Resin Glycosides. XIII.[1] Operculins VI, XI, XII, XIII, XIV and XV, the Ether-Soluble Resin Glycosides (Jalapin) from Rhizoma Jalapae Braziliensis (Roots of *Ipomoea operculata*)

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Six new ether-soluble resin glycosides (jalapin), operculins VI, XI, XII, XIII, XIV and XV, isolated previously from Rhizoma Jalapae Braziliensis (roots of *Ipomoea operculata*), have been characterized on the bases of chemical and spectral data.

Keywords resin glycoside; jalapin; Rhizoma Jalapae Braziliensis; *Ipomoea operculata*; Convolvulaceae; operculin

In the preceding papers,[2,3] we reported the isolation of eighteen ether-soluble resin glycosides (jalapin), operculins I—XVIII, from Rhizoma Jalapae Braziliensis (roots of *Ipomoea operculata* (GOMES) MART), and the structures of operculins I—V, VII—X and XVI—XVIII. This paper concerns the structure elucidation of six minor jalapins, operculins VI (**1**), XI (**2**), XII (**3**), XIII (**4**), XIV (**5**) and XV (**6**), isolated previously.[2,3]

Operculin VI (**1**), $C_{64}H_{114}O_{20}$, showed an $[M-H]^-$ ion peak at *m/z* 1201 in the negative ion fast atom bombardment mass spectrum (negative FAB-MS), and signals due to four anomeric (δ 98.6, 100.2, 103.5 and 104.4) and three ester carbonyl (δ 173.1, 173.3 and 173.5) carbons in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (Table I). It furnished, on alkaline hydrolysis, *n*-dodecanoic acid and operculinic acid C (**7**),[4] *viz.* (11*S*)-11-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-fucopyranoside. These data suggested that **1** consists of 2 mol of *n*-dodecanoic acid and 1 mol of **7** with an intramolecular ester structure.

TABLE I. ^{13}C-NMR Spectral Data for **1**, **2**, **3**, **4**, **5** and **6** (in Pyridine-d_5, 100 MHz)

	1	2	3	4	5	6
Fuc-1	104.4	101.5	101.7	104.3	104.3	104.4
Fuc-2	80.0	73.1	73.0	79.9	79.9	79.8
Fuc-3	73.5	76.7	76.9	73.4	73.4	73.4
Fuc-4	72.9	73.5	73.6	72.9	72.9	72.8
Fuc-5	70.8	71.2	71.2	70.8	70.8	70.8
Fuc-6	17.3	17.2	17.2	17.3	17.3	17.3
Rha-1	98.6	100.2	100.2	98.5	98.5	98.4
Rha-2	73.7	69.6	69.7	73.6	73.6	73.7
Rha-3	69.8	77.9	78.9	69.3	69.4	69.7
Rha-4	81.0	79.3	76.2	81.5	81.5	81.9
Rha-5	68.7	67.7	67.4	68.9	69.0	69.1
Rha-6	19.3	18.9	19.3	19.1	19.1	19.2
Rha′-1	100.2	100.7	102.5	100.0	100.0	103.5
Rha′-2	74.2	74.3	70.4	73.2	73.2	71.8
Rha′-3	70.9	70.9	75.5	80.2	80.2	82.3
Rha′-4	80.5	80.7	78.2	78.2	78.3	79.0
Rha′-5	68.5	68.5	69.0	68.6	68.6	68.6
Rha′-6	18.9	18.7	18.5	18.8	18.8	18.9
Rha″-1	103.5	103.6	103.5	103.4	103.4	102.9
Rha″-2	72.4	72.3	72.6	72.4	72.5	72.5
Rha″-3	70.3	70.2	70.1	72.9	72.9	70.3
Rha″-4	75.4	75.4	75.0	73.9	74.0	75.4
Rha″-5	68.1	68.0	68.1	70.7	70.7	68.0
Rha″-6	18.0	18.0	17.9	18.5	18.5	17.9
Glc-1				105.4	105.4	105.3
Glc-2				75.2	75.2	75.0
Glc-3				78.4	78.4	78.3
Glc-4				71.4	71.5	71.8
Glc-5				78.1	78.1	78.1
Glc-6				62.9	63.0	62.8
Ag-11	82.4	79.3	79.8	82.4	82.4	82.4
Ag-16	14.3	14.3	14.3	14.3	14.3	14.3
C=O	173.5	174.8	174.3	173.1	173.1	173.1
	173.3	173.5	173.5	173.6	173.6	173.5
	173.1	173.2	172.6			

δ in ppm from TMS. Fuc, fucopyranosyl; Rha, rhamnopyranosyl; Glc, glucopyranosyl; Ag, aglycone ((*S*)-jalapinolic acid). All assignments are based on the HETCOR spectral data.

The ^{1}H-NMR signals of **1** were assigned by referring to the ^{1}H–^{1}H shift correlated 2D-NMR (COSY) and nuclear Overhauser effect 2D-NMR (NOESY) spectra (Table II). When compared with those of **7**,[4] the signals due to 2-H (δ 4.63) of the first rhamnose (Rha), 2-H (δ 4.74) of the second rhamnose (Rha′) and 4-H (δ 4.23) of the third rhamnose (Rha″) in **7** were shifted downfied by 1.24, 1.20 and 1.56 ppm, respectively. The three ester linkages are therefore located at 2-OH of Rha, 2-OH of Rha′ and 4-OH of Rha″.

In the negative FAB-MS of **1** and **7**, besides the common fragment peaks at *m/z* 271 [272 (jalapinolic acid)$-$H]$^-$ and 417 [272+146 (deoxyhexose unit)$-$H]$^-$, **1** showed the diagnostically important peak at *m/z* 545 [272+2×146$-$18 (H_2O)$-$H]$^-$, in place of that at *m/z* 563 [272+2×146$-$H]$^-$ observed in the spectrum of **7**. The presence of the former, 18 mass units less than the latter, suggested that the ester linkage of jalapinolic acid involves Rha,[3] and hence the two dodecanoyl groups are in Rha′ and Rha″, respectively. This suggestion was verified by measurement of the electron-impact mass spectrum (EI-MS) of the peracetate of **1** (**8**), demonstrating the fragment ion peaks at *m/z* 413, 655 and 783 ascribable to the fragments *a*, *b* and *c* in Fig. 1.

Consequently, the structure of **1** was defined as (*S*)-jalapinolic acid 11-*O*-(4-*O*-*n*-dodecanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-(2-*O*-*n*-dodecanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside, intramolecular 1,2″-ester (Fig. 2).

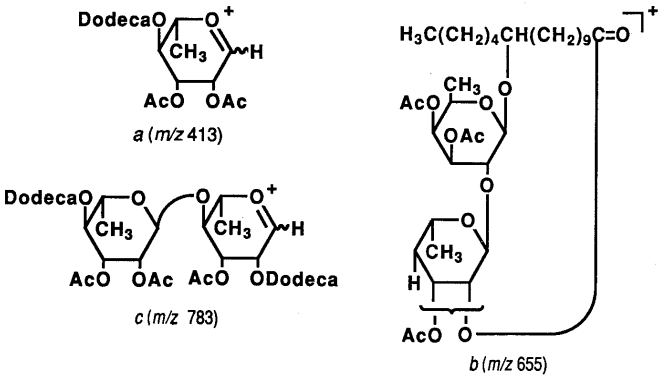
Operculin XI (**2**), $C_{64}H_{114}O_{20}$ and operculin XII (**3**), $C_{46}H_{114}O_{20}$, gave the same organic acid and glycosidic acid as those from **1** by alkaline hydrolysis.

The negative FAB-MS of **2** and **3** were almost superimposable on that of **1**, in which the $[M-H]^-$ and fragment ion peaks were seen at *m/z* 1201, 545, 417 and 271. Furthermore, the EI-MS of the peracetate of **2** (**9**), showed the same fragment ion peaks as those of **8** at *m/z* 413 (*a*), 655 (*b*) and 783 (*c*) (Fig. 1). Therefore, it is

TABLE II. ^{1}H-NMR Spectral Data for **1**, **2**, **3**, **4**, **5** and **6** (in Pyridine-d_5, 400 MHz)

	1	2	3	4	5	6
Fuc-1	4.66, d (7.5)	4.74, d (7.6)	4.75, d (7.8)	4.68, d (7.2)	4.70, d (7.5)	4.70, d (7.5)
Fuc-2	4.09, dd (7.5, 9.5)	4.48, dd (7.6, 9.5)	4.49, dd (7.8, 9.5)	4.11, dd (7.2, 9.0)	4.14, dd (7.5, 9.5)	4.14, dd (7.5, 9.5)
Fuc-3	3.98, dd (9.5, 3.5)	4.13, dd (9.5, 3.4)	4.15, dd (9.5, 3.5)	4.03, dd (9.0, 3.5)	4.05, dd (9.5, 4.0)	4.04, dd (9.5, 3.5)
Fuc-4	3.94, d (3.5)	3.88, d (3.4)	3.90, d (3.5)	3.93, d (3.5)	3.96, dd (4.0, 0.5)	3.96, dd (3.5, 0.5)
Fuc-5	3.72, q (6.4)	3.78, q (6.4)	3.79, q (6.4)	3.72, q (6.4)	3.73, dq (0.5, 6.4)	3.73, dq (0.5, 6.4)
Fuc-6	1.47, d (6.4)	1.49, d (6.4)	1.50, d (6.4)	1.49, d (6.4)	1.50, d (6.4)	1.50, d (6.4)
Rha-1	5.46, d (1.5)	6.31, d (1.2)	6.33, d (1.2)	5.47, d (1.5)	5.49, d (1.5)	5.50, d (1.5)
Rha-2	5.87, dd (1.5, 3.1)	5.23, dd (1.2, 2.8)	5.21, dd (1.2, 3.0)	5.88, dd (1.5, 3.0)	5.91, dd (1.5, 3.5)	5.88, dd (1.5, 3.5)
Rha-3	4.94, dd (3.1, 9.5)	5.54, dd (2.8, 10.1)	5.63, dd (3.0, 9.5)	4.96, dd (3.0, 9.0)	4.99, dd (3.5, 9.5)	5.01, dd (3.5, 9.5)
Rha-4	4.16, dd (9.5, 9.5)	4.54, dd (10.1, 10.1)	4.67, dd (9.5, 9.5)	4.11, dd (9.0, 9.0)	4.14, dd (9.5, 9.5)	4.14, dd (9.5, 9.5)
Rha-5	4.41[a]	4.96, dq (10.1, 6.1)	5.04, dq (9.5, 6.1)	4.43, dq (9.0, 6.4)	4.46, dq (9.5, 6.1)	4.49, dq (9.5, 6.4)
Rha-6	1.62, d (6.4)	1.56, d (6.1)	1.56, d (6.1)	1.60, d (6.4)	1.62, d (6.1)	1.67, d (6.4)
Rha′-1	5.97, d (1.5)	5.51, d (1.5)	5.85, s	5.83, d (1.5)	5.86, d (1.5)	5.98, d (1.5)
Rha′-2	5.94, dd (1.5, 3.5)	5.74, dd (1.5, 3.1)	4.67[a]	6.27, dd (1.5, 3.0)	6.30, dd (1.5, 3.5)	5.12, dd (1.5, 3.0)
Rha′-3	4.63, dd (3.5, 9.5)	4.56[a]	5.69, dd (3.0, 9.5)	4.73, dd (3.0, 9.0)	4.76, dd (3.5, 9.0)	4.69, dd (3.0, 9.0)
Rha′-4	4.25, dd (9.5, 9.5)	4.21, dd (9.5, 9.5)	4.52, dd (9.5, 9.5)	4.33[a]	4.35[a]	4.49, dd (9.0, 9.0)
Rha′-5	4.35, dq (9.5, 6.1)	4.32, dq (9.5, 6.1)	4.36, dq (9.5, 6.1)	4.33[a]	4.35[a]	4.36[a]
Rha′-6	1.68, d (6.1)	1.64, d (6.1)	1.56, d (6.1)	1.62, d (6.4)	1.64, d (6.2)	1.63, d (6.1)
Rha″-1	6.15, d (1.3)	6.12, d (1.8)	5.64, d (1.5)	6.20, d (1.2)	6.24, d (1.5)	6.20, d (1.5)
Rha″-2	4.76, dd (1.3, 3.5)	4.73, dd (1.8, 3.4)	4.45, dd (1.5, 3.5)	4.91, dd (1.2, 3.5)	4.96, dd (1.5, 3.5)	4.91[a]
Rha″-3	4.52, dd (3.5, 9.5)	4.46, dd (3.4, 9.8)	4.38, dd (3.5, 9.5)	4.48, dd (3.5, 9.0)	4.51, dd (3.5, 9.0)	4.57, dd (3.0, 9.0)
Rha″-4	5.79, dd (9.5, 9.5)	5.79, dd (9.8, 9.8)	5.75, dd (9.5, 9.5)	4.26, dd (9.0, 9.0)	4.28, dd (9.0, 9.0)	5.77, dd (9.0, 9.0)
Rha″-5	4.41[a]	4.37, dq (9.8, 6.4)	4.27, dq (9.5, 6.4)	4.33[a]	4.35[a]	4.36[a]
Rha″-6	1.45, d (6.4)	1.44, d (6.4)	1.35, d (6.4)	1.64, d (6.4)	1.66, d (6.1)	1.37, d (6.4)
Glc-1				5.03, d (7.8)	5.07, d (7.5)	5.13, d (7.1)
Glc-2				3.94, dd (7.8, 9.0)	3.97, dd (7.5, 9.0)	3.94, dd (7.1, 9.0)
Glc-3				4.02, dd (9.0, 9.0)	4.04, dd (9.0, 9.0)	4.09, dd (9.0, 9.0)
Glc-4				3.91, dd (9.0, 9.0)	3.95, dd (9.0, 9.0)	3.99, dd (9.0, 9.0)
Glc-5				3.73, ddd (3.0, 6.0, 9.0)	3.76, ddd (3.0, 5.0, 9.0)	3.78, ddd (2.5, 6.0, 9.0)
Glc-6				4.07, dd (6.0, 12.0)	4.09, dd (5.0, 12.0)	4.07, dd (6.0, 11.0)
				4.38, dd (3.0, 12.0)	4.40, dd (3.0, 12.0)	4.41, dd (2.5, 11.0)
Ag- 2	2.23, m	2.22, ddd (3.7, 7.0, 14.0)	2.13, ddd (3.0, 6.5, 14.0)	2.25, ddd (4.0, 8.0, 15.0)	2.27, ddd (5.0, 7.0, 15.0)	2.38, m
	2.39, m	2.68, ddd (2.5, 11.0, 14.0)	2.27[a]	2.44, ddd (5.5, 8.0, 15.0)	2.46, ddd (5.5, 7.5, 15.0)	2.23, m
Ag-11	3.82, m	3.83, m	3.88, m	3.82, m	3.84, m	3.83, m
Ag-16	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)
Org-2	2.29, t (7.5)	2.31, m	2.28[a]	2.32, ddd (3.0, 7.0, 7.0)	2.33, ddd (4.0, 7.0, 7.0)	2.48, ddd (2.0, 7.0, 7.0)
	2.45, ddd (4.0, 7.5, 7.5)	2.45, m	2.40, m			
CH_3	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)	0.85, t (7.0)	0.88, t (7.0)
	0.87, t (7.0)	1.00, t (7.0)	0.98, t (7.0)			

δ in ppm from TMS (J values in Hz are given in parentheses). Fuc, fucopyranosyl; Rha, rhamnopyranosyl; Glc, glucopyranosyl; Ag, aglycone ((*S*)-jałapinolic acid); Org, *n*-dodecanoyl or *n*-decanoyl. *a*) Signals are overlapping. All assignments are based on the ^{1}H–^{1}H COSY and NOESY spectral data.



Ac: acetyl; Dodeca: *n*-dodecanoyl

Fig. 1

considered that **2** and **3** are positional isomers of **1** as to ester linkages, and that their two *n*-dodecanoyl groups and intramolecular ester linkage belong respectively to Rha′, Rha″ and Rha.

The ^{1}H-NMR spectrum of **2**, compared with that of **1**, exhibited a remarkable downfield shift (0.60 ppm) at 3-H of Rha along with an upfield shift (0.64 ppm) at 2-H of Rha, whereas 2-H of Rha′ and 4-H of Rha″ resonated at similar chemical shifts to those of **1** (Table II), indicating **2** to be an isomer of **1** whose jalapinolic acid ester group is rearranged from 2-OH to 3-OH of Rha. This was supported by acylation shifts observed in the spectrum of **2**, where the signals due to 3-H of Rha, 2-H of Rha′ and 4-H of Rha″ in **7**[4] were shifted downfield by 0.96, 1.00 and 1.56 ppm, respectively.

Accordingly, **2** was concluded to be (*S*)-jalapinolic acid 11-*O*-(4-*O*-*n*-dodecanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-(2-*O*-*n*-dodecanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside, intramolecular 1,3″-ester (Fig. 2).

On the other hand, though the signals owing to 3-H of Rha and 4-H of Rha″ of **3** were observed at quite similar positions to those of **2**, the signals due to 2- and 3-H of Rha′ were each shifted upfield (1.07 ppm) and downfield (1.13 ppm), respectively (Talbe II).

Consequently, **3** was defined as the positional isomer of **2** of which the *n*-dodecanoic acid residue at 2-OH of Rha′ migrates to 3-OH in the same sugar unit (Fig. 2).

Both operculin XIII (**4**), $C_{58}H_{102}O_{24}$, and operculin XV (**6**), $C_{58}H_{102}O_{24}$, afforded, on alkaline hydrolysis, *n*-dodecanoic acid and operculinic acid A (**10**), that is, the common glycosidic acid for operculins I (**11**), II, V (**12**), VII and VIII obtained previously in the same plant.[4]

The negative FAB-MS of **4** and **6** were almost superimposable on each other and exhibited the $[M-H]^-$ ion

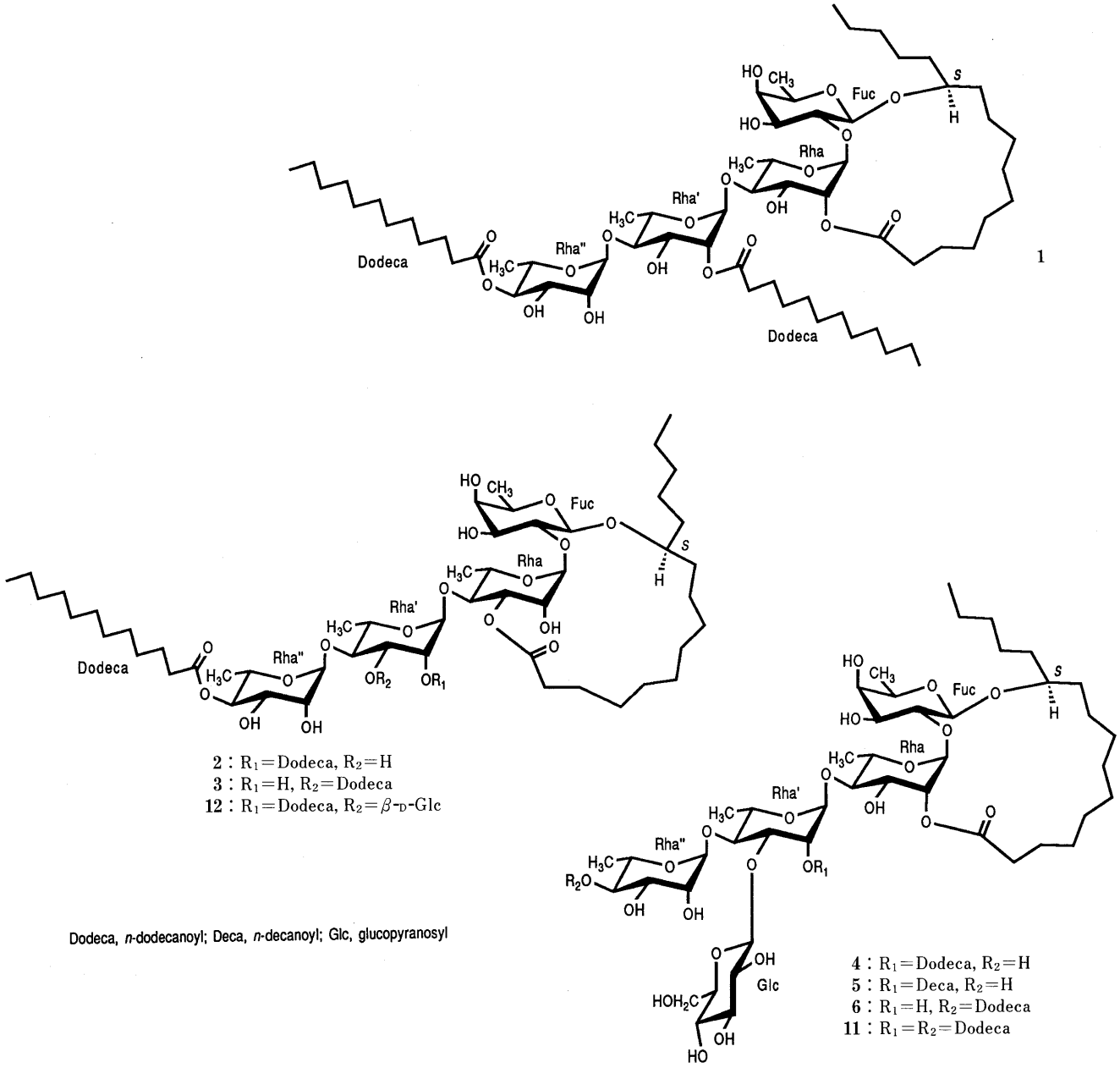


Fig. 2. Structures of **1**—**6**, **11** and **12**

peak at *m/z* 1181 along with fragment peaks at *m/z* 999, 837, 545, 417 and 271 which were explained as $[1181-182$ (dodecanoic acid $-H_2O)]^-$, $[999-162$ (hexose unit)$]^-$, $[837-2\times146$ (deoxyhexose unit)$]^-$, $[545-128$ (deoxyhexose $-18)]^-$ and $[417-146]^-$, respectively. These data demonstrated that **4** and **6** are, like **1**—**3**, isomeric to each other and consist of 1 mol each of *n*-dodecanoic acid and **10** with cyclic ester structure, where the carboxyl groups are intramolecularly linked to the first rhamnose (Rha) as judged by the fragment peaks at *m/z* 545 and 417 (*vide supra*). These results suggested **4** and **6** to be partially deacylated derivatives of **11** and/or **12**.

In a comparison of the ^{1}H-NMR spectrum of **4** with those of **11** and **12**, the signals due to the sugar moiety of **4** were quite similar to those of **11**, except for the signal due to 4-H of Rha″ being shifted upfield by 1.52 ppm from that (δ 5.78) of **11**.[4]

Accordingly, **4** was characterized as (*S*)-jalapinolic acid 11-*O*-β-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→4)]-*O*-(2-*O*-*n*-dodecanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranoside, intramolecular 1,2″-ester (Fig. 2).

In the ^{1}H-NMR spectrum of **6**, compared with that of **4**, a pronounced downfield shift was observed at 4-H of Rha″ (1.51 ppm) along with an upfield shift of 2-H of Rha′ (1.15 ppm) (Table II).

Consequently, compound **6** is another deacyl derivative of **11**, from which the dodecanoic acid group at 2-OH of Rha′ is removed (Fig. 2).

Operculin XIV (**5**), $C_{56}H_{98}O_{24}$, yielded, on alkaline hydrolysis, *n*-decanoic acid and **10**. The negative FAB-MS of **5** exhibited the $[M-H]^-$ ion peak at *m/z* 1153 together with the same fragment peaks as those of **4** and **6** at *m/z* 545, 417 and 271, and the ^{13}C-NMR spectrum showed five anomeric and two ester carbonyl carbon signals (Table I). Further, the ^{1}H-NMR spectrum of **5** was quite similar to

that of **4**, and, in particular, the chemical shifts of the signals due to 2-H of Rha and 2-H of Rha′ were identical with those of **4** (Table II).

Accordingly, the structure of **5** was concluded to be (*S*)-jalapinolic acid 11-*O*-*β*-D-glucopyranosyl-(1→3)-*O*-[α-L-rhamnopyranosyl-(1→4)]-*O*-(2-*O*-*n*-decanoyl)-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-*β*-D-fucopyranoside, intramolecular 1,2″-ester (Fig. 2).

The eighteen operculins isolated from this crude drug resemble the other known jalapins[1-3,5-8] in that they are monomers with similar macrocyclic ester structures in the glycosidic acid moieties. However, their component organic acids, *n*-decanoic and *n*-dodecanoic acids, are characteristically different from those of the other known resin glycosides, *viz.* isobutyric, 2-methylbutyric, tiglic and nilic acids.[5-8]

Although the operculins are classified to three types according to the component glycosidic acids, operculinic acids A, B and C, they fall into two types from a different viewpoint, that is, one with an 18-membered ring with the intramolecular ester group attached to 2-OH of the second sugar unit (Rha) and the other with a 19-membered ring with an ester linkage at 3-OH of Rha. Further, it is noteworthy that the positions of ester linkages of organic acids are restricted to 2-OH or 3-OH of the third sugar unit (Rha′) and 4-OH of the fourth (terminal) sugar unit (Rha″).

Experimental

All instruments and materials used were as cited in the preceding report[4] unless otherwise specified.

Isolation of 1—6 The procedure for separation **1**—**6** was described in the previous report.[2,3]

1: A white powder (Et_2O–*n*-hexane), mp 90—97 °C, $[\alpha]_D^{21}$ −32.3° (*c*=2.1, MeOH). IR (KBr) cm^{-1}: 3400 (OH), 1725 (C=O). Negative FAB-MS *m/z* (%): 1201 (14) $[M-H]^-$, 1019 (9) [1201−182 (dodecanoic acid unit)]$^-$, 837 (9) [1201−2×182]$^-$, 691 (7) [837−146 (deoxyhexose unit)]$^-$, 545 (19) [691−146]$^-$, 417 (100) [545−128 (deoxyheose unit $-H_2O$)]$^-$, 271 (74) [417−146]$^-$. *Anal.* Calcd for $C_{64}H_{114}O_{20}\cdot H_2O$: C, 62.93; H, 9.57. Found: C, 62.79; H, 9.40.

2: A white powder (Et_2O–*n*-hexane), mp 105—113 °C, $[\alpha]_D^{22}$ −62.7° (*c*=0.9, MeOH). IR (KBr) cm^{-1}: 3400 (OH), 1730 (C=O). Negative FAB-MS *m/z* (%): 1201 (51) $[M-H]^-$, 1019 (17) [1201−182]$^-$, 837 (11) [1201−2×182]$^-$, 691 (7) [837−146]$^-$, 545 (33) [691−146]$^-$, 417 (100) [545−128]$^-$, 271 (100) [417−146]$^-$. *Anal.* Calcd for $C_{64}H_{114}O_{20}$: C, 63.87; H, 9.55. Found: C, 63.91; H, 9.59.

3: A white powder (Et_2O–*n*-hexane), mp 107—116 °C, $[\alpha]_D^{22}$ −33.0° (*c*=0.8, MeOH). IR (KBr) cm^{-1}: 3400 (OH), 1730 (C=O). Negative FAB-MS *m/z* (%): 1201 (100) $[M-H]^-$, 1019 (23) [1201−182]$^-$, 837 (9) [1201−2×182]$^-$, 691 (7) [837−146]$^-$, 545 (17) [691−146]$^-$, 417 (68) [545−128]$^-$, 271 (16) [417−146]$^-$. *Anal.* Calcd for $C_{64}H_{114}O_{20}$: C, 63.87; H, 9.55. Found: C, 63.88; H, 9.65.

4: A white powder (Et_2O–*n*-hexane), mp 137—142 °C, $[\alpha]_D^{21}$ −28.1° (*c*=1.0, MeOH). IR (KBr) cm^{-1}: 3400 (OH), 1730 (C=O). Negative FAB-MS *m/z* (%): 1181 (56) $[M-H]^-$, 1035 (4) [1181−146]$^-$, 1019 (3) [1181−162 (hexose unit)]$^-$, 999 (23) [1181−182]$^-$, 853 (5) [999−146]$^-$, 837 (7) [999−162]$^-$, 545 (40) [837−2×146]$^-$, 417 (100) [545−128]$^-$, 271 (90) [417−146]$^-$. *Anal.* Calcd for $C_{58}H_{102}O_{24}$: C, 58.87; H, 8.69. Found: C, 58.95; H, 8.73.

5: A white powder (Et_2O–*n*-hexane), mp 137—142 °C, $[\alpha]_D^{21}$ −31.1° (*c*=1.0, MeOH). IR (KBr) cm^{-1}: 3400 (OH), 1725 (C=O). Negative FAB-MS *m/z* (%): 1153 (87) $[M-H]^-$, 999 (46) [153−154 (decanoic acid unit)]$^-$, 853 (7) [999−146]$^-$, 837 (7) [999−162]$^-$, 545 (47) [837−2×146]$^-$, 417 (100) [545−128]$^-$, 271 (83) [417−146]$^-$. *Anal.* Calcd for $C_{56}H_{98}O_{24}$: C, 58.22; H, 8.55. Found: C, 58.41; H, 8.69.

6: A white powder (Et_2O–*n*-hexane), mp 146—155 °C, $[\alpha]_D^{21}$ −32.9° (*c*=1.0, MeOH). IR (KBr) cm^{-1}: 3400 (OH), 1725 (C=O). Negative FAB-MS *m/z* (%): 1181 (59) $[M-H]^-$, 999 (9) [1181−182]$^-$, 853 (10) [999−146]$^-$, 837 (4) [999−162]$^-$, 545 (8) [837−2×146]$^-$, 417 (100) [545−128]$^-$, 271 (28) [417−128]$^-$. *Anal.* Calcd for $C_{58}H_{102}O_{24}$: C, 58.87; H, 8.69. Found: C, 58.81; H, 8.67.

Alkaline Hydrolysis of 1—6 Suspensions of **1** (18 mg), **2** (18 mg), **3** (22 mg), **4** (10 mg), **5** (7 mg) and **6** (8 mg) in 3% aqueous KOH–1,4-dioxane (1:1, 2 ml) were each heated at 95 °C for 1 h. The reaction mixture was adjusted to pH 4 with 1 N HCl and diluted with H_2O (10 ml). The mixture was extracted with ether (3×5 ml). The ether layer was treated with diazomethane in ether, followed by removal of the solvent. The residue was subjected to GC (column, Unisole 3000, 3.2 mm i.d. × 2 m glass column; column temperature, 160 °C; carrier gas N_2 (1.25 kg/cm^2); t_R (min): 8.36 (methyl *n*-dodecanoate) for **1**, 8.37 (methyl *n*-dodecanoate) for **2**, 8.36 (methyl *n*-dodecanoate) for **3**, 8.36 (methyl *n*-dodecanoate) for **4**, 4.18 (methyl *n*-decanoate) for **5**, 8.38 (methyl *n*-dodecanoate) for **6**.

The aqueous layer was desalted by chromatography over MCI-gel CHP 20P to give a glycosidic acid as a white powder (11 mg from **1**, mp 110—114 °C, 13 mg from **2**, mp 114—117 °C, 10 mg from **3**, mp 113—117 °C, 7 mg from **4**, mp 173—176 °C, 4 mg from **5**, mp 170—174 °C, and 5 mg from **6**, mp 170—175 °C. The glycosidic acids derived from **1**, **2** and **3** were each shown to be identical with operculinic acid C (**7**) (mp 116—120 °C), and those from **4**, **5** and **6** to be identical with operculinic acid A (**10**) (mp 172—174 °C) by comparison of the ^{1}H-NMR spectra with those of authentic samples (in pyridine-d_5, 400 MHz).

Acetylation of 1 and 2 Solutions of **1** (10 mg) and **2** (12 mg) in Ac_2O–pyridine (1:1, 2 ml) were each left to stand at room temperature overnight. the solvent was removed under an N_2 stream to give **8** (12 mg from **1**) and **9** (14 mg from **2**). **8**: A white powder, mp 51—54 °C, $[\alpha]_D^{17}$ −12.4° (*c*=1.4, MeOH). IR (KBr) cm^{-1}: 1750 (C=O). EI-MS *m/z*: 413 (*a*), 655 (*b*), 783 (*c*) (Fig. 1). ^{1}H-NMR (pyridine-d_5, 400 MHz) *δ*: 2.00, 2.04, 2.04, 2.23, 2.27, 2.37 ($OCOCH_3$). **9**: A white powder, mp 55—58 °C, $[\alpha]_D^{24}$ −45.3° (*c*=1.6, MeOH). EI-MS *m/z* (%): 783 (5), 655 (6), 413 (100).

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