Resin Glycosides. XVI.[1] Marubajalapins I—VII, New Ether-Soluble Resin Glycosides from *Pharbitis purpurea*

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Fifteen new resin glycosides, marubajalapins I—XV, were isolated from the jalapin fraction of the aerial part (leaves and stems) of *Pharbitis purpurea*. Among them, the structures of marubajalapins I—VII have been determined on the basis of chemical and spectral data. They are the first examples of jalapins with operculinic acid E obtained previously as a minor glycosidic acid of the crude jalapin from Jalapae Braziliensis.

Keywords resin glycoside; jalapin; marubajalapin; operculinic acid E; *Pharbitis purpurea*; Convolvulaceae; *n*-octanoic acid

In 1908, Power and Rogerson reported a chemical investigation on the resin glycoside obtained from the stems of *Pharbitis purpurea* VOIGT, showing that the alkaline hydrolysis of the glycoside yielded three organic acids, formic, butyric and 2-methylbutyric acids along with a glycosidic acid composed of D-glucose, hydroxylauric and ipurolic acids.[2] As a continuation of our studies on resin glycosides, which are characteristic of Convolvulaceae plants, we examined the aerial part, leaves and stems, of this plant and isolated fifteen new jalapins named marubajalapins I—XV after "maruba-asagao", the Japanese name of this plant. This paper deals with the structure elucidation of marubajalapins I(**1**), II(**2**), III(**3**), IV(**4**), V(**5**), VI(**6**) and VII (**7**).

The MeOH extractive of the fresh aerial part (leaves and stems) was treated with $CHCl_3$–MeOH–H_2O (2 : 1 : 1). The bottom layer was concentrated and the residue was chromatographed over silica gel and Sephadex LH-20 to give the ether-soluble resin glycoside (jalapin)[3] fraction (yield; 0.078%). The alkaline hydrolysis product of the jalapin fraction was fractionated into organic and glycosidic acid fractions. The former was methylated with diazomethane and the product was subjected to gas chromatography (GC) to show the presence of methyl *n*-octanoate and methyl *n*-decanoate. Methylation and subsequent purification by preparative high performance liquid chromatography (HPLC) of the latter fraction provided a glycosidic acid methyl ester (**8**), which was identical with the methyl ester of operculinic acid E (**9**), *viz.*, 11*S*-hydroxyhexadecanoic acid ((*S*)-jalapinolic acid) 11-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, by comparison of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum with that of an authentic sample obtained previously as a minor glycosidic acid of the jalapin fraction from Jalapae Braziliensis.[4] Repeated preparative HPLC over octadecyl silica (ODS) of the jalapin fraction gave marubajalapins I—XV.

Marubajalapin I (**1**), $C_{56}H_{98}O_{21}$, furnished, on alkaline hydrolysis, *n*-octanoic acid and operculinic acid E (**9**). The signals due to three carboxy carbons along with four anomeric carbons in the ^{13}C-NMR spectrum (Table I) and the $[M-H]^-$ ion peak at *m/z* 1105 in the negative ion fast atom bombardment mass spectrum (FAB-MS) as well as the nonequivalent 2-H_2 signals owing to the jalapinolic acid group (Jla) in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum (Table II) indicated that **1** consists of 1 mol of **9** and 2 mol of *n*-octanoic acids, and that the carboxyl group of Jla is also intramolecularly linked with a hydroxy group of the sugar moiety to form a macrocyclic ester ring, as in all the jalapins so far isolated.[5-9]

The ^{1}H signals due to sugar moiety of **1** were assigned by referring to the ^{1}H–^{1}H shift-correlated two dimensional (2D)-NMR (COSY), nuclear Overhauser effect 2D-NMR (NOESY) and ^{1}H–^{13}C heteronuclear shift-correlated 2D-NMR (HETCOR) spectra. A comparison of the signals with those of **8** indicated that 2-H of the first rhamnose (Rha), 2-H of the second rhamnose (Rha′) and 4-H of the third rhamnose (Rha″) were shifted downfield by 1.41, 1.24 and 1.61 ppm, respectively. Therefore, the ester linkages are concluded to be located at 2-OH of Rha, 2-OH of Rha′ and 4-OH of Rha″.

TABLE I. ^{13}C-NMR Spectral Data for **1**—**7** (in Pyridine-d_5)

		1[a]	**2**[a]	**3**[a]	**4**[b]	**5**[a]	**6**[a]	**7**[b]
Glc	-1	104.5	104.4	104.5	104.4	101.6	104.5	104.5
	2	81.8	82.0	81.8	82.0	75.1	82.0	81.8
	3	76.6	76.5	76.6	76.5	79.9	76.5	76.6
	4	71.9	71.9	71.8	71.9	72.1	71.9	71.9
	5	78.0	78.0	77.9	77.9	78.1	78.0	78.0
	6	62.9	62.8	62.8	62.8	62.9	62.9	62.9
Rha	-1	98.6	98.6	98.5	98.6	100.3	98.6	98.6
	2	73.6	73.7	73.5	73.7	69.6	73.8	73.6
	3	69.9	70.3[c]	69.9	70.2	78.9	70.3[c]	69.9
	4	80.7	80.9	80.7	81.0	76.2	81.0	80.9
	5	68.8	68.7[d]	68.8	68.7[c]	67.6	68.8[d]	68.8
	6	19.3	19.3	19.3	19.3	19.5	19.3	19.3
Rha′	-1	100.1	103.3	100.1	103.3	102.6	103.4	100.2
	2	74.2	70.1	74.2	70.1	70.4	70.1	74.1
	3	71.0	75.1[e]	70.9	75.1[d]	75.6	75.1[e]	70.6
	4	80.5	78.6	80.4	78.6	78.2	78.7	80.1
	5	68.6	68.8[d]	68.5	68.8[c]	69.1	68.9[d]	68.3
	6	18.9	18.7	18.8	18.7	18.5	18.7	18.9
Rha″	-1	103.5	103.5	103.5	103.4	103.6	103.5	100.2
	2	72.4	72.8	72.4	72.7	72.6	72.8	73.6
	3	70.3	70.2[c]	70.3	70.2	70.1	70.2[c]	68.1[c]
	4	75.4	75.8[e]	75.4	75.8[d]	75.1	75.8[e]	75.1
	5	68.1	68.2	68.1	68.2	68.2	68.3	68.0[c]
	6	18.1	17.9	18.0	17.9	17.9	17.9	18.0
Jla	-11	82.9	82.8	82.8	82.8	79.9	82.8	82.9
C=O		173.5	173.5	173.5	173.4	174.4	173.5	173.5
		173.4	173.4	173.3	173.3	173.5	173.4	173.4
		173.3	173.4	173.3	173.3	172.7	173.4	173.3
								173.1

a) 150 MHz. *b*) 100 MHz. *δ* in ppm from TMS. Glc, glucopyranosyl; Rha, rhamnopyranosyl; Jla, (*S*)-jalapinolic acid group. *c*—*e*) Assignments may be interchanged in each column.

TABLE II. ^{1}H-NMR Spectral Data for **1**—**7** (in Pyridine-d_5)

		1[a]	**2**[a]	**3**[a]	**4**[b]
Glc	-1	4.89, d (7.7)	4.93, d (7.7)	4.88, d (7.3)	4.91, d (7.6)
	2	3.89, dd (7.7, 9.2)	3.90, dd (7.7, 9.0)	3.88, dd (7.3, 9.0)	3.87, dd (7.6, 9.0)
	3	*ca.* 4.14	4.18, dd (9.0, 9.0)	*ca.* 4.13	4.15, dd (9.0, 9.0)
	4	*ca.* 4.12	4.13, dd (9.0, 9.0)	*ca.* 4.11	4.10, dd (9.0, 9.0)
	5	3.84, ddd (2.6, 5.2, 9.2)	3.87, ddd (2.8, 5.2, 9.0)	3.84, ddd (2.4, 4.8, 9.0)	*ca.* 3.84
	6	4.31, dd (5.2, 11.2)	4.31, dd (5.2, 11.3)	4.29, dd (4.8, 11.7)	4.28, dd (5.5, 12.0)
		4.45, dd (2.6, 11.2)	4.46, dd (2.8, 11.3)	*ca.* 4.45	*ca.* 4.43
Rha	-1	5.60, d (1.6)	5.60, d (1.8)	5.59, d (1.8)	5.57, d (1.5)
	2	6.05, dd (1.6, 3.4)	6.03, dd (1.8, 3.6)	6.04, dd (1.8, 3.3)	6.00, dd (1.5, 3.5)
	3	5.08, dd (3.4, 9.3)	5.07, dd (3.6, 9.5)	5.07, dd (3.3, 9.5)	5.04, dd (3.5, 9.1)
	4	4.24, dd (9.3, 9.3)	4.26, dd (9.5, 9.5)	4.23, dd (9.5, 9.5)	4.23, dd (9.1, 9.1)
	5	4.42, dq (9.3, 6.1)	*ca.* 4.43	4.41, dq (9.5, 6.2)	*ca.* 4.41
	6	1.63, d (6.1)	1.63, d (6.1)	1.62, d (6.2)	1.61, d (6.4)
Rha′	-1	6.08, d (1.6)	6.21, d (1.6)	6.07, d (1.8)	6.18, d (1.5)
	2	6.00, dd (1.6, 3.3)	*ca.* 4.92	5.99, dd (1.8, 3.3)	*ca.* 4.90
	3	4.68, dd (3.3, 9.3)	5.83, dd (3.2, 9.5)	4.67, dd (3.3, 9.5)	5.81, dd (3.2, 9.6)
	4	4.30, dd (9.3, 9.3)	4.59, dd (9.5, 9.5)	4.29, dd (9.5, 9.5)	4.56, dd (9.6, 9.6)
	5	4.38, dq (9.3, 6.5)	*ca.* 4.43	4.37, dq (9.5, 6.2)	*ca.* 4.41
	6	1.71, d (6.5)	1.66, d (6.1)	1.70, d (6.2)	1.64, d (6.1)
Rha″	-1	6.21, d (1.5)	5.77, d (1.2)	6.21, d (1.8)	5.74, d (1.0)
	2	4.81, dd (1.5, 3.4)	*ca.* 4.58	4.81, dd (1.8, 3.3)	*ca.* 4.56
	3	4.58, dd (3.4, 9.7)	4.53, dd (2.8, 9.4)	4.57, dd (3.3, 9.5)	4.50, dd (3.0, 9.5)
	4	5.86, dd (9.7, 9.7)	5.84, dd (9.4, 9.4)	5.85, dd (9.5, 9.5)	5.81, dd (9.5, 9.5)
	5	*ca.* 4.43	4.37, dq (9.4, 6.1)	*ca.* 4.43	4.34, dq (9.5, 6.1)
	6	1.47, d (6.5)	1.40, d (6.1)	1.47, d (6.2)	1.39, d (6.1)
Jla	-11	*ca.* 3.88	*ca.* 3.90	*ca.* 3.87	*ca.* 3.87
	2	*ca.* 2.41	*ca.* 2.43	*ca.* 2.41	*ca.* 2.41
		ca. 2.26	*ca.* 2.25	*ca.* 2.26	*ca.* 2.25
CH_3		0.83, t (7.0)	0.83, t (6.9)	0.85, t (7.0)	0.85, t (7.0)
		0.81, t (7.2)	0.81, t (7.3)	0.82, t (7.0)	0.83, t (7.3)
		0.81, t (7.2)	0.79, t (7.3)	0.81, t (7.3)	0.78, t (7.0)

		5[a]	**6**[a]	**7**[b]
Glc	-1	4.99, d (7.7)	4.93, d (7.5)	4.85, d (7.5)
	2	*ca.* 4.29	3.90, dd (7.5, 9.0)	3.84, dd (7.5, 9.2)
	3	*ca.* 4.30	4.17, dd (9.0, 9.0)	*ca.* 4.09
	4	4.15, dd (9.2, 9.2)	4.12, dd (9.0, 9.0)	*ca.* 4.07
	5	3.90, ddd (2.8, 5.1, 9.2)	3.87, ddd (2.6, 5.1, 9.0)	3.79, ddd (2.8, 4.2, 9.2)
	6	4.36, dd (5.1, 11.7)	4.31, dd (5.1, 11.7)	4.25, dd (4.2, 11.5)
		4.50, dd (2.8, 11.7)	4.46, dd (2.6, 11.7)	4.39, dd (2.8, 11.5)
Rha	-1	6.49, d (1.8)	5.60, d (1.8)	5.56, d (1.6)
	2	5.24, dd (1.8, 2.9)	6.03, dd (1.8, 3.1)	*ca.* 5.98
	3	5.68, dd (2.9, 9.5)	5.07, dd (3.1, 9.5)	5.01, dd (3.5, 9.2)
	4	4.75, dd (9.5, 9.5)	4.26, dd (9.5, 9.5)	4.17, dd (9.2, 9.2)
	5	5.15, dq (9.5, 6.2)	4.43, dq (9.5, 5.9)	*ca.* 4.35
	6	1.74, d (6.2)	1.63, d (5.9)	1.59, d (6.2)
Rha′	-1	5.90, d (1.5)	6.21, d (1.8)	5.99, d (1.0)
	2	4.71, dd (1.5, 2.9)	*ca.* 4.92	*ca.* 5.97
	3	5.72, dd (2.9, 9.5)	5.84, dd (3.1, 9.5)	4.65, dd (3.5, 9.5)
	4	4.56, dd (9.5, 9.5)	4.60, dd (9.5, 9.5)	4.23, dd (9.5, 9.5)
	5	*ca.* 4.42	4.43, dq (9.5, 6.2)	*ca.* 4.33
	6	1.61, d (6.2)	1.66, d (6.2)	1.66, d (6.0)
Rha″	-1	5.68, d (1.8)	5.77, d (1.8)	6.06, s
	2	4.49, dd (1.8, 3.3)	4.59, dd (1.8, 3.3)	6.04, d (3.5)
	3	4.43, dd (3.3, 9.5)	4.53, dd (3.3, 9.5)	4.69, dd (3.5, 9.5)
	4	5.80, dd (9.5, 9.5)	5.84, dd (9.5, 9.5)	5.67, dd (9.5, 9.5)
	5	4.32, dq (9.5, 6.2)	4.37, dq (9.5, 6.2)	4.41, dq (9.5, 6.0)
	6	1.38, d (6.2)	1.41, d (6.2)	1.49, d (6.0)
Jla	-11	3.95, m	*ca.* 3.90	*ca.* 3.86
	2	*ca.* 2.27	*ca.* 2.43	*ca.* 2.41
		ca. 2.15	2.24, m	*ca.* 2.28
CH_3		0.99, t (7.3)	0.85, t (7.0)	0.83, t (7.0)
		0.85, t (7.2)	0.84, t (7.3)	0.82, t (7.0)
		0.81, t (7.2)	0.83, t (7.0)	0.82, t (6.5)
				0.81, t (6.5)

a) 600 MHz. *b*) 400 MHz. δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses); Glc, glucopyranosyl; Rha, rhamnopyranosyl; Jla, (*S*)-jalapinolic acid group.

In the negative FAB-MS of **1** and **9**, besides the common fragment peaks observed at *m/z* 271 and 433, **1** showed a peak at *m/z* 561 in place of that at *m/z* 579 $[M-H-2\times 146$ (deoxyhexose unit)$]^-$ observed in the spectrum of **9**.[4] The difference of 18 mass units suggested that the ester linkage of Jla involves Rha. This was confirmed by the electron impact mass spectrum (EI-MS) of the peracetate of **1** (**10**) which revealed peaks at *m/z* 357, 671 and 713 ascribable to the fragments a, c and e, respectively (Fig. 1).

Consequently, the structure of **1** was concluded to be (*S*)-jalapinolic acid 11-*O*-(4-*O*-*n*-octanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-(2-*O*-*n*-octanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, intramolecular 1,2″-ester, as shown in Fig. 2.

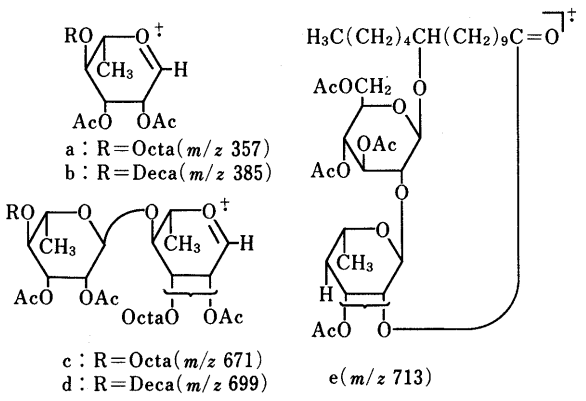

Fig. 1. Mass Fragment Ions of **10**—**13**
Ac, acetyl; Octa, *n*-octanoyl; Deca, *n*-decanoyl.

Marubajalapin II (**2**), $C_{56}H_{98}O_{21}$, gave the same components as those of **1** by alkaline hydrolysis and its negative FAB-MS was almost superimposable on that of **1**, showing $[M-H]^-$ and fragment ion peaks at *m/z* 1105, 561, 433 and 271. Therefore, **2** was considered to be a positional isomer of **1** with a macrocyclic ester group situated in Rha. In the ^{1}H-NMR spectrum of **2**, compared with that of **1**, a downfield shift of 3-H of Rha′ (1.15 ppm) along with an upfield shift of 2-H of Rha′ (*ca.* 1.08 ppm) were observed, whereas 2-H of Rha and 4-H of Rha″ resonated at quite similar positions to those of **1** (Table II). Accordingly, the structure of **2** was characterized as (*S*)-jalapinolic acid 11-*O*-(4-*O*-*n*-octanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-(3-*O*-*n*-octanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, intramolecular 1,2″-ester, as shown in Fig. 2.

Marubajalapins III (**3**), $C_{58}H_{102}O_{21}$, IV (**4**), $C_{58}H_{102}O_{21}$, and V (**5**), $C_{58}H_{102}O_{21}$, each afforded *n*-decanoic and *n*-octanoic acids in the ratio of about 1 : 1 (GC) on alkaline hydrolysis, along with **9**. Their negative FAB-MS were almost superimposable on each other, exhibiting $[M-H]^-$ and fragment ion peaks at *m/z* 1133, 1007, 853, 707, 561, 433 and 271. Furthermore, the EI-MS of their peracetates (**11**, **12** and **13**) showed the same fragment ion peaks at *m/z* 385 (b), 699 (d) and 713 (e) (Fig. 1). The ^{1}H-NMR signals due to the sugar moieties of **3** and **4** were quite similar to those of **1** and of **2**, respectively (Table II). Accordingly, the structures of **3** and **4** were concluded to be (*S*)-jalapinolic

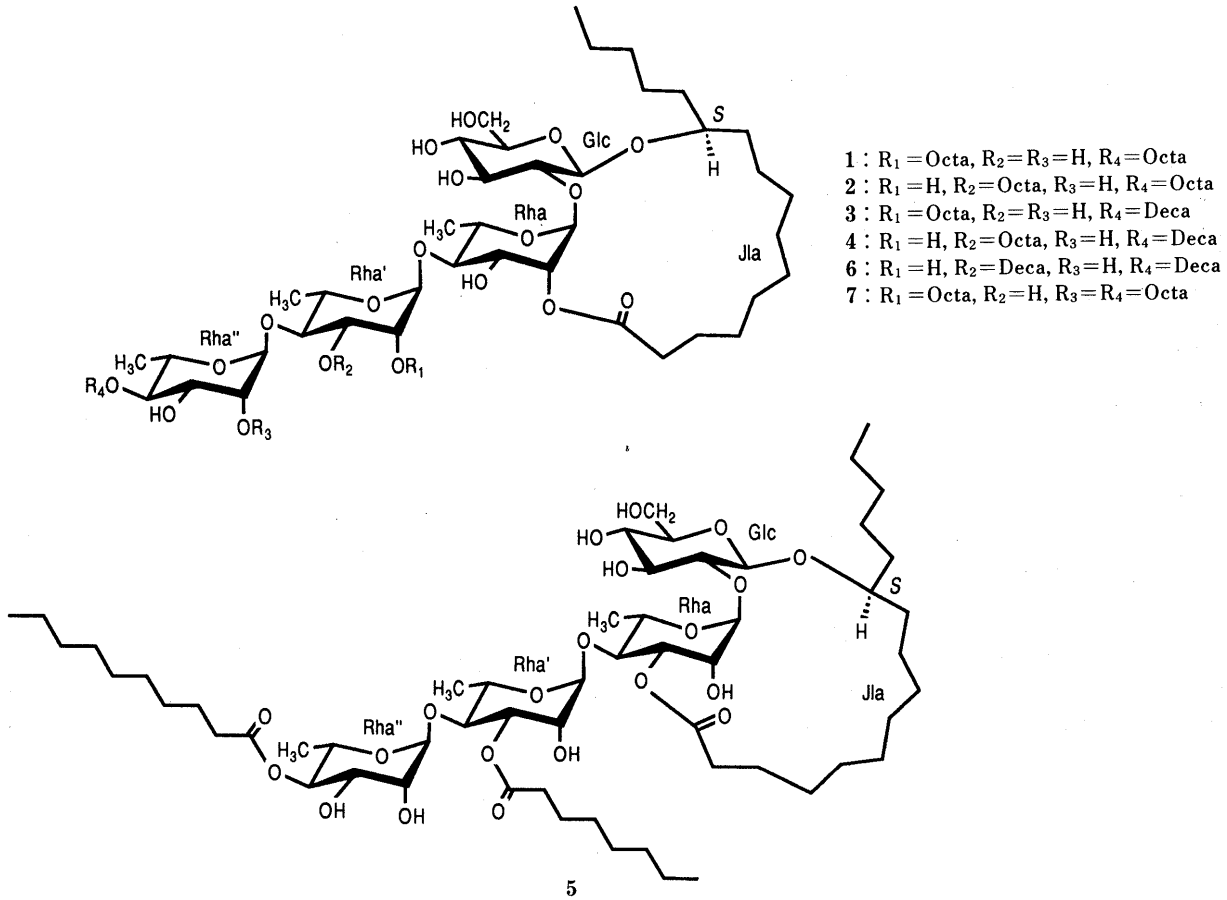

Fig. 2. Structures of **1**—**7**
Octa, *n*-octanoyl; Deca, *n*-decanoyl.

acid 11-*O*-(4-*O*-*n*-decanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-(2-*O*-*n*-octanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, intramolecular 1,2″-ester and the positional isomer of **3** in which the *n*-octanoic acid residue at 2-OH of Rha′ is transferred to 3-OH of Rha′ (Fig. 2). On the other hand, the ^{1}H-NMR spectrum of **5** exhibited, in comparison with that of **8**, acylation shifts of 1.07, 1.17 and 1.55 ppm at 3-H of Rha, 3-H of Rha′ and 4-H of Rha″, respectively. Therefore, compound **5** was characterized as an isomer of **4**, in which the cyclic ester group is transferred from 2-OH to 3-OH in the same sugar moiety (Rha) (Fig. 2).

Marubajalapin VI (**6**), $C_{60}H_{106}O_{21}$, gave *n*-decanoic acid and **9** on alkaline hydrolysis. The negative FAB-MS exhibited the $[M-H]^-$ ion peak at *m/z* 1161, 28 (C_2H_4) mass units larger than that of **4**, together with the same fragment ion peaks as those of **4** at *m/z* 853, 707, 561, 433 and 271. The ^{1}H-NMR signals due to the sugar moiety including the deshielded signals due to 2-H of Rha, 3-H of Rha′ and 4-H of Rha″ were quite similar to those of **4** (Table II). Consequently, **6** was concluded to be a homologue of **4** in which the *n*-octanoic acid group at 3-OH of Rha′ is replaced by an *n*-decanoic acid group, as shown in Fig. 2.

Marubajalapin VII (**7**), $C_{64}H_{112}O_{22}$, afforded, on alkaline hydrolysis, *n*-octanoic acid and **9**. The negative FAB-MS of **7** showed the $[M-H]^-$ ion peak at *m/z* 1231, 126 (*n*-octanoyl residue) mass units larger than that of **1**, and the same fragment ion peaks as those of **1**—**6** at *m/z* 561, 433 and 271. The ^{13}C-NMR spectrum exhibited four ester carbonyl carbon signals (Table I). From these data, **7** was considered to be a derivative of **1** in which one of the free hydroxy groups in **1** was acylated by *n*-octanoic acid. In the ^{1}H-NMR spectrum of **7**, compared with that of **1**, the signal ascribable to 2-H of Rha″ was shifted downfield by 1.23 ppm, while the other signals were observed at similar positions to those of **1** (Table II). Consequently, the structure of **7** was concluded to be (*S*)-jalapinolic acid 11-*O*-(2,4-di-*O*-*n*-octanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-(2-*O*-*n*-octanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside, intramolecular 1,2″-ester, as shown in Fig. 2.

Marubajalapins I—VII resemble the jalapins obtained from Jalapae Braziliensis regarding their component organic acids, that is, they have no volatile acids but fatty acids. They are the first examples of jalapins with operculinic acid E.

In this study, we could not find either organic acids such as formic, butyric and 2-methylbutyric acids or hydroxylauric and ipurolic acids, reported by Power and Rogerson.[2] However, in our preliminary investigation on the seeds of this plant, we found an ether-insoluble resin glycoside (convolvulin) which showed quite similar behavior on TLC to pharbitin obtained from the seeds of *Pharbitis nil*, which has ipurolic acid as a component hydroxyfatty acid.[10]

Experimental

The instruments and materials used were as cited in the preceding report[1] unless otherwise specified.

Extraction and Preparation of Jalapin Fraction The fresh leaves and stems (3 kg) of *Pharbitis purpurea*, cultivated in the botanical garden of this university, were collected in October 1990, and extracted with MeOH (33 l) at room temperature. The extract was evaporated under reduced pressure to afford a dark green syrup (103.47 g). This was treated with $CHCl_3$–MeOH–H_2O (2:1:1, 1.2 l), and the bottom layer was concentrated to give fr. 1 (21.21 g). Fraction 1 was chromatographed over silica gel (Merck Art. 7734, *n*-hexane→*n*-hexane–AcOEt (3:1→1:1→1:2→1:5)→MeOH) to afford fr. 2 (1.27 g), fr. 3 (5.74 g), fr. 4 (5.01 g) and fr. 5 (3.19 g). Chromatography of fr. 4 on a Sephadex LH-20 (MeOH) afforded fr. 6 (0.44 g), fr. 7 (2.34 g, jalapin fraction) and fr. 8 (1.99 g).

Alkaline Hydrolysis of Jalapin Fraction The jalapin fraction (512 mg) was dissolved in 1 N KOH–1,4-dioxane (2:3, 5 ml) and heated at 95 °C for 2 h. After cooling, the reaction mixture was adjusted to pH 3 with 1 N HCl and extracted with ether (10 ml × 3). The ether layer was dried over $MgSO_4$ and evaporated under reduced pressure to give an oil (160 mg, organic acid fraction). Aliquots of this fraction were methylated with diazomethane in ether, then analyzed by GC [condition 1: column, Unisole 3000, 3.2 mm i.d. × 2 m glass column; column temperature, 150 °C; carrier gas N_2 (1.0 kg/cm^2) t_R (min): 5.40 (methyl *n*-decanoate), 2.80 (methyl *n*-octanoate)]. The H_2O layer was desalted by chromatography over MCI gel CHP 20 to give a white powder (236 mg, glycosidic acid fraction). This was dissolved in MeOH (3 ml), then treated with diazomethane in ether. The mixture was subjected to preparative HPLC (GL Sciences, Inertsil ODS, 2.0 cm × 25 cm, 75% MeOH) to give **8** (206 mg), a white powder, mp 86—88 °C, $[\alpha]_D^{22}$ −88.1° (*c*=17.4, MeOH), which was identical with the methyl ester of operculinic acid E on the basis of ^{13}C-NMR data (in pyridine-d_5, 100 MHz).

Isolation of Marubajalapins I—XV The jalapin fraction (2.34 g) was chromatographed over silica gel [Merck Art. 9385, $CHCl_3$–MeOH (14:1→10:1→2:1)] to afford fr. 9 (100 mg), fr. 10 (1120 mg), fr. 11 (340 mg), fr. 12 (60 mg) and fr. 13 (660 mg). Fraction 10 was subjected to HPLC (Tosoh, TSK gel ODS-80TM, 21.5 mm i.d. × 300 mm, MeOH) to give fr. 14 (137 mg), fr. 15 (70 mg), fr. 16 (220 mg), fr. 17 (300 mg) and fr. 18 (100 mg). HPLC [a combination of Inertsil ODS-2 (6 mm i.d. × 250 mm) and Nacalai Tesque, COSMOSIL ODS 5C18-Ar (6 mm i.d. × 250 mm), 99% MeOH] of fr. 14 gave fr. 19 (11 mg), marubajalapin XI (10 mg) and fr. 20 (80 mg). Fraction 16 was subjected to HPLC (Inertsil ODS, 99.5% MeOH) to afford fr. 21 (81 mg), marubajalapin VIII (50 mg) and fr. 22 (65 mg). HPLC (99.5% MeOH) of fr. 22 as described for fr. 14 gave fr. 23 (3 mg) and marubajalapin IX (55 mg). HPLC of fr. 17 under the same condition as for fr. 16 furnished fr. 24 (85 mg), marubajalapin XIV (52 mg) and fr. 25 (97 mg). Fraction 25 was subjected to HPLC under the same condition as for fr. 22 to give fr. 26 (12 mg), **7** (19 mg) and fr. 27 (28 mg). HPLC (COSMOSIL ODS 5C18-Ar) of fr. 18 gave fr. 28 (5 mg), marubajalapin XII (5 mg) and marubajalapin XIII (19 mg). Fraction 11 and fr. 13 were each subjected to HPLC (Inertsil ODS, 99% MeOH) to give marubajalapin X (12 mg) and marubajalapin XV (18 mg) from fr. 11, and **5** (20 mg), **2** (13 mg), **4** (34 mg), **1** (19 mg), **3** (25 mg), fr. 29 (33 mg) and **6** (6 mg) from fr. 13.

1: A white powder, mp 86—87 °C, $[\alpha]_D^{24}$ −46.0° (*c*=2.4, MeOH). Negative FAB-MS *m/z* (%): 1105 (65) $[M-H]^-$, 979 (24) [1105−126 (octanoic acid unit)]$^-$, 853 (11) [979−126]$^-$, 707 (9) [853−146 (deoxyhexose unit)]$^-$, 561 (40) [707−146]$^-$, 433 (100) [561−128 (146−18 (H_2O))]$^-$, 271 (89) [433−162 (hexose unit), jalapinolic acid-H]$^-$. ^{13}C- and ^{1}H-NMR δ: see Tables I and II. *Anal.* Calcd for $C_{56}H_{98}O_{21}$: C, 60.74; H, 8.92. Found: C, 60.47; H, 8.95.

2: A white powder, mp 84—87 °C, $[\alpha]_D^{31}$ −44.7° (*c*=1.3, MeOH). Negative FAB-MS *m/z* (%): 1105 (75) $[M-H]^-$, 979 (32) [1105−126]$^-$, 853 (13) [979−126]$^-$, 707 (10) [853−146]$^-$, 561 (40) [707−146]$^-$, 433 (100) [561−128]$^-$, 271 (100) [433−162]$^-$. ^{13}C- and ^{1}H-NMR δ: see Tables I and II. *Anal.* Calcd for $C_{56}H_{98}O_{21}\cdot H_2O$: C, 59.77; H, 8.96. Found: C, 59.89; H, 8.97.

3: A white powder, mp 95—99 °C, $[\alpha]_D^{30}$ −48.5 °C (*c*=2.6, MeOH). Negative FAB-MS *m/z* (%): 1133 (81) $[M-H]^-$, 1007 (26) [1133−126]$^-$, 979 (14) [1133−154 (decanoic acid unit)]$^-$, 853 (19) [1007−154 and/or 979−126]$^-$, 707 (13) [853−146]$^-$, 561 (47) [707−146]$^-$, 433 (100) [561−128]$^-$, 271 (100) [433−162]$^-$. ^{13}C- and ^{1}H-NMR δ: see Tables I and II. *Anal.* Calcd for $C_{58}H_{102}O_{21}\cdot H_2O$: C, 60.40; H, 9.09. Found: C, 60.50; H, 8.98.

4: A white powder, mp 95—99 °C, $[\alpha]_D^{30}$ −48.5° (*c*=2.6, MeOH). Negative FAB-MS *m/z* (%): 1133 (49) $[M-H]^-$, 1007 (17) [1133−126]$^-$, 979 (6) [1133−154]$^-$, 853 (12) [1007−154 and/or 979−126]$^-$, 707 (12) [853−146]$^-$, 561 (40) [707−146]$^-$, 433 (100) [561−128]$^-$, 271 (100) [433−162]$^-$. ^{13}C- and ^{1}H-NMR δ: see Tables I and II. *Anal.* Calcd for $C_{58}H_{102}O_{21}\cdot 3/2H_2O$: C, 59.93; H, 9.10. Found: C, 60.04; H, 9.06.

5: A white powder, mp 100—104 °C, $[\alpha]_D^{21}$ −77.6° (*c*=2.0, MeOH). Negative FAB-MS *m/z* (%): 1133 (51) $[M-H]^-$, 1007 (14) [1133−

126]$^-$, 979 (10) [1133−154]$^-$, 853 (12) [1007−154 and/or 979−126]$^-$, 707 (11) [853−146]$^-$, 561 (43) [707−146]$^-$, 433 (100) [561−128]$^-$, 271 (88) [433−162]$^-$. ^{13}C- and ^{1}H-NMR δ: see Tables I and II. *Anal.* Calcd for $C_{58}H_{102}O_{21}$: C, 61.35; H, 9.05. Found: C, 61.06; H, 9.18.

6: A white powder, mp 91−93 °C, $[\alpha]_D^{24}$ −47.0° (c=0.7, MeOH). Negative FAB-MS m/z (%): 1161 (36) [M−H]$^-$, 1007 (15) [1161−154]$^-$, 853 (12) [1007−154]$^-$, 707 (9) [853−146]$^-$, 561 (33) [707−146]$^-$, 433 (100) [561−128]$^-$, 271 (100) [433−162]$^-$. ^{13}C- and ^{1}H-NMR δ: see Tables I and II. *Anal.* Calcd for $C_{60}H_{106}O_{21}\cdot 1/4H_2O$: C, 61.70; H, 9.19. Found: C, 61.53; H, 9.19.

7: A white powder, mp 70—73 °C, $[\alpha]_D^{29}$ −28.8° (c=1.6, MeOH). Negative FAB-MS m/z (%): 1231 (55) [M−H]$^-$, 1105 (26) [1231−126]$^-$, 707 (13) [1105−126×2−146]$^-$, 561 (30) [707−146]$^-$, 433 (100) [561−128]$^-$, 271 (80) [433−162]$^-$. ^{13}C- and ^{1}H-NMR δ: see Tables I and II. *Anal.* Calcd for $C_{64}H_{112}O_{22}\cdot 2/3H_2O$: C, 61.71; H, 9.17. Found: C, 61.97; H, 9.52.

Alkaline Hydrolysis of 1—7 Solutions of **1** (2 mg), **2** (1 mg), **3** (8 mg), **4** (8 mg), **5** (3 mg), **6** (1 mg) and **7** (7 mg) in 1,4-dioxane–1 N KOH (1 : 1, 2 ml) were each heated at 95 °C for 1 h. The reaction mixture was adjusted to pH 3 with 1 N HCl, then diluted with H_2O (20 ml), and extracted with ether (4×10 ml). The ether layer was dried over $MgSO_4$ and treated with diazomethane in ether. After removal of the solvent the residue was subjected to GC [condition 1: t_R (min): 2.81 (methyl *n*-octanoate), 5.42 (methyl *n*-decanoate)], 2.81 for **1**, **2** and **7**, 2.81, 5.42 for **3**, **4** and **5**, and 5.42 for **6**.

The aqueous layer was desalted by chromatography over MCI gel CHP 20 to give a white powder (glycosidic acid) (1 mg from **1**, 0.5 mg from **2**, 3 mg from **3**, 5 mg from **4**, 2 mg from **5**, 0.5 mg from **6**, 4 mg from **7**). The glycosidic acids were each identical with operculinic acid E[4] on high performance thin layer chromatography [HPTLC Si, Merck Art. 5628, $CHCl_3$–MeOH–H_2O (6 : 4 : 1): *Rf* 0.57].

Acetylation of 1, 3, 4 and 5 Solutions of **1** (1 mg), **3** (5 mg), **4** (1 mg) and **5** (3 mg) in Ac_2O–pyridine (1 : 1, 1 ml) were each left to stand at room temperature overnight. After removal of the reagent under a stream of N_2, the residue was partitioned between ether (0.3 ml) and H_2O (0.3 ml). The ether layer was concentratd to afford a white powder, [**10**: 1 mg (EI-MS m/z (%): 357 (100), 671 (4), 713 (4)) from **1**, **11**: 5 mg (EI-MS m/z (%): 385 (100), 699 (9), 713 (6)) from **3**, **12**: 1 mg (EI-MS m/z (%): 385 (100), 699 (7), 713 (4)) from **4**, **13**: 3 mg (EI-MS m/z (%): 385 (100), 699 (19), 713 (3)) from **5**].

Acknowledgment The authors are indebted to Mr. M. Nishi and Mr. S. Inoue of this university for the measurements of the NMR spectra, MS and elemental analyses.

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