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), C₆₄H₁₁₄O₂₀, 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 (¹³C-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*)-jalapinic acid) 11-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 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.

The ¹H-NMR signals of 1 were assigned by referring to the ¹H–¹H 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 downfield 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 (jalapinic acid)–H][–] and 417 [272 + 146 (deoxyhexose unit)–H][–], 1 showed the diagnostically important peak at *m/z* 545 [272 + 2 $\times$ 146 – 18 (H₂O)–H][–], in place of that at *m/z* 563 [272 + 2 $\times$ 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 jalapinic 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*)-jalapinic acid 11-*O*-(4-*O*-*n*-dodecanoyl)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-*O*-(2-*O*-*n*-dodecanoyl)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-fucopyranoside, intramolecular 1,2''-ester (Fig. 2).

Operculin XI (2), C₆₄H₁₁₄O₂₀ and operculin XII (3), C₄₆H₁₁₄O₂₀, 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 I. ¹³C-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*)-jalapinic acid). All assignments are based on the HETCOR spectral data.

TABLE II. ¹H-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)
Ag-2	2.23, m	2.22, ddd (3.7, 7.0, 14.0)	2.13, ddd (3.0, 6.5, 14.0)	4.38, dd (3.0, 12.0)	4.40, dd (3.0, 12.0)	4.41, dd (2.5, 11.0)
	2.39, m	2.68, ddd (2.5, 11.0, 14.0)	2.27 ^{a)}	2.25, ddd (4.0, 8.0, 15.0)	2.27, ddd (3.0, 5.0, 15.0)	2.38, m
Ag-11	3.82, m	3.83, m	3.88, m	2.44, ddd (5.5, 8.0, 15.0)	2.46, ddd (5.5, 7.5, 15.0)	2.23, m
Ag-16	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)	3.82, m	3.84, m	3.83, m
Org-2	2.29, t (7.5)	2.31, m	2.28 ^{a)}	0.87, t (7.0)	0.87, t (7.0)	0.87, t (7.0)
	2.45, ddd (4.0, 7.5, 7.5)	2.45, m	2.40, m	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)
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*)-jalapinic acid); Org, *n*-dodecanoyl or *n*-decanoyl. ^{a)} Signals are overlapping. All assignments are based on the ¹H-¹H COSY and NOESY spectral data.

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 ¹H-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 jalapinic 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*)-jalapinic 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 (Table 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**), C₅₈H₁₀₂O₂₄, and operculin XV (**6**), C₅₈H₁₀₂O₂₄, 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 $[1181 - 182 (\text{dodecanoic acid} - \text{H}_2\text{O})]^-$, $[999 - 162 (\text{hexose unit})]^-$, $[837 - 2 \times 146 (\text{deoxyhexose unit})]^-$, $[545 - 128 (\text{deoxyhexose} - 18)]^-$ 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 $^1\text{H-NMR}$ 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*)-jalapinic acid

11-*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 3)-*O*-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-*O*-(2-*O*-*n*-dodecanoyl)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-fucopyranoside, intramolecular 1,2''-ester (Fig. 2).

In the $^1\text{H-NMR}$ 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), $\text{C}_{56}\text{H}_{98}\text{O}_{24}$, yielded, on alkaline hydrolysis, *n*-decanoic acid and 10. The negative FAB-MS of 5 exhibited the $[\text{M} - \text{H}]^-$ 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 $^{13}\text{C-NMR}$ spectrum showed five anomeric and two ester carbonyl carbon signals (Table I). Further, the $^1\text{H-NMR}$ 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)-jalapinic acid 11-O- β -D-glucopyranosyl-(1 $\rightarrow$ 3)-O-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]-O-(2-O-*n*-decanoyl)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 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 report⁴) 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 (Et₂O-*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 $\times$ 182][–], 691 (7) [837–146 (deoxyhexose unit)][–], 545 (19) [691–146][–], 417 (100) [545–128 (deoxyhexose unit–H₂O)][–], 271 (74) [417–146][–]. Anal. Calcd for C₆₄H₁₁₄O₂₀·H₂O: C, 62.93; H, 9.57. Found: C, 62.79; H, 9.40.

2: A white powder (Et₂O-*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 $\times$ 182][–], 691 (7) [837–146][–], 545 (33) [691–146][–], 417 (100) [545–128][–], 271 (100) [417–146][–]. Anal. Calcd for C₆₄H₁₁₄O₂₀: C, 63.87; H, 9.55. Found: C, 63.91; H, 9.59.

3: A white powder (Et₂O-*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 $\times$ 182][–], 691 (7) [837–146][–], 545 (17) [691–146][–], 417 (68) [545–128][–], 271 (16) [417–146][–]. Anal. Calcd for C₆₄H₁₁₄O₂₀: C, 63.87; H, 9.55. Found: C, 63.88; H, 9.65.

4: A white powder (Et₂O-*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 $\times$ 146][–], 417 (100) [545–128][–], 271 (90) [417–146][–]. Anal. Calcd for C₅₈H₁₀₂O₂₄: C, 58.87; H, 8.69. Found: C, 58.95; H, 8.73.

5: A white powder (Et₂O-*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 $\times$ 146][–], 417 (100) [545–128][–], 271 (83) [417–146][–]. Anal. Calcd for C₅₆H₉₈O₂₄: C, 58.22; H, 8.55. Found: C, 58.41; H, 8.69.

6: A white powder (Et₂O-*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 $\times$ 146][–], 417 (100) [545–128][–], 271 (28) [417–128][–]. Anal. Calcd for C₅₈H₁₀₂O₂₄: 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 H₂O (10 ml). The mixture was extracted with ether (3 $\times$ 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. $\times$ 2 m glass column; column temperature, 160°C; carrier gas N₂ (1.25 kg/cm²); *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 ¹H-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 Ac₂O–pyridine (1:1, 2 ml) were each left to stand at room temperature overnight. The solvent was removed under an N₂ 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). ¹H-NMR (pyridine-*d*₅, 400 MHz) δ : 2.00, 2.04, 2.04, 2.23, 2.27, 2.37 (OCOCH₃). **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).

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

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