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Resin Glycosides. IV.[1] Two New Resin Glycosides, Muricatins VII and VIII, from the Seeds of *Ipomoea muricata*

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Two resin glycosides, muricatins VII (**1**) and VIII (**2**) were isolated from the seeds of *Ipomoea muricata* (L.) JACQ. (Convolvulaceae). They were respectively characterized as 11*R*-jalapinolic acid 11-*O*-(4-*O*-(3*R*-hydroxy-2*R*-methylbutyryl))-β-D-fucopyranosyl-(1→4)-(2-*O*-(2*S*-methylbutyryl))-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl(qui′)-(1→2)-β-D-quinovopyranosyl-1,3(qui′)-olide and 11*R*-jalapinolic acid 11-*O*-(α-L-rhamnopyranosyl-(1→2))-β-D-quinovopyranosyl(qui″)-(1→3)-β-D-quinovopyranosyl-(1→2)-β-D-quinovopyranosyl-1,2(qui″)-olide on the basis of chemical and spectral data. Muricatic acid C previously obtained was also characterized as the glycosidic acid of **2**.

Keywords——resin glycoside; *Ipomoea muricata*; Convolvulaceae; muricatin VII; muricatin VIII; intramolecular macrocyclic ester; muricatic acid C

In the preceding paper[1] we reported six ether-soluble resin glycosides, muricatins I—VI, from the seeds of *Ipomoea muricata* (L.) JACQ. All of them were found to possess characteristic macrocyclic ester structures similar to those of four resin glycosides, orizabins I—IV, from the roots of *I. orizabensis* (Pellet) LEDAN.[2] In a continuation of our studies on the resin glycosides of this plant, we have isolated two compounds, muricatins VII (**1**) and VIII (**2**).

Each fraction (fr. 7 and fr. 9) previously obtained[1b] was subjected to preparative high performance liquid chromatography (preparative HPLC) to give compounds **1** and **2**, respectively, in yields of 0.1 and 0.04% based on the seeds.

Muricatin VII (**1**), white powder, mp 118—120 °C (dec.), $[\alpha]_D$ −18.0° showed an $(M-H)^-$ ion peak at *m/z* 1021 in the negative ion fast atom bombardment mass spectrum (FAB-MS). It was saponified with 5% KOH to provide a mixture of organic acids together with a glycosidic acid which was identified as muricatic acid A, 11*R*-jalapinolic acid 11-*O*-β-D-fucopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl-(1→2)-β-D-quinovopyranoside (**3**),[1a] by comparison of their proton nuclear magnetic resonance (^{1}H-NMR) spectra. The former was treated with diazomethane and examined by gas chromatography (GC), which revealed the presence of 2-methylbutyric and nilic (3-hydroxy-2-methylbutyric) acids. Therefore, in conjunction with the previous study on the components obtained by hydrolyses of the crude resin,[1a] **1** consists of 1 mol each of muricatic acid A, 2*S*-methylbutyric acid and (2*R*,3*R*)-nilic acid.

The ^{1}H-NMR spectrum of **1** showed, when compared with that of **3**, remarkable downfield shifts of 4-H of fucose (1.61 ppm), 2-H of rhamnose (1.04 ppm) and 3-H of quinovose (1.58 ppm), and instead of the triplet at δ 2.52 (2H, J=7.0) in **3**, two signals at δ 2.42 and 2.83 (each 1H, ddd) due to the nonequivalent 2-H_2 of the jalapinolic acid group were observed (Table I).

TABLE I. ^{1}H-NMR Spectral Data for Muricatin VII (1) and Derivatives (400 MHz)

	1	4	5	6	3
qui-1	4.75 (d, 7.0)	4.72 (d, 8.0)	4.77 (d, 7.5)	4.76 (d, 7.8)	4.85 (d, 8.0)
qui-2	4.44 (dd, 7.0, 9.0)	4.30 (dd, 8.0, 9.5)	4.44 (dd, 7.5, 9.0)	4.47 (dd, 7.8, 9.1)	4.31 (dd, 8.0, 8.0)
qui-3	4.25 (dd, 9.0, 9.0)	4.54 (dd, 9.5, 9.5)	4.28 (dd, 9.0, 9.0)	4.24 (dd, 9.1, 9.1)	4.47 (dd, 8.0, 9.0)
qui-4	3.60 (dd, 9.0, 9.0)	3.62 (dd, 9.5, 9.5)	3.61 (dd, 9.0, 9.0)	3.62 (dd, 9.1, 9.1)	3.69 (dd, 9.0, 9.0)
qui-5	3.63 (dq, 9.0, 5.5)	3.67 (dq, 9.5, 6.0)	3.69 (dq, 9.0, 6.0)	3.65 (dq, 9.1, 6.0)	3.70 (dq, 9.0, 6.0)
qui-6	1.60 (d, 5.5)	1.61 (d, 6.0)	1.60 (d, 6.0)	1.48 (d, 6.0)	1.59 (d, 5.5)
qui′-1	5.86 (d, 7.5)	5.80 (d, 7.0)	5.83 (d, 7.5)	5.84 (d, 7.1)	5.82 (d, 8.0)
qui′-2	4.12 (dd, 7.5, 9.5)	4.24 (d, 7.0, 9.0)	4.09 (dd, 7.5, 9.0)	4.10 (dd, 7.1, 8.8)	4.22 (dd, 8.0, 8.8)
qui′-3	5.71 (dd, 9.5, 9.5)	5.70 (dd, 9.0, 9.0)	5.67 (dd, 9.0, 9.0)	5.70 (dd, 8.8, 8.8)	4.13 (dd, 8.8, 8.8)
qui′-4	3.82 (dd, 9.5, 9.5)	3.83 (dd, 9.0, 9.0)	3.82 (dd, 9.0, 9.0)	3.81 (dd, 8.8, 8.8)	3.65 (dd, 8.8, 9.0)
qui′-5	3.65 (dq, 9.5, 6.0)	3.75 (dq, 9.0, 6.0)	3.66 (dq, 9.0, 6.0)	3.80 (dq, 8.8, 6.0)	3.71 (dq, 9.0, 6.0)
qui′-6	1.48 (d, 6.0)	1.52 (d, 6.0)	1.47 (d, 6.0)	1.52 (d, 6.0)	1.47 (d, 6.0)
rha-1	5.53 (d, 1.0)	5.69 (d, 1.7)	5.47 (d, 1.6)	5.47 (d, 1.6)	6.33 (d, 1.2)
rha-2	5.79 (dd, 1.0, 3.0)	4.67 (dd, 1.7, 3.0)	5.74 (dd, 1.6, 3.5)	5.79 (dd, 1.6, 3.5)	4.75 (dd, 1.2, 3.0)
rha-3	4.72 (dd, 3.0, 9.5)	6.08 (dd, 3.0, 9.8)	4.62 (dd, 3.5, 9.5)	4.63 (dd, 3.5, 9.5)	4.83 (dd, 3.0, 9.0)
rha-4	4.25 (dd, 9.5, 9.5)	4.61 (dd, 9.8, 9.8)	4.24 (dd, 9.5, 9.5)	4.29 (dd, 9.5, 9.5)	4.46 (dd, 9.0, 9.0)
rha-5	4.77 (dq, 9.5, 6.1)	4.99 (dq, 9.8, 6.0)	4.75 (dq, 9.5, 6.2)	4.77 (dq, 9.5, 6.1)	5.05 (dq, 9.0, 6.2)
rha-6	1.88 (d, 6.1)	1.84 (d, 6.0)	1.89 (d, 6.2)	1.92 (d, 6.1)	1.93 (d, 6.2)
fuc-1	5.22 (d, 7.5)	4.94 (d, 7.1)	5.25 (d, 8.0)	5.16 (d, 8.0)	5.19 (d, 7.9)
fuc-2	4.28 (dd, 7.5, 9.5)	4.10 (dd, 7.1, 9.5)	4.56 (dd, 8.0, 10.0)	4.36 (dd, 8.0, 9.5)	4.38 (dd, 7.9, 9.8)
fuc-3	4.24 (dd, 9.5, 3.6)	4.15 (dd, 9.5, 3.5)	5.37 (dd, 10.0, 3.5)	4.05 (dd, 9.5, 3.4)	4.12 (dd, 9.8, 3.5)
fuc-4	5.58 (dd, 3.6, 1.0)	5.54 (dd, 3.5, 0.6)	4.22 (dd, 3.5, 0.9)	3.97 (dd, 3.4, 1.0)	3.97 (d, 3.5)
fuc-5	3.94 (dq, 1.0, 6.0)	3.84 (dq, 0.6, 6.0)	3.78 (dq, 0.9, 6.5)	3.63 (dq, 1.0, 6.0)	3.70 (q, 5.5)
fuc-6	1.37 (d, 6.0)	1.34 (d, 6.0)	1.43 (d, 6.5)	1.62 (d, 6.0)	1.55 (d, 5.5)
jla-2	2.42 (ddd, 1.0, 9.5, 17.0)	2.37 (ddd, 2.0, 8.0, 17.0)	2.41 (ddd, 1.0, 9.5, 17.0)	2.42 (ddd, 1.0, 9.5, 17.0)	2.52 (t, 7.0)
	2.83 (ddd, 2.0, 8.0, 17.0)	2.44 (ddd, 2.0, 8.0, 17.0)	2.84 (ddd, 2.0, 8.0, 17.0)	2.90 (ddd, 2.0, 8.0, 17.0)	2.52 (t, 7.0)
jla-11	3.82 (br s)	3.83 (br s)	3.84 (br s)	3.86 (br s)	3.90 (br s)
jla-16	0.85 (t, 7.0)	0.86 (t, 7.0)	0.86 (t, 7.0)	0.85 (t, 7.0)	0.86 (t, 7.0)
mba-2	2.55 (tq, 7.0, 7.0)	2.58 (tq, 7.0, 7.0)	2.55 (tq, 7.0, 7.0)	2.56 (tq, 7.0, 7.0)	
mba-3	1.55[a)]	1.56[a)]	1.52[a)]	1.54[a)]	
	1.79[a)]	1.83[a)]	1.79[a)]	1.83[a)]	
mba-4	0.95 (t, 7.0)	0.87 (t, 7.0)	0.96 (t, 7.0)	0.96 (t, 7.0)	
mba-5	1.24 (d, 7.0)	1.21 (d, 7.0)	1.24 (d, 7.0)	1.24 (d, 7.0)	
nla-2	2.72 (dq, 7.0, 7.0)	2.76 (dq, 7.0, 7.0)	2.73 (dq, 7.0, 7.0)		
nla-3	4.25 (dq, 7.0, 7.0)	4.26 (dq, 7.0, 7.0)	4.25 (dq, 7.0, 7.0)		
nla-4	1.30 (d, 6.5)	1.33 (d, 6.5)	1.35 (d, 6.5)		
nla-5	1.20 (d, 7.0)	1.23 (d, 7.0)	1.23 (d, 7.0)		

Spectra were taken in 0.02 M solution in pyridine-d_5; δ in ppm from tetramethylsilane (TMS) (coupling constants (J) in Hz are given in parentheses); fuc, fucose; rha, rhamnose; qui, quinovose; jla, jalapinolic acid; mba, 2-methylbutyric acid; nla, nilic acid. *a)* Signals are overlapping. All assignments were based on ^{1}H–^{1}H COSY.

TABLE II. ^{1}H-NMR Spectral Data for Muricatin VIII (**2**) and Derivatives (400 MHz)

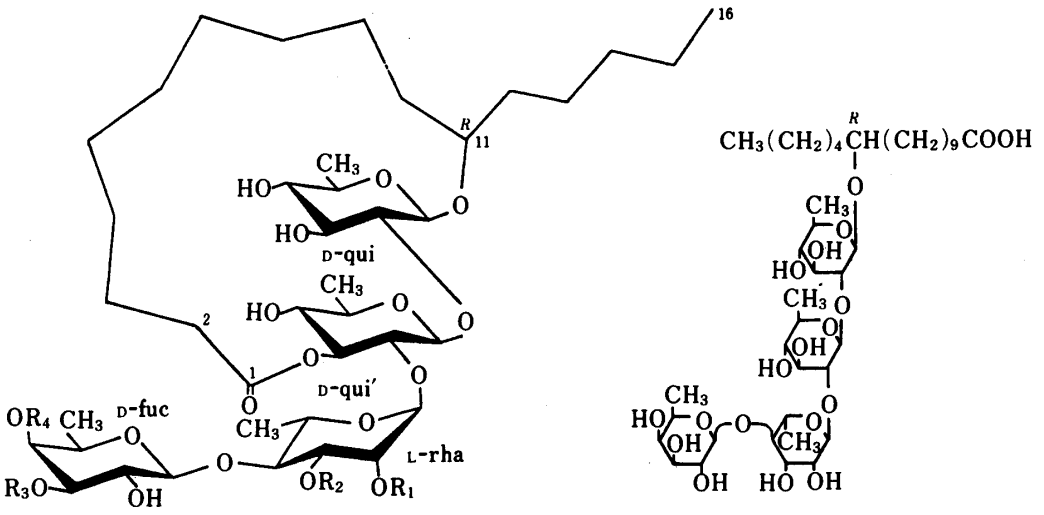
	2	**7a**	**8a**	**9a**
qui-1	4.83 (d, 7.5)	4.85 (d, 7.5)	4.71 (d, 8.5)	5.02 (d, 7.5)
qui-2	4.28 (dd, 7.5, 9.0)	3.97 (dd, 7.5, 9.0)	4.10 (dd, 8.5, 9.9)	4.21 (dd, 7.5, 9.5)
qui-3	4.46 (dd, 9.0, 9.0)	4.03 (dd, 9.0, 9.0)	5.53 (dd, 9.5, 9.5)	3.85 (dd, 9.5, 9.5)
qui-4	3.62 (dd, 9.0, 9.0)	3.64 (dd, 9.0, 9.0)	4.97 (dd, 9.5, 9.5)	3.41 (dd, 9.5, 9.5)
qui-5	3.65 (dq, 9.0, 6.0)	3.61 (dq, 9.0, 6.0)	4.75 (dq, 9.5, 6.0)	3.79 (dq, 9.5, 6.0)
qui-6	1.49 (d, 6.0)	1.59 (d, 6.0)	1.36 (d, 6.0)	1.42 (d, 6.0)
qui′-1	5.67 (d, 7.5)	5.78 (d, 7.8)	4.84 (d, 8.0)	4.71 (d, 7.5)
qui′-2	4.11 (dd, 7.5, 9.0)	4.18 (dd, 7.8, 9.0)	4.03 (dd, 8.0, 9.5)	3.98 (dd, 7.5, 9.0)
qui′-3	4.08 (dd, 9.0, 9.0)	3.89 (dd, 9.0, 9.0)	4.44 (dd, 9.5, 9.5)	4.22 (dd, 9.0, 9.5)
qui′-4	3.49 (dd, 9.0, 9.0)	3.57 (dd, 9.0, 9.0)	4.97 (dd, 9.5, 9.5)	4.93 (dd, 9.5, 9.5)
qui′-5	3.54 (dq, 9.0, 6.0)	3.78 (dq, 9.0, 6.0)	3.72 (dq, 9.5, 6.0)	3.97 (dq, 9.5, 6.0)
qui′-6	1.60 (d, 6.0)	1.55 (d, 6.0)	1.23 (d, 6.0)	1.28 (d, 6.0)
qui″-1	5.10 (d, 8.0)	4.89 (d, 7.5)	5.21 (d, 8.0)	5.03 (d, 7.0)
qui″-2	5.65 (dd, 8.0, 9.0)	4.32 (dd, 7.5, 9.0)	5.46 (dd, 8.0, 9.3)	5.47 (dd, 8.0, 9.5)
qui″-3	4.04 (dd, 9.0, 9.0)	4.46 (dd, 9.0, 9.0)	5.57 (dd, 9.3, 9.3)	5.54 (dd, 9.5, 9.5)
qui″-4	3.66 (dd, 9.0, 9.0)	3.65 (dd, 9.0, 9.0)	5.13 (dd, 9.3, 9.3)	5.16 (dd, 9.5, 9.5)
qui″-5	3.71 (dq, 9.0, 6.0)	3.72 (dq, 9.0, 6.0)	3.72 (dq, 9.3, 6.0)	3.82 (dq, 9.5, 6.0)
qui″-6	1.49 (d, 6.0)	1.55 (d, 6.0)	1.27 (d, 6.0)	1.38 (d, 6.0)
rha-1	5.92 (d, 0.6)	6.25 (d, 0.9)	5.91 (s)	5.85 (s)
rha-2	4.74 (0.6, 3.0)	4.82 (dd, 0.9, 3.0)	4.75 (d, 6.0)	4.63 (d, 6.0)
rha-3	4.67 (dd, 3.0, 9.5)	4.62 (dd, 3.0, 9.5)	4.92 (dd, 6.5, 8.0)	4.52 (dd, 6.0, 8.0)
rha-4	4.34 (dd, 9.5, 9.5)	4.29 (dd, 9.5, 9.5)	5.39 (dd, 8.0, 10.5)	5.37 (dd, 8.0, 10.5)
rha-5	5.07 (dq, 9.5, 6.0)	4.98 (dq, 9.5, 6.0)	4.53 (dq, 10.5, 6.5)	4.60 (dq, 10.5, 6.0)
rha-6	1.82 (d, 6.0)	1.90 (d, 6.0)	1.57 (d, 6.5)	1.51 (d, 6.0)
jla-2	2.49 (ddd, 4.0, 8.0, 16.0) 3.34 (ddd, 2.5, 9.0, 16.0)	2.32 (t, 7.5, 7.5) 2.32 (t, 7.5, 7.5)	2.52 (ddd, 2.5, 10.0, 13.5) 2.89 (ddd, 4.0, 12.0, 13.5)	2.53 (ddd, 3.0, 7.0, 16.0) 2.88 (ddd, 2.5, 8.0, 16.0)
jla-11	3.79 (br s)	3.92 (br s)	3.71 (br s)	3.79 (br s)
jla-16	0.87 (t, 7.0)	0.86 (t, 7.5)	0.88 (t, 7.0)	0.88 (t, 6.5)
$COOCH_3$		3.61		
OAc			2.01, 2.02, 2.02, 2.03 2.08, 2.11 (each 3H, s)	2.05, 2.06, 2.07, 2.10 (each 3H, s)
CH_3			1.62, 1.75 (each 3H, s)	1.58, 1.65, 1.69, 1.72 (each 3H, s)

Spectra were taken in 0.02 M solution in pyridine-d_5; δ in ppm from TMS. All assignments were based on ^{1}H–^{1}H COSY.

These observations indicated that **1** has, like muricatins I—VI,[1b] a macrocyclic ester structure formed by linkage between the carboxy group of the jalapinolic acid and one of the hydroxy groups in the sugar moiety, and that the acyl groups are located at 4-OH of fucose, 2-OH of rhamnose and 3-OH of one of the two quinovoses.

In order to specify the sites of ester linkages of the respective organic acids and jalapinolic acid, partial deacylation was examined. Compound **1** was treated with a mixture of trimethylamine and methanol (1 : 6) for 30 min at room temperature and the products were separated by HPLC to give **4** (2.0%), **5** (4.3%) and **6** (1.9%), together with unreacted **1**. The ^{1}H-NMR spectrum of **6** showed, in comparison with that of **1**, an upfield shift (1.53 ppm) of 4-H of fucose and loss of the signals attributable to the nilic acid moiety, and was found to be identical with that of muricatin V.[1b] Therefore, the nilic acid is located at 4-OH of fucose, and the 2-methylbutyric acid and jalapinolic acid are linked with 2-OH of rhamnose and 3-OH of the second quinovose (qui′), respectively.

The *J* values of the anomeric and methine proton signals of the respective sugar units



1: R_1 = mba, R_2 = R_3 = H, R_4 = nla (muricatin VII)
4: R_1 = R_3 = H, R_2 = mba, R_4 = nla
5: R_1 = mba, R_2 = R_4 = H, R_3 = nla
6: R_1 = mba, R_2 = R_3 = R_4 = H (muricatin V)

mba: $CH_3CH_2\underset{CH_3}{\overset{S}{C}}H-CO$ nla: $CH_3\overset{R}{C}H(OH)-\overset{R}{C}H(CH_3)-CO$

qui: quinovose rha: rhamnose fuc: fucose

Fig. 1

showed the rhamnose unit to be in $^1C_4$ conformation and the other three sugar units in $^4C_1$.

From all the above data, the full structure of muricatin VII (**1**) is defined as 11*R*-jalapinolic acid 11-*O*-(4-*O*-(3*R*-hydroxy-2*R*-methylbutyryl))-β-D-fucopyranosyl-(1→4)-(2-*O*-(2*S*-methylbutyryl))-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl(qui')-(1→2)-β-D-quinovopyranosyl-1,3(qui')-olide (Fig. 1).

Compounds **4** and **5** gave almost the same negative ion FAB-MS as that of **1**, suggesting that they are isomeric to one another. The ^{1}H-NMR spectrum of **4** showed, in comparison with that of **1**, upfield (1.12 ppm) and downfield (1.36 ppm) shifts, respectively, of 2- and 3-H of rhamnose, while **5** exhibited downfield (1.13 ppm) and upfield (1.36 ppm) shifts, respectively, of 3- and 4-H of fucose. Accordingly, the partial deacylation reaction of **1** was accompanied with acyl migration: the 2-methylbutyric acid moiety originally combined with 2-OH of rhamnose had shifted to 3-OH of rhamnose, forming **4**, while the nilic acid moiety had transferred from 4- to 3-OH of fucose, producing **5** (Fig. 1).

Muricatin VIII (**2**), white powder, mp 155—158 °C (dec.), $[\alpha]_D$ −58.3°, exhibited an $(M-H)^-$ ion peak at *m/z* 837 in the negative ion FAB-MS, and one ester carbonyl and four anomeric carbon signals at δ 174.0, 103.4, 101.9, 101.7 and 101.0 in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum. On treatment with 5% KOH, **2** gave no organic acid but a glycosidic acid, which was identical with muricatic acid C (**7**), previously reported as an unknown minor component of the crude resin.[1a] Permethylation and methanolysis of **7** liberated methyl 3,4-di-*O*-methyl-, methyl 4-*O*-methyl- and methyl 2,3,4-tri-*O*-methylquinovopyranosides, methyl 2,3,4-tri-*O*-methylrhamnopyranoside and methyl jalapinolate. These data indicated that **2** is composed of only muricatic acid C, a branched tetrasaccharide of jalapinolic acid, and that the carboxy group of the jalapinolic acid forms an ester linkage with a hydroxy group of the sugar moiety.

To determine the sequence of the sugar residues of **7**, a number of unsuccessful partial

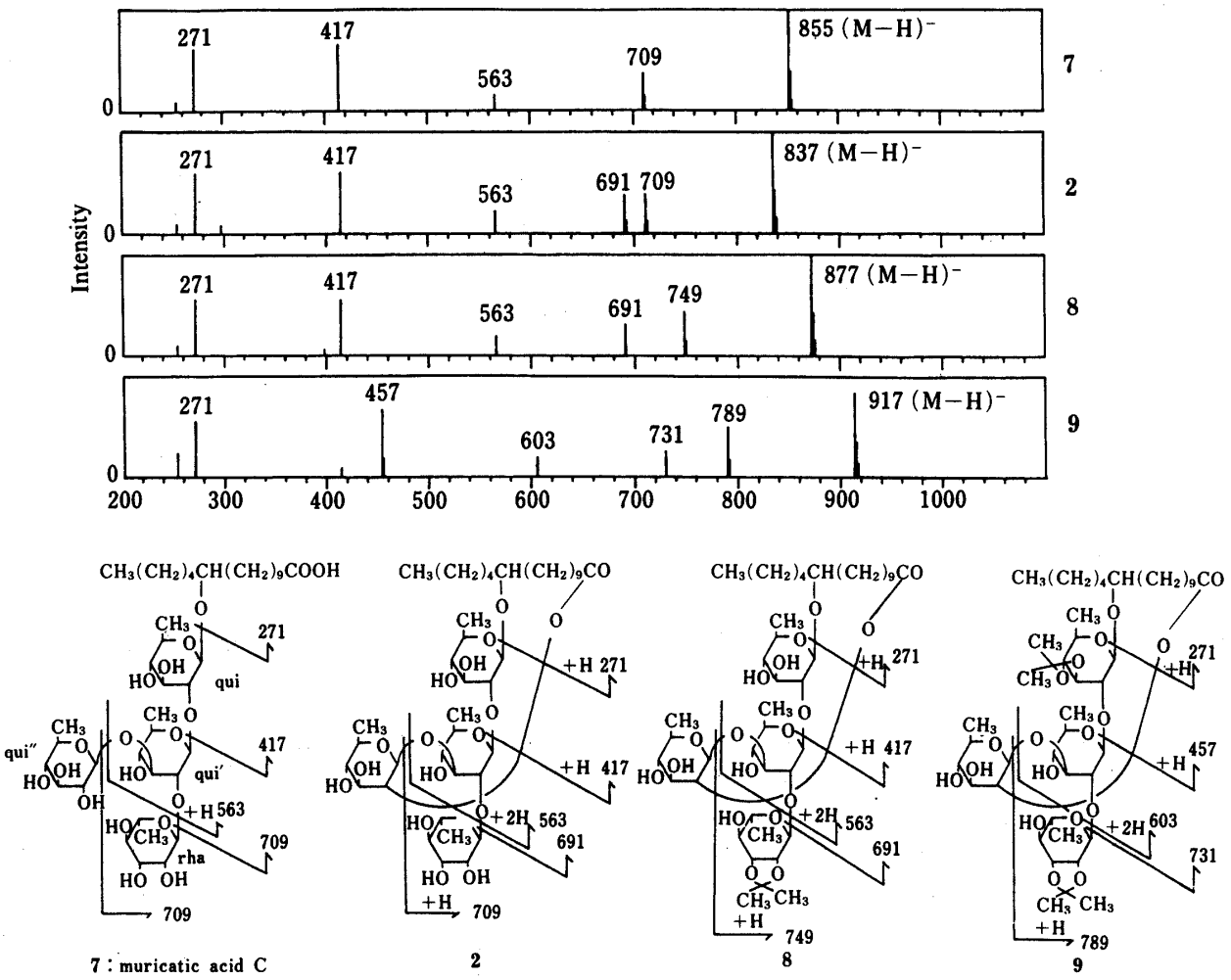


Fig. 2. Negative Ion FAB-MS of **7**, **2**, **8** and **9**

hydrolyses under a variety of conditions were attempted. Then, we tried to characterize the structure of **2** itself.

In comparison with the negative ion FAB-MS of **7**, fragment ion peaks at *m/z* 691 and 709 were assignable, respectively, to $(M-H-146\ (\text{methylpentose unit}))^-$ and $(M-H-(146-H_2O))^-$, suggesting that the carboxyl of the jalapinolic acid is combined with the terminal quinovose or rhamnose to form a macrocyclic ring (Fig. 2).

The ^{1}H-NMR spectrum of **2**, compared with that of the methyl ester (**7a**) of **7**, showed a considerable downfield shift (1.33 ppm) of 2-H of quinovose. Hence, the ester linkage is located at 2-OH of the terminal quinovose.

Compound **2** was treated with 2,2-dimethoxypropane in the presence of a small amount of *p*-toluenesulfonic acid to afford two compounds, **8** and **9**, and their negative ion FAB-MS were examined in comparison with that of **2** (Fig. 2).

Compound **8** exhibited an $(M-H)^-$ ion peak at *m/z* 877 and a fragment peak at *m/z* 749 in place of those at *m/z* 837 ($(M-H)^-$) and 709 in **2**, besides fragment peaks at *m/z* 691, 563, 417 and 271 in common with **2** (Fig. 2). Therefore, **8** is a monoacetonide in which the isopropyridene group is situated in the terminal rhamnose. Compound **9** showed an $(M-H)^-$ ion peak at *m/z* 917 indicating **9** to be a diacetonide. Furthermore, its spectrum showed fragment peaks at *m/z* 789, 731, 603 and 457 which are, respectively, 40 mass units larger than those at *m/z* 749, 691, 563 and 417 of **8**, suggesting that one of the two isopropylidene moieties was combined with the first quinovose (qui) counted from the aglycone. Thus, the terminal

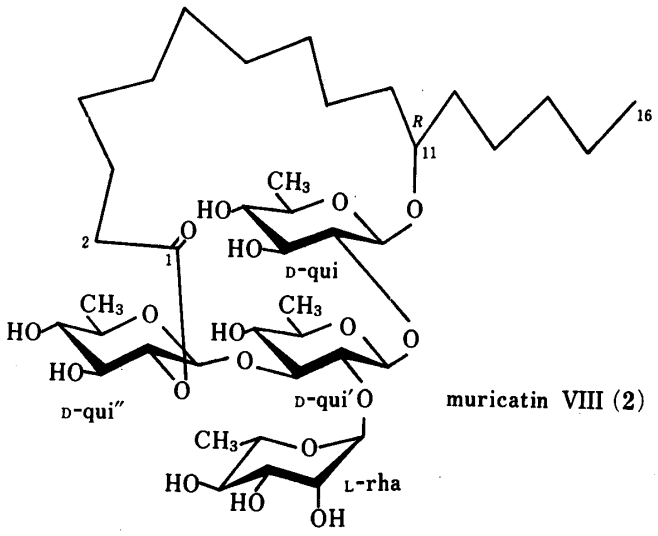


Fig. 3

rhamnose and quinovose (qui'') are placed on 2- and 3-OH of the second quinovose (qui'). Compounds **8** and **9** were each acetylated to give compounds **8a** and **9a**. Their ^{1}H-NMR spectral data supported the above conclusion (Table II), but the sites of glycosidic linkages of the respective terminal rhamnose and qui'' at qui' remained unsolved.

The two-dimensional nuclear Overhauser effect (NOESY) spectrum of **8a** showed cross peaks between 1-H of rhamnose and 2-H of qui', and 1-H of qui'' and 3-H of qui', but no cross peak between 1-H of rhamnose and 3-H of qui' or 1-H of qui'' and 2-H of qui' was observed. Therefore, the rhamnose and qui'' are, respectively, linked with 2- and 3-OH of qui'.

The J values of the anomeric and methine proton signals due to the sugar moiety in the ^{1}H-NMR of **2** indicated that the glycosidic linkage of the rhamnose unit is α in $^1C_4$ conformation and those of the other three quinovoses are β in $^4C_1$.

Accordingly, the structures of muricatic acid C (**7**) and muricatin VIII (**2**) are defined, respectively, as 11*R*-jalapinolic acid 11-*O*-(α-L-rhamnopyranosyl-(1→2))-β-D-quinovopyranosyl(qui'')-(1→3)-β-D-quinovopyranosyl-(1→2)-β-D-quinovopyranoside and its 1,2(qui'')-olide (Fig. 3).

It should be noted that muricatin VIII (**2**) is different from all the resin glycosides so far isolated in that **2** contains no organic acid as a component.

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as in the previous paper[1a] unless otherwise specified. The NOESY spectrum was measured by the use of a correlation sequence with a 45° mixing pulse and N-type peak selection (mixing time: PI_3 150 ms). Data processing was performed with the standard JEOL software with a 512 × 2048 data point matrix. The abbreviations used are as follows: s, singlet; d, doublet; dd, double-doublet; dq, double-quartet; ddd, double-double-doublet; tq, triple-quartet; br s, broad singlet. Specific rotations were measured at 24 °C. The assignments of carbon signals were based on ^{1}H–^{13}C shift-correlated spectra.

Isolation of Muricatins VII (1) and VIII (2)——The fr. 7 (2.7 g) and fr. 9 (14.5 g), obtained previously[1a] from the crude resin glycoside fraction were each subjected to repetitive preparative HPLC ($CHCl_3$–MeOH, 8:2) to afford muricatin VII (**1**) (2.5 g) and muricatin VIII (**2**) (0.92 g). Muricatin VII (**1**): white powder, mp 118—120 °C (dec.), $[\alpha]_D$ −18.2° (c = 1.0, MeOH). Infrared spectrum (IR) (KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS m/z: 1021 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR: Table I. *Anal.* Calcd for $C_{50}H_{86}O_{21}$: C, 58.69; H, 8.47. Found: C, 58.41, H, 8.50. Muricatin VIII (**2**): white powder, mp 155—158 °C (dec.), $[\alpha]_D$ −58.3° (c = 1.0, MeOH). Negative ion FAB-MS: Fig. 2. ^{13}C-NMR (pyridine-d_5) δ: 103.4, 79.6, 78.8, 77.2, 72.2, 18.7 (C_1–C_6 of qui), 101.9, 79.3, 84.8, 76.8,

72.1, 18.2 (C_1–C_6 of qui'), 101.0, 74.6, 75.8, 74.5, 73.6, 18.9 (C_1–C_6 of qui''), 101.7, 72.6, 72.5, 73.9, 69.5, 19.2 (C_1–C_6 of rhamnose), 174.0 (ester carbonyl C). ^{1}H-NMR: Table II. *Anal.* Calcd for $C_{40}H_{70}O_{18}$: C, 58.69; H, 8.47. Found: C, 58.49; H, 8.43.

Saponification of 1——A solution of **1** (12 mg) in 5% KOH (H_2O–1,4-dioxane, 3 : 1) (10 ml) was refluxed for 1 h. The reaction mixture was made acidic to pH 4.0 with 2 N HCl, and extracted with ether (10 ml). The organic layer was treated with diazomethane and the product was examined by GC (Unisol F-200, 4 mm i.d. × 2 m glass column; column temperature, 70 °C; N_2, 2 kg/cm^2). t_R (min): 1.9 (methyl 2-methylbutyrate), 24.0 (methyl nilate).

The aqueous phase was extracted with *n*-BuOH (5 ml) and the organic layer was concentrated *in vacuo* to give muricatic acid A[1a] (**3**) (5 mg), white powder, mp 104—110 °C (dec.).

Partial Deacylation of 1——Compound **1** (350 mg) in triethylamine–MeOH (1 : 6) (10 ml) was left standing for 30 min at room temperature. The reaction mixture was made acidic (pH 4.0), diluted with water and then extracted with ether (10 ml). The organic layer was reduced and subjected to preparative HPLC ($CHCl_3$–MeOH–H_2O, 9 : 1 : 0.1) to afford **4** (12 mg), **5** (15 mg) and muricatin V (**6**)[1b] (8 mg), along with unreacted **1** (310 mg). Compound **4**: colorless needles (*n*-hexane–acetone, 3 : 1), mp 113—118 °C (dec.). $[\alpha]_D$ −48.4° (c = 2.0, MeOH). Negative ion FAB-MS *m/z*: 1021 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR: Table I. *Anal.* Calcd for $C_{50}H_{86}O_{21}$: C, 58.69; H, 8.47. Found: C, 58.60; H, 8.49. Compound **5**: colorless needles (*n*-hexane–acetone, 3 : 1), mp 176—185 °C (dec.). $[\alpha]_D$ −27.3° (c = 0.5, MeOH). Negative ion FAB-MS *m/z*: 1021 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR: Table I. *Anal.* Calcd for $C_{50}H_{86}O_{21}$: C, 58.69; H, 8.47. Found: C, 58.47; H, 8.50.

Saponification of 2——Compound **2** (10 mg) was saponified and worked up in the same way as described for **1** to give compound **7** (5 mg), white powder, mp 105—109 °C (dec.). $[\alpha]_D$ −51.2° (c = 1.0, MeOH). IR (KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS *m/z*: 855 $(M-H)^-$, 709, 563, 417, 271. *Anal.* Calcd for (in the form of peracetate) $C_{58}H_{90}O_{28}$: C, 56.39; H, 7.34. Found: C, 56.25; H, 7.43. **7** was identical with muricatic acid C[1a] by ^{1}H-NMR comparison.

Compound **7** was treated with diazomethane to give **7a** (5 mg), white powder, mp 114—117 °C (dec.). ^{13}C-NMR (pyridine-d_5) δ: 102.3, 79.6, 79.3, 77.2, 72.5, 18.5 (C_1–C_6 of qui), 101.6, 78.1, 88.7, 74.9, 72.3, 18.1 (C_1–C_6 of qui'), 104.7, 75.0, 78.2, 76.3, 73.4, 18.6 (C_1–C_6 of qui''), 102.2, 72.2, 72.8, 74.3, 69.7, 19.0 (C_1–C_6 of rhamnose). ^{1}H-NMR: Table II.

Permethylation and Methanolysis of 7——Compound **7** (6 mg) was methylated according to Hakomori,[3] and the permethylate was methanolyzed in the usual way. The product was analyzed by GC. Condition 1 (10% 1,4-butanediol succinate on Chromosorb W (60—80 mesh), 4 mm i.d. × 1.2 m glass column; column temperature, 120 °C; N_2, 1.1 kg/cm^2), t_R (min): 1.6, 2.4 (methyl 2,3,4-tri-*O*-methylquinovopyranoside), 2.5 (methyl 2,3,4-tri-*O*-methylrhamnopyranoside), 5.6, 7.2 (methyl 3,4-di-*O*-methylquinovopyranoside), 10.4, 15.0 (methyl 4-*O*-methylquinovopyranoside). Condition 2 (5% SE-52 on Chromosorb W (60—80 mesh), 4 mm i.d. × 1.9 m glass column; column temperature, 190 °C; N_2, 2 kg/cm^2), t_R (min): 4.1 (methyl jalapinolate).

Preparation of 8 and 9——A mixture of **2** (30 mg), 2,2-dimethoxypropane (3 ml), *p*-toluenesulfonic acid (trace) and molecular sieve (4 Å, 400 mg) was left standing for 30 min at room temperature with stirring. The reaction mixture was diluted with water (20 ml) and extracted with ether (20 ml). After removal of the solvent, the residue was chromatographed on silica gel ($CHCl_3$–MeOH, 9 : 1) to yield **8** (4 mg) and **9** (6 mg). Compound **8**: white powder, mp 138—142 °C (dec.), $[\alpha]_D$ −42.1° (c = 1.8, MeOH). Negative ion FAB-MS: Fig. 2. *Anal.* Calcd for $C_{43}H_{74}O_{18}\cdot 2H_2O$; C, 56.44; H, 8.59. Found: C, 56.73; H, 8.55. Compound **9**: white powder, mp 114—117 °C (dec.), $[\alpha]_D$ −37.1° (c = 2.3, MeOH). Negative ion FAB-MS: Fig. 2. *Anal.* Calcd for $C_{46}H_{78}O_{18}\cdot H_2O$: C, 58.95; H, 8.60. Found: C, 59.28; H, 8.46.

Preparation of 8a and 9a——Compounds **8** (3 mg) and **9** (3 mg) were each acetylated with acetic anhydride (0.2 ml) and pyridine (0.2 ml) at room temperature. Usual work-up yielded the hexaacetate (**8a**) (3 mg), white powder, mp 121—130 °C (dec.), ^{1}H-NMR: Table II, and the tetraacetate (**9a**) (3 mg), white powder, mp 101—104 °C (dec.), ^{1}H-NMR: Table II.

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