obtained from **1** (7 mg) and **2** (5 mg) was treated with *S*-1-phenylethylamine (50 mg) in the same manner as reported for quamoclins[9g] to furnish colorless needles (*n*-hexane–AcOEt) (9 and 2 mg), mp 83—87 °C. The products were each shown to be identifical with an authentic sample of (*S*)-*N*-1-phenylethyl-2(*S*)-methylbutyrylamide by ^{1}H-NMR ($CDCl_3$, 400 MHz) and HPLC.[9g]

Acidic Hydrolysis of 3 A mixture of **3** (100 mg) and 1 N HCl (1 ml) was heated at 95 °C for 30 min. The mixture was diluted with H_2O (10 ml) then extracted with Et_2O (3×10 ml). The Et_2O layer was washed with H_2O (10 ml) and concentrated *in vacuo*. Treatment of the residue with CH_2N_2 in Et_2O followed by evaporation yielded **4** (7 mg), colorless needles (hexane–AcOEt), mp 42—44 °C. ^{13}C-NMR (in $CDCl_3$, 100 MHz) δ: 174.4, 72.1, 51.4, 37.5, 34.1, 32.0, 29.7, 29.6, 29.4, 29.3, 29.2, 25.7, 25.4, 25.0, 22.7, 14.1, which was identical with an authentic sample of methyl jalapinolate. A solution of **4** (2 mg) in pyridine (0.5 ml), CCl_4 (5 drop) and (+)-α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) chloride (15 mg) was left to stand at room temperature overnight. The mixture was worked up in the same way as previously reported[1] to afford a syrup (3 mg). The ^{1}H-NMR spectral data [(in $CDCl_3$, 600 MHz) δ: 5.082 (1H, dd, J=5.5, 6.7 Hz, 11-H), 2.299 (2H, t, J=6.7 Hz, 2-H_2), 0.877 (3H, t, J=7.0 Hz, 16-H_3)] were in good accordance with those of the (+)-MTPA ester of methyl 11(*S*)-jalapinolate.

The aqueous layer was neutralized with 1 N KOH and desalted (Sephadex LH-20, MeOH) to afford a sugar mixture (64 mg), which was subjected to TLC analysis [HPTLC, Silica gel 60 F_{254} (Merck Art 5628), $CHCl_3$–MeOH–H_2O, 6:4:1. *Rf*: 0.29 (glucose), 0.54 (rhamnose); TLC

Table III. ^{1}H-NMR Data for **7**, **8** and **9** (in Pyridine-d_5, 600 MHz)

	7	**8**	**9**
Glc -1	4.97, d (7.7)	4.95, d (7.7)	4.99, d (7.7)
-2	4.31, dd (7.7, 8.9)	4.38, dd (7.7, 9.2)	4.35, dd (7.7, 9.2)
-3	4.50, dd (8.9, 8.9)	4.45, dd (9.2, 9.2)	4.54, dd (9.2, 9.2)
-4	4.10, dd (8.9, 8.9)	4.09, dd (9.2, 9.2)	4.10, dd (9.2, 9.2)
-5	*ca.* 3.87	*ca.* 3.89	*ca.* 3.89
-6	*ca.* 4.31	4.33, dd (5.1, 11.7)	4.31, dd (5.1, 11.7)
	4.44, dd (2.4, 11.7)	4.50, dd (2.2, 11.7)	4.45, dd (2.6, 11.7)
Glc′ -1	5.65, d (7.7)	5.74, d (8.1)	5.68, d (7.7)
-2	4.13, dd (7.7, 8.9)	4.15, dd (8.1, 8.8)	4.18, dd (7.7, 8.6)
-3	3.81, dd (8.9, 8.9)	3.78, dd (8.8, 8.8)	3.78, dd (8.6, 8.6)
-4	3.95, dd (8.9, 8.9)	3.94, dd (8.8, 8.8)	*ca.* 3.96
-5	3.68, ddd (2.2, 5.2, 8.8)	3.71, ddd (2.5, 5.9, 8.8)	3.71, ddd (2.2, 5.9, 8.7)
-6	*ca.* 4.19	*ca.* 4.20	*ca.* 4.19
	ca. 4.33	4.40, dd (2.2, 11.7)	4.39, dd (2.2, 11.4)
Glc″ -1	4.84, d (8.1)	4.84, d (7.7)	4.88, d (8.1)
-2	*ca.* 3.86	3.95, dd (7.7, 9.2)	*ca.* 3.96
-3	5.61, dd (9.3, 9.3)	4.12, dd (9.2, 9.2)	4.12, dd (9.2, 9.2)
-4	5.33, dd (9.3, 10.1)	*ca.* 3.92	3.94, dd (9.2, 9.2)
-5	4.23, ddd (2.5, 7.2, 10.1)	*ca.* 4.21	*ca.* 4.21
-6	*ca.* 3.88	*ca.* 3.89	*ca.* 3.89
	4.39, dd (2.4, 10.5)	5.01, dd (2.2, 10.3)	4.99, dd (2.2, 11.1)
Glc‴ -1	4.78, d (7.7)	4.78, d (7.7)	4.78, d (7.7)
-2	4.01, dd (7.7, 8.9)	4.04, dd (7.7, 8.8)	4.04, dd (7.7, 8.8)
-3	4.19, dd (8.9, 8.9)	4.20, dd (8.8, 8.8)	4.20, dd (8.8, 8.8)
-4	4.26, dd (8.9, 8.9)	4.26, dd (8.8, 8.8)	4.26, dd (8.8, 8.8)
-5	3.84, ddd (2.2, 4.6, 8.9)	*ca.* 3.89	*ca.* 3.89
-6	*ca.* 4.31	4.35, dd (4.0, 11.1)	4.35, dd (5.1, 11.4)
	4.41, dd (2.2, 11.9)	4.48, dd (2.2, 11.1)	4.48, dd (2.6, 11.4)
Rha -1	6.22, d (1.2)	6.41, d (1.8)	6.32, d (1.8)
-2	*ca.* 6.00	4.98, dd (1.8, 2.9)	4.97, dd (1.8, 3.1)
-3	*ca.* 6.00	5.99, dd (2.9, 9.6)	5.96, dd (3.1, 9.7)
-4	4.19, dd (8.9, 8.9)	6.03, dd (9.6, 9.6)	4.48, dd (9.7, 9.7)
-5	5.11, dq (8.9, 6.5)	5.26, dq (9.6, 6.2)	5.12, dq (9.7, 6.2)
-6	1.79, d (6.5)	1.62, d (6.2)	1.80, d (6.2)
Ag -16	0.82, t (7.0)	0.83, t (7.0)	0.82, t (7.0)
-11	*ca.* 3.93	*ca.* 3.94	*ca.* 3.96
-2	2.34, t (7.7)	2.32, t (7.5)	2.32, t (7.5)
$COOCH_3$	3.67, s	3.63, s	3.62, s
Mba -2	2.50, ddq (6.9, 6.9, 6.9)	2.52, ddq (7.0, 7.0, 7.0)	2.42, ddd (7.0, 7.0, 7.0)
	2.45, ddq (6.9, 6.9, 6.9)	2.35, ddq (7.0, 7.0, 7.0)	
	2.41, ddq (6.9, 6.9, 6.9)		
	2.28, ddq (6.9, 6.9, 6.9)		
Mba -4	0.98, t (7.5)	0.96, t (7.5)	0.85, t (7.0)
	0.93, t (7.5)	0.82, t (7.5)	
	0.86, t (7.3)		
	0.85, t (7.2)		
Mba -5	1.28, d (7.0)	1.31, d (7.0)	1.07, d (7.0)
	1.22, d (7.0)	1.03, d (7.0)	
	1.19, d (7.0)		
	1.10, d (7.0)		

δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses); Glc, glucopyranosyl; Rha, rhamnopyranosyl; Ag, aglycone ((*S*)-jalapinolic acid); Mba, 2(*S*)-methylbutyryl.

[Funakoshi Avicel SF, *n*-BuOH–pyridine–H_2O (6:2:3) top layer + pyridine (1)] *Rf*: 0.39 (glucose), 0.65 (rhamnose)]. This mixture (6 mg) was derived into TMS ethers of the methyl thiazolidine 4(*R*)-carboxylate derivatives and the product was subjected to GC analysis according to the method reported by Hara *et al.*[6] [Hitachi G-3000 gas chromatograph; column, fused silica capillary column Bonded MPS-50 (Quadrex), 0.25 i.d. mm × 50 m; film thickness, 0.25 μm; carrier gas, He (30 ml/min); column temperature, 220 °C; t_R (min), 19.43 (L-rhamnose), 26.96 (D-glucose)].

Acetylation of 3 A solution of **3** (15 mg) in Ac_2O–pyridine (1:1, 1 ml) was left to stand overnight at room temperature. The solvent was removed under an N_2 stream to give a residue. The residue was chromatographed over silica gel [Kusano CIG Si-gel, 2.2 cm i.d. × 10 cm, *n*-hexane–AcOEt (4:5→3:5→2:5)] to afford a white powder (**5**) (14 mg), mp 69—80 °C, $[\alpha]_D^{23}$ −20.5° (*c*=1.8, MeOH). ^{1}H-NMR δ: see Table I.

Acetylation of 1 and 2 Compounds **1** (10 mg) and **2** (10 mg) were each dissolved in Ac_2O–pyridine (1:1, 2 ml) and the solution was heated at 50 °C for 24 h. The solvent was removed under an N_2 stream to give a residue. The residue was subjected to HPLC (Inertsil ODS-2, 6 mm i.d. × 250 mm, MeOH) to afford **6** (11 mg from **1**), white powder, mp 76—84 °C. ^{1}H-NMR (pyridine-d_5, 600 MHz) δ: 1.986, 2.007, 2.010, 2.027 × 2, 2.076, 2.116, 2.251, 2.279, 2.286 (each 3H, s, $OCOCH_3$). EI-MS *m/z*: 525 (10), 357 (100), 315 (4), and **11** (12 mg from **2**), white powder, mp 87—89 °C, ^{1}H-NMR (pyridine-d_5, 600 MHz) δ: 2.001, 2.020, 2.025, 2.041 × 2, 2.089, 2.131, 2.262, 2.292 × 2 (each 3H, s, $OCOCH_3$). EI-MS *m/z*: 511 (7), 357 (100), 315 (88), 273 (53).

Partial Solvolysis of 1 Compound **1** (161 mg) was dissolved in 3% triethylamine–MeOH (5 ml) and the solution was refluxed for 3 h. The reaction mixture was neutralized with 1 N HCl then desalted (Sephadex LH-20, MeOH) to afford a residue, which was chromatographed on a CIG Si-gel column [($CHCl_3$–MeOH–H_2O, 8:2:0.2→7:3:0.5→6:4:1)→MeOH] to give fr. 13 (45 mg), fr. 14 (25 mg), fr. 15 (23 mg) and fr. 16 (13 mg), which were purified by HPLC (Inertsil ODS, 90% MeOH) to afford **7** (12 mg), **8** (9 mg), **9** (12 mg) and **10** (10 mg), respectively.

7: White powder, mp 98—103 °C, $[\alpha]_D^{21}$ −11.2° (*c*=1.5, MeOH). Negative FAB-MS *m/z* (%): 1415 (100) $[M-H]^-$, 1401 (16) $[M-H-14(CH_2)]^-$, 1331 (22) $[M-H-84$ (isovaleric acid$-H_2O]^-$, 1101 (28) $[M-H-146$ (rhamnose unit)$-2\times84]^-$, 609 (19) $[1101-2\times162$ (glucose unit)$-2\times84)]^-$, 415 (72) $[609-162-32$ (MeOH)$]^-$. ^{1}H-NMR δ: see Table III. **8**: White powder, mp 117—122 °C, $[\alpha]_D^{21}$ −32.7° (*c*=1.2, MeOH). Negative FAB-MS *m/z* (%): 1247 (100) $[M-H]^-$, 1233 (22) $[M-H-14\ (CH_2)]^-$, 1163 (16) $[M-H-162]^-$, 1085 (13) $[M-H-162]^-$, 933 (66) $[M-H-146-2\times84]^-$, 771 (51) $[933-162]^-$, 609 (14) $[771-162]^-$, 447 (13) $[609-162]^-$, 415 (74) $[447-32]^-$. ^{1}H-NMR δ: see Table III.

9: White powder, mp 129—132 °C, $[\alpha]_D^{21}$ −29.5° (*c*=1.4, MeOH). Negative FAB-MS *m/z* (%): 1163 (100) $[M-H]^-$, 1149 (22) $[M-H-14]^-$, 1079 (16) $[M-H-84]^-$, 933 (29) $[1079-146]^-$, 771 (10) $[933-162]^-$, 609 (10) $[771-162]^-$, 447 (13) $[609-162]^-$, 415 (74) $[447-32]^-$. ^{1}H-NMR δ: see Table III. **10**: White powder, mp 144—148 °C, $[\alpha]_D^{18}$ −37.0° (*c*=1.3, MeOH). Negative FAB-MS *m/z* (%): 1079 (100) $[M-H]^-$, 1065 (10) $[M-H-14\ (CH_2)]^-$, 933 (22) $[M-H-146]^-$, 917 (16) $[M-H-162]^-$, 771 (8) $[933-162]^-$, 755 (24) $[917-162]^-$, 609 (6) $[771-162]^-$, 447 (5) $[609-162]^-$, 415 (28) $[447-32]^-$. ^{1}H-NMR (in pyridine-d_5, 600 MHz) δ: 6.29 (1H, d, *J*=1.5 Hz, Rha-1), 5.78 (1H, d, *J*=7.7, Glc′-1), 5.00 (1H, d, *J*=7.7 Hz, Glc-1), 4.87 (1H, d, *J*=7.7 Hz, Glc″-1), 4.80 (1H, d, *J*=7.7 Hz, Glc‴-1), 3.63 (3H, s, $COOCH_3$), 2.33 (2H, t, *J*=7.5 Hz, 2-H_2), 1.80 (3H, d, *J*=6.2 Hz, Rha-6), 0.83 (3H, t, *J*=7.1 Hz, 15-CH_3).

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