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Resin Glycosides. III.[1] Isolation and Structural Study of the Genuine Resin Glycosides, Muricatins I—VI, from the Seeds of *Ipomoea muricata*

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Six kinds of so-called resin glycoside, muricatins I—VI, were isolated from the seeds of *Ipomoea muricata* JACQ. (Convolvulaceae). Their structures including the stereochemistry have been determined on the basis of chemical and spectral data. Similar to the resin glycosides previously isolated from the roots of *I. orizabensis* (PELLET) LEDAN., all of them were monomers of a jalapinolic acid tetraglycoside in which the sugar moiety is partially acylated by organic acids and also combined with the carboxy group of the aglycone to form a macrocyclic ester structure.

Keywords——resin glycoside; *Ipomoea muricata*; Convolvulaceae; muricatin I—VI; partially acylated jalapinolic acid tetraglycoside; intramolecular macrocyclic ester

In the preceding paper,[1] we reported the structures of two glycosidic acids, muricatic acids A and B, as well as three organic acids, isobutyric, 2*S*-methylbutyric and 2*R*,3*R*-nilic acids, formed by alkaline hydrolysis of the crude resin glycoside from the seeds of *Ipomoea muricata* JACQ. This paper is concerned with the isolation and structural elucidation of six resin glycosides.

The MeOH extract of the seeds was defatted with *n*-hexane and the residue was treated with ether to afford ether-soluble and insoluble portions. The former was subjected successively to silica gel and Sephadex LH-20 chromatographies to give a crude resin glycoside, which was separated on a Lobar silica gel column into three fractions. The final purification was achieved by the repetitive preparative silica gel high performance liquid chromatography (HPLC) of the respective fractions to provide six pure resin glycosides named muricatins I (**1**), II (**2**), III (**3**), IV (**4**), V (**5**) and VI (**6**) in the yields of 2.0, 1.6, 0.3, 0.1, 0.4 and 0.4%, respectively, based on the seeds.

Muricatin I (**1**), colorless needles, mp 119—123 °C (dec.), $[\alpha]_D$ −18.2°, gave, on alkaline hydrolysis, 2-methylbutyric acid and a glycosidic acid which was identified as muricatic acid A[1] (**7**) from the proton nuclear magnetic resonance (^{1}H-NMR) spectrum. The negative ion fast atom bombardment mass spectrum (FAB-MS)[2] of **1** showed a peak at *m/z* 1005 $(M-H)^-$ but no peak in the higher region up to *m/z* 3000, indicating the molecular weight of **1** to be 1006. It exhibited four anomeric proton signals at δ 4.71, 5.17, 5.49 and 5.80 and signals assignable to two moles of 2-methylbutyric acid group in the ^{1}H-NMR spectrum as well as signals due to four anomeric (δ 99.2, 99.6, 102.6 and 106.1) and three ester carbonyl carbons (δ 172.4, 176.0 and 176.6) in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum. These data suggested that **1** consists of one mole of muricatic acid A (**7**) and two moles of 2-methylbutyric acid which are combined with the hydroxy groups of the sugar

TABLE I. ^{1}H-NMR Spectral Data for Resin Glycosides (**1**—**6**) and Their Derivatives (400 MHz)

	1	**2**	**3**	**4**	**5**
qui-1	4.71 (d, 7.5)	4.74 (d, 7.5)	4.71 (d, 7.1)	4.70 (d, 7.8)	4.76 (d, 7.8)
qui-2	4.39 (dd, 7.5, 9.3)	4.42 (dd, 7.5, 9.5)	4.29 (dd, 7.1, 8.1)	4.29 (dd, 7.8, 9.0)	4.47 (dd, 7.8, 9.1)
qui-3	4.25 (dd, 9.3, 9.3)	4.28 (dd, 9.5, 9.5)	4.56 (dd, 8.1, 8.3)	4.54 (dd, 9.0, 9.0)	4.24 (dd, 9.1, 9.1)
qui-4	3.60 (dd, 9.3, 9.3)	3.61 (dd, 9.5, 9.5)	3.62 (dd, 8.3, 8.3)	3.61 (dd, 9.0, 9.0)	3.62 (dd, 9.1, 9.1)
qui-5	3.58 (dq, 9.3, 5.5)	3.59 (dq, 9.5, 5.5)	3.58 (dq, 8.3, 6.0)	3.73 (dq, 9.0, 6.0)	3.65 (dq, 9.1, 6.0)
qui-6	1.56 (d, 5.5)	1.58 (d, 5.5)	1.58 (d, 6.0)	1.58 (d, 6.0)	1.48 (d, 6.0)
qui′-1	5.80 (d, 7.5)	5.84 (d, 7.4)	5.78 (d, 7.0)	5.78 (d, 7.0)	5.84 (d, 7.1)
qui′-2	4.09 (dd, 7.5, 8.5)	4.11 (dd, 7.4, 9.0)	4.25 (dd, 7.0, 8.1)	4.26 (dd, 7.0, 8.5)	4.10 (dd, 7.1, 8.8)
qui′-3	5.66 (dd, 8.5, 9.2)	5.68 (dd, 9.0, 9.0)	5.70 (dd, 8.1, 8.1)	5.70 (dd, 8.5, 8.5)	5.70 (dd, 8.8, 8.8)
qui′-4	3.79 (dd, 9.2, 9.2)	3.80 (dd, 9.0, 9.0)	3.83 (dd, 8.1, 8.1)	3.79 (dd, 8.5, 8.5)	3.81 (dd, 8.8, 8.8)
qui′-5	3.62 (dq, 9.2, 6.0)	3.63 (dq, 9.0, 6.0)	3.67 (dq, 8.1, 6.0)	3.62 (dq, 8.5, 6.1)	3.80 (dq, 8.8, 6.0)
qui′-6	1.46 (d, 6.0)	1.47 (d, 6.0)	1.58 (d, 6.0)	1.52 (d, 6.1)	1.52 (d, 6.0)
rha-1	5.49 (d, 1.1)	5.50 (d, 1.4)	5.68 (d, 1.6)	5.64 (d, 1.6)	5.47 (d, 1.6)
rha-2	5.74 (dd, 1.1, 3.5)	5.76 (dd, 1.4, 3.5)	4.65 (dd, 1.6, 3.0)	4.66 (dd, 1.6, 3.0)	5.79 (dd, 1.6, 3.5)
rha-3	4.68 (dd, 3.5, 9.5)	4.69 (dd, 3.5, 9.5)	6.11 (dd, 3.0, 9.5)	6.10 (dd, 3.0, 9.9)	4.63 (dd, 3.5, 9.5)
rha-4	4.20 (dd, 9.5, 9.5)	4.24 (dd, 9.5, 9.5)	4.62 (dd, 9.5, 9.5)	4.62 (dd, 9.9, 9.9)	4.29 (dd, 9.5, 9.5)
rha-5	4.74 (dq, 9.5, 6.0)	4.77 (dq, 9.5, 6.0)	4.99 (dq, 9.5, 6.2)	4.98 (dq, 9.9, 6.1)	4.77 (dq, 9.5, 6.1)
rha-6	1.86 (d, 6.0)	1.88 (d, 6.0)	1.86 (d, 6.2)	1.86 (d, 6.1)	1.92 (d, 6.1)
fuc-1	5.17 (d, 7.1)	5.20 (d, 7.5)	4.95 (d, 7.1)	4.96 (d, 7.5)	5.16 (d, 8.0)
fuc-2	4.21 (dd, 7.1, 10.0)	4.25 (dd, 7.5, 10.0)	4.10 (dd, 7.1, 9.5)	4.13 (dd, 7.5, 10.0)	4.36 (dd, 8.0, 9.5)
fuc-3	4.17 (dd, 10.0, 3.8)	4.20 (dd, 10.0, 3.5)	4.13 (dd, 9.5, 3.4)	4.14 (dd, 10.0, 3.0)	4.05 (dd, 9.5, 3.4)
fuc-4	5.50 (dd, 3.8, 1.0)	5.51 (dd, 3.5, 0.9)	5.57 (dd, 3.4, 0.9)	5.56 (dd, 3.0, 0.9)	3.97 (dd, 3.4, 1.0)
fuc-5	3.87 (dq, 1.0, 6.2)	3.88 (dq, 0.9, 6.2)	3.80 (dq, 0.9, 6.5)	3.87 (dq, 0.9, 6.5)	3.63 (dq, 1.0, 6.0)
fuc-6	1.27 (d, 6.2)	1.28 (d, 6.2)	1.26 (d, 6.5)	1.27 (d, 6.5)	1.62 (d, 6.0)
qui″-1					
qui″-2					
qui″-3					
qui″-4					
qui″-5					
qui″-6					
jla- 2	2.40 (ddd, 1.0, 9.5, 17.0)	2.41 (ddd, 1.0, 9.5, 17.0)	2.33[b] ($W_{h/2}$, 17.5)	2.33[b] ($W_{h/2}$, 17.5)	2.42 (ddd, 1.0, 9.5, 17.0)
	2.80 (ddd, 2.0, 8.0, 17.0)	2.83 (ddd, 2.0, 8.0, 17.0)	2.39[b] ($W_{h/2}$, 17.0)	2.40[b] ($W_{h/2}$, 17.5)	2.90 (ddd, 2.0, 8.0, 17.0)
jla-11	3.81 (br s)	3.82 (br s)	3.73 (br s)	3.73 (br s)	3.86 (br s)
jla-16	0.85 (t, 7.0)	0.85 (t, 7.0)	0.86 (t, 7.0)	0.86 (t, 7.0)	0.85 (t, 7.0)
mba-2	2.52 (tq, 7.0, 7.0)	2.54 (tq, 7.0, 7.0)	2.58 (tq, 7.0, 7.0)	2.60 (tq, 7.0, 7.0)	2.56 (tq, 7.0, 7.0)
mba-3	1.55[a]	1.56[a]	1.55[a]	1.56[a]	1.54[a]
	1.81[a]	1.82[a]	1.90 (ddq, 7.0, 7.0, 7.0)	1.91 (ddq, 7.0, 0, 7.0)	1.83[a]
mba-4	0.95 (t, 7.0)	0.95 (t, 7.0)	0.96 (t, 7.0)	0.87 (t, 7.0)	0.96 (t, 7.0)
mba-5	1.22 (d, 7.0)	1.23 (d, 7.0)	1.24 (d, 7.0)	1.24 (d, 7.0)	1.24 (d, 7.0)
mba′-2	2.47 (tq, 7.0, 7.0)		2.46 (tq, 7.0, 7.0)		
mba′-3	1.53[a]		1.53[a]		
	1.79[a]		1.80 (ddq, 7.0, 7.0, 7.0)		
mba′-4	0.90 (t, 7.0)		0.87 (t, 7.0)		
mba′-5	1.17 (d, 7.0)		1.19 (d, 7.0)		
iba-2		2.63 (sept, 7.0)		2.60 (sept, 7.0)	
iba-3		1.16 (d, 7.0)		1.19 (d, 7.0)	
iba-3′		1.17 (d, 7.0)		1.21 (d, 7.0)	

moiety of **7**, and that, similar to the resin glycosides previously isolated from *I. orizabensis* (PELLET) LEDAN.,[3] the carboxy group of the aglycone, jalapinolic acid, is also intramolecularly linked with a hydroxy group of the sugar moiety. The latter suggestion was

TABLE I. (continued)

	6	7	8	9	10
qui-1	4.77 (d, 7.8)	4.85 (d, 8.0)	4.88 (d, 7.0)	4.77 (d, 7.5)	4.63 (d, 7.8)
qui-2	4.43 (dd, 7.8, 9.1)	4.31 (dd, 8.0, 8.0)	4.26 (dd, 7.0, 8.0)	4.44 (dd, 7.5, 9.0)	4.49 (dd, 7.8, 8.5)
qui-3	4.29 (dd, 9.1, 9.1)	4.47 (dd, 8.0, 9.0)	4.47 (dd, 8.0, 8.0)	4.29 (dd, 9.0, 9.0)	4.25 (dd, 8.5, 8.5)
qui-4	3.58 (dd, 9.1, 9.1)	3.69 (dd, 9.0, 9.0)	3.58 (dd, 8.0, 8.0)	3.66 (dd, 9.0, 9.0)	3.58 (dd, 8.5, 8.5)
qui-5	3.61 (dq, 9.1, 6.1)	3.70 (dq, 9.0, 6.0)	3.6[a]	3.68 (dq, 9.0, 6.0)	3.59 (dq, 8.5, 6.0)
qui-6	1.59 (d, 6.1)	1.59 (d, 5.5)	1.51 (d, 6.0)	1.61 (d, 6.0)	1.47 (d, 6.0)
qui′-1	5.83 (d, 7.1)	5.82 (d, 8.0)	5.77 (d, 7.2)	5.84 (d, 7.2)	5.76 (d, 7.2)
qui′-2	4.12 (dd, 7.1, 8.8)	4.22 (dd, 8.0, 8.0)	4.19 (dd, 7.2, 8.0)	4.10 (dd, 7.2, 8.8)	4.20 (dd, 7.2, 8.5)
qui′-3	5.69 (dd, 8.8, 8.8)	4.13 (dd, 8.8, 8.8)	4.10 (dd, 8.0, 8.0)	5.68 (dd, 8.8, 8.8)	5.70 (dd, 8.5, 8.5)
qui′-4	3.80 (dd, 8.8, 8.8)	3.65 (dd, 8.8, 9.0)	3.6[a]	3.81 (dd, 8.8, 8.8)	3.82 (dd, 8.5, 6.0)
qui′-5	3.66 (dq, 8.8, 6.0)	3.71 (dq, 9.0, 6.0)	3.73 (dq, 9.0, 6.0)	3.68 (dq, 8.8, 6.0)	3.65 (dq, 8.5, 6.0)
qui′-6	1.48 (d, 6.0)	1.47 (d, 6.0)	1.52 (d, 6.0)	1.48 (d, 6.0)	1.49 (d, 6.0)
rha-1	5.50 (d, 1.6)	6.33 (d, 1.2)	6.31 (d, 1.2)	5.48 (d, 1.4)	5.62 (d, 1.8)
rha-2	5.75 (dd, 1.6, 3.2)	4.75 (dd, 1.2, 3.0)	4.67 (dd, 1.2, 3.0)	5.74 (dd, 1.4, 3.5)	4.62 (dd, 1.8, 3.1)
rha-3	4.66 (dd, 3.2, 9.5)	4.83 (dd, 3.0, 9.0)	4.82 (dd, 3.0, 9.0)	4.63 (dd, 3.5, 9.0)	6.11 (dd, 3.1, 9.9)
rha-4	4.24 (dd, 9.5, 9.5)	4.46 (dd, 9.0, 9.0)	4.41 (dd, 9.0, 9.0)	4.26 (dd, 9.0, 9.0)	4.63 (dd, 9.9, 9.9)
rha-5	4.78 (dq, 9.5, 6.1)	5.05 (dq, 9.0, 6.2)	5.06 (dq, 9.0, 6.0)	4.77 (dq, 9.0, 6.2)	4.98 (dq, 9.9, 6.0)
rha-6	1.92 (d, 6.1)	1.93 (d, 6.2)	1.89 (d, 6.0)	1.90 (d, 6.2)	1.86 (d, 6.0)
fuc-1		5.19 (d, 7.9)		5.25 (d, 8.0)	4.92 (d, 8.0)
fuc-2		4.38 (dd, 7.9, 9.8)		4.56 (dd, 8.0, 10.0)	4.26 (dd, 8.0, 10.0)
fuc-3		4.12 (dd, 9.8, 3.5)		5.35 (dd, 10.0, 3.2)	4.00 (dd, 10.0, 3.5)
fuc-4		3.97 (d, 3.5)		4.22 (dd, 3.2, 0.9)	4.01 (dd, 3.5, 1.0)
fuc-5		3.70 (q, 5.5)		3.78 (dq, 0.9, 6.5)	3.68 (dq, 1.0, 6.0)
fuc-6		1.55 (d, 5.5)		1.46 (d, 6.5)	1.53 (d, 6.0)
qui″-1	5.25 (d, 7.5)		5.24 (d, 7.2)		
qui″-2	3.97 (dd, 7.5, 9.0)		4.00 (dd, 7.2, 8.0)		
qui″-3	4.06 (dd, 9.0, 9.0)		4.08 (dd, 8.0, 8.0)		
qui″-4	3.62 (dd, 9.0, 9.0)		3.6[a]		
qui″-5	3.68 (dq, 9.0, 6.0)		3.6[a]		
qui″-6	1.58 (d, 6.0)		1.5 (d, 6.0)		
jla- 2	2.42 (ddd, 1.0, 9.5, 17.0)	2.52 (t, 7.0)	2.49 (t, 7.0)	2.42 (ddd, 1.0, 9.5, 17.0)	2.36[b] ($W_{h/2}$, 17.5)
	2.85 (ddd, 2.0, 8.0, 17.0)	2.52 (t, 7.0)	2.49 (t, 7.0)	2.83 (ddd, 2.0, 8.0, 17.0)	2.38[b] ($W_{h/2}$, 17.0)
jla-11	3.84 (br s)	3.90 (br s)	3.88 (br s)	3.84 (br s)	3.75 (br s)
jla-16	0.86 (t, 7.0)	0.86 (t, 7.0)	0.86 (t, 7.0)	0.86 (t, 7.0)	0.86 (t, 7.0)
mba-2	2.53 (tq, 7.0, 7.0)			2.55 (tq, 7.0, 7.0)	2.62 (tq, 7.0, 7.0)
mba-3	1.54[a]			1.74[a]	1.75[a]
	1.82[a]			1.82[a]	1.95 (ddq, 7.0, 7.0, 7.0)
mba-4	0.94 (t, 7.0)			0.95 (t, 7.0)	0.88 (t, 7.0)
mba-5	1.23 (d, 7.0)			1.24 (d, 7.0)	1.26 (d, 7.0)
mba′-2				2.43 (tq, 7.0, 7.0)	
mba′-3				1.53[a]	
				1.78[a]	
mba′-4				0.87 (t, 7.0)	
mba′-5				1.13 (d, 7.0)	
iba-2					
iba-3					
iba-3′					

supported by the nonequivalent 2-H_2 signals of the jalapinolic acid moiety observed at δ 2.40 and 2.80 (each 1H, ddd).

In order to clarify the positions of the ester linkages of the three acyl groups, detailed

TABLE I. (continued)

	11	13	14	15	16
qui-1	4.76 (d, 7.8)	5.18 (d, 8.0)	4.76 (d, 7.5)	4.72 (d, 7.8)	4.77 (d, 7.5)
qui-2	4.47 (dd, 7.8, 9.1)	3.96 (dd, 8.0, 8.5)	4.44 (dd, 7,5, 9.5)	4.43 (dd, 7.8, 8.5)	4.44 (dd, 7.5, 9.0)
qui-3	4.35 (dd, 9.1, 9.1)	3.95 (dd, 8.5, 8.5)	4.25 (dd, 9.5, 9.5)	4.28 (dd, 8.5, 8.5)	4.38 (dd, 9.0, 9.0)
qui-4	3.63 (dd, 9.1, 9.1)	3.42 (dd, 8.5, 8.5)	3.61 (dd, 9.5, 9.5)	3.62 (dd, 8.5, 8.5)	3.61 (dd, 9.0, 9.0)
qui-5	3.62 (dq, 9.1, 6.0)	3.65 (dq, 8.5, 6.2)	3.65 (dq, 9.5, 6.0)	3.65 (dq, 8.5, 6.0)	3.62 (dq, 9.0, 6.0)
qui-6	1.49 (d, 6.0)	1.44 (d, 6.2)	1.61 (d, 6.0)	1.56 (d, 6.0)	1.59 (d, 6.0)
qui′-1	5.40 (d, 7.1)	5.28 (d, 7.5)	5.83 (d, 7.2)	5.77 (d, 7.0)	5.90 (d, 7.0)
qui′-2	4.16 (dd, 7.1, 8.0)	4.12 (dd, 7.5, 8.5)	4.08 (dd, 7.2, 9.0)	4.27 (dd, 7.0, 8.5)	4.18 (dd, 7.0, 8.5)
qui′-3	5.70 (dd, 8.0, 8.0)	5.55 (dd, 8.5, 8.5)	5.67 (dd, 9.0, 9.0)	5.70 (dd, 8.5, 8.5)	5.70 (dd, 8.5, 8.5)
qui′-4	3.85 (dd, 8.0, 8.0)	5.11 (dd, 8.5, 8.5)	3.80 (dd, 9.0, 9.0)	3.82 (dd, 8.5, 8.5)	3.86 (dd, 8.5, 8.5)
qui′-5	3.67 (dq, 8.0, 6.5)	3.72 (dq, 8.5, 6.0)	3.67 (dq, 9.0, 6.0)	3.65 (dq, 8.5, 6.0)	3.68 (dq, 8.5, 6.0)
qui′-6	1.48 (d, 6.0)	1.17 (d, 6.0)	1.47 (d, 6.0)	1.53 (d, 6.0)	1.49 (d, 6.0)
rha-1	5.67 (d, 1.6)	5.45 (d, 1.6)	5.47 (d, 1.5)	5.63 (d, 1.2)	5.68 (d, 1.0)
rha-2	4.62 (dd, 1.6, 3.5)	5.64 (dd, 1.6, 3.5)	5.73 (dd, 1.5, 3.1)	4.62 (dd, 1.2, 3.0)	4.59 (dd, 1.0, 3.0)
rha-3	4.61 (dd, 3.5, 9.3)	5.84 (dd, 3.5, 10.0)	4.61 (dd, 3.1, 9.5)	6.12 (dd, 3.0, 9.8)	4.64 (dd, 3.0, 9.5)
rha-4	4.39 (dd, 9.3, 9.3)	4.27 (dd, 10.0, 10.0)	4.29 (dd, 9.5, 9.5)	4.63 (dd, 9.8, 9.8)	4.38 (dd, 9.5, 9.5)
rha-5	4.76 (dq, 9.3, 6.1)	4.74 (dq, 10.0, 6.2)	4.74 (dq, 9.5, 6.2)	4.98 (dq, 9.8, 6.0)	4.78 (dq, 9.5, 6.0)
rha-6	1.86 (d, 6.1)	1.87 (d, 6.2)	1.89 (d, 6.2)	1.88 (d, 6.0)	1.88 (d, 6.0)
fuc-1	5.09 (d, 8.0)	4.67 (d, 7.0)	5.25 (d, 8.0)		
fuc-2	4.37 (dd, 8.0, 9.0)	4.39 (dd, 7.0, 10.0)	4.56 (dd, 8.0, 10.0)		
fuc-3	4.07 (dd, 9.0, 3.4)	3.86 (dd, 10.0, 3.0)	5.32 (dd, 10.0, 3.2)		
fuc-4	3.97 (dd, 3.4, 1.0)	5.58 (dd, 3.0, 1.0)	4.22 (dd, 3.2, 0.9)		
fuc-5	3.63 (dq, 1.0, 6.0)	3.90 (dq, 1.0, 6.1)	3.79 (dq, 0.9, 6.5)		
fuc-6	1.62 (d, 6.0)	1.28 (d, 6.1)	1.45 (d, 6.5)		
qui″-1				5.00 (d, 7.8)	5.17 (d, 7.8)
qui″-2				3.84 (dd, 7.8, 8.5)	4.01 (dd, 7.8, 8.0)
qui″-3				4.03 (dd, 8.5, 8.5)	4.09 (dd, 8.0, 8.0)
qui″-4				3.64 (dd, 8.5, 8.5)	3.64 (dd, 8.0, 8.0)
qui″-5				3.64 (dq, 8.5, 6.0)	3.64 (dq, 8.0, 6.0)
qui″-6				1.53 (d, 6.0)	1.55 (d, 6.0)
jla- 2	2.32 (ddd, 1.0, 9.5, 17.0)	2.49 (ddd, 1.0, 9.5, 17.0)	2.40 (ddd, 1.0, 9.5, 17.0)	2.36[b] ($W_{h/2}$, 17.0)	2.33 (ddd, 1.0, 9.5, 17.0)
	2.47 (ddd, 2.0, 8.0, 17.0)	2.83 (ddd, 2.0, 8.0, 17.0)	2.84 (ddd, 2.0, 8.0, 17.0)	2.38[b] ($W_{h/2}$, 17.0)	2.37 (ddd, 2.0, 8.0, 17.0)
jla-11	3.85 (br s)	3.72 (br s)	3.84 (br s)	3.82 (br s)	3.84 (br s)
jla-16	0.86 (t, 7.0)	0.87 (t, 7.0)	0.85 (t, 7.0)	0.84 (t, 7.0)	0.86 (t, 7.0)
mba-2		2.50 (tq, 7.0, 7.0)	2.55 (tq, 7.0, 7.0)	2.56 (tq, 7.0, 7.0)	
mba-3		1.51[a]	1.73[a]	1.87[a]	
		1.72[a]	1.82[a]	1.78[a]	
mba-4		0.93 (t, 7.0)	0.95 (t, 7.0)	0.85 (t, 7.0)	
mba-5		1.18 (d, 7.0)	1.23 (d, 7.0)	1.21 (d, 7.0)	
mba′-2		2.37 (tq, 7.0, 7.0)			
mba′-3		1.50[a]			
		1.70[a]			
mba′-4		0.92 (t, 7.0)			
mba′-5		1.13 (d, 7.0)			
iba-2			2.54 (sept, 7.0, 7.0)		
iba-3			1.12 (d, 7.0)		
iba-3′			1.12 (d, 7.0)		

A 0.02 M solution in pyridine-d_5; δ in ppm from tetramethylsilane (coupling constants (J) in Hz are given in parentheses). fuc, fucose; rha, rhamnose; qui, quinovose; jla, jalapinolic acid; iba, isobutyric acid; mba, 2-methylbutyric acid; nla, nilic acid. *a*) Signals are overlapping. *b*) Splitting patterns are complicated.

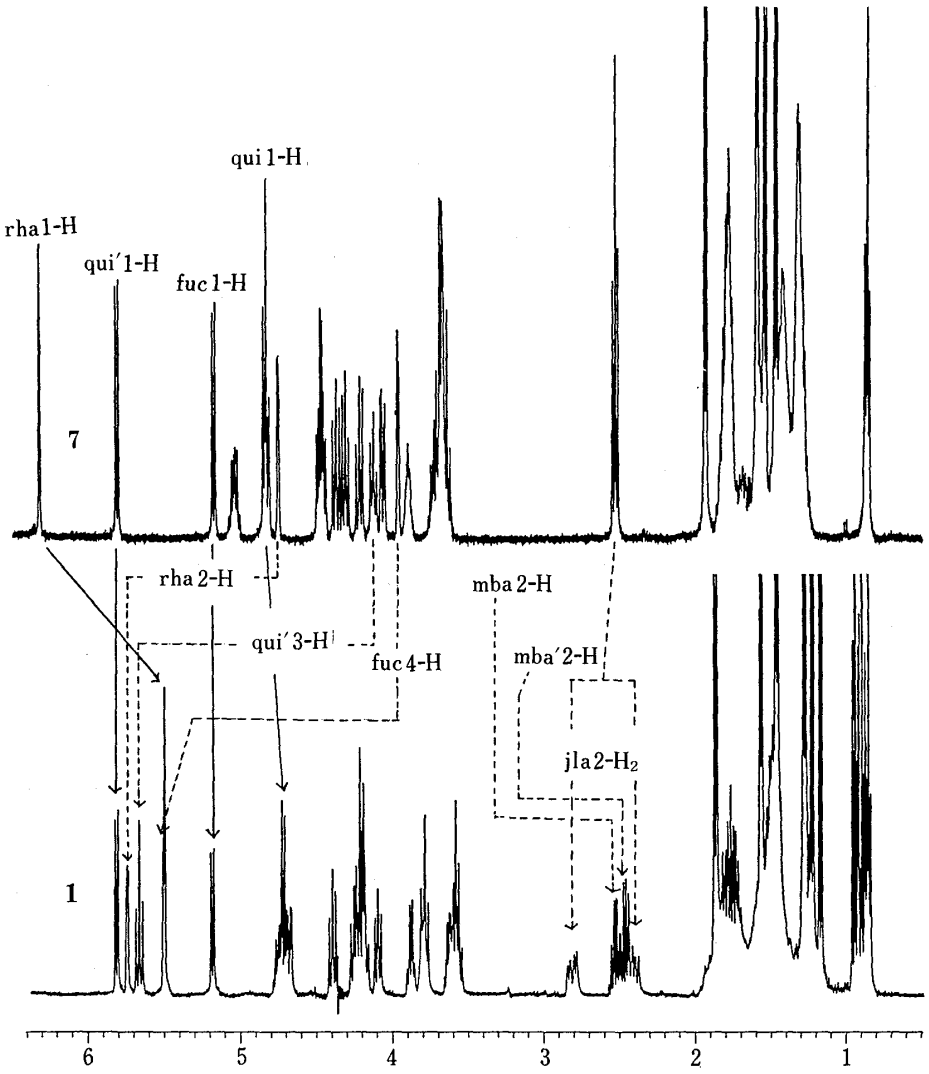


Fig. 1. ^{1}H-NMR Spectra of **1** and **7** (400 MHz, in Pyridine-d_5)

assignments of proton and carbon signals of **1** were performed by using ^{1}H–^{1}H and ^{13}C–^{1}H two-dimensional shift correlation NMR techniques (Table I). The ^{1}H-NMR spectrum of **1** showed, when compared with that of **7**, remarkable downfield shifts due to acylation at 3-H of quinovose (1.53 ppm), 2-H of rhamnose (0.99 ppm) and 4-H of fucose (1.53 ppm) (Fig. 1). Therefore, the acyl groups are concluded to be located at 3-OH of one of two quinovoses, 2-OH of rhamnose and 4-OH of fucose. However, specification of the sites of ester linkages of the respective organic acids and jalapinolic acid as well as discrimination of the quinovose-bearing ester group were not possible even by using nuclear Overhauser effect spectroscopy (NOESY) and partially relaxed Fourier-transform (PRFT) methods. Next, to solve the problem, partial deacylation was conducted according to the procedure used previously for the resin glycosides of *I. orizabensis*.[3]

Compound **1** was treated with 7% NH_3–MeOH (1 : 6) for 1.5 h at room temperature and the products were separated by HPLC to give three compounds, **3** (2.9%), **5** (2.2%) and **9** (3.7%) together with unreacted **1**. The ^{1}H-NMR spectrum of **5** exhibited, compared with that of **1**, an upfield shift (1.53 ppm) of 4-H of fucose along with disappearance of the signals due to one mole of 2-methylbutyric acid residue. Therefore, one of the two 2-methylbutyric acids in **1** is considered to be linked with 4-OH of fucose (Fig. 2).

Compound **5** was further treated with mild alkali to yield **10** (4.4%) and **11** (1.7%). In the

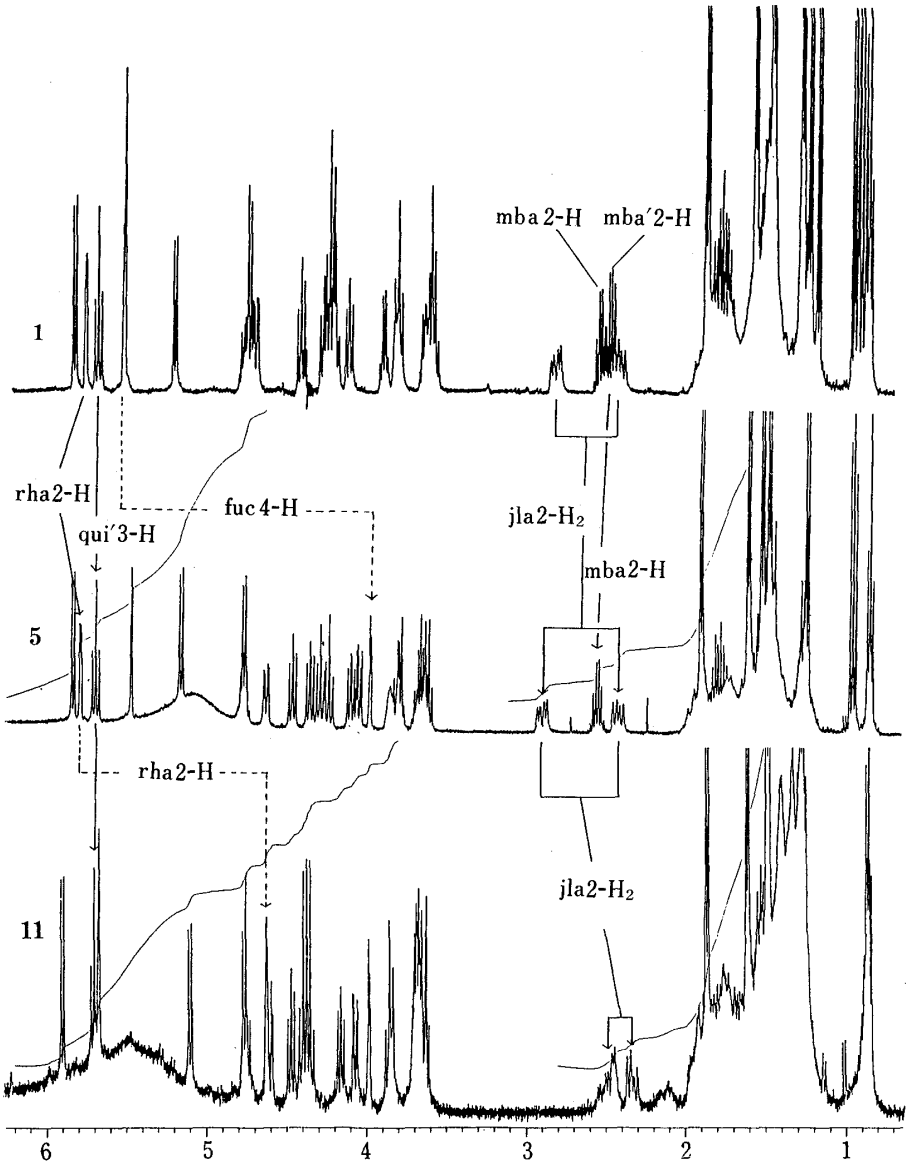


Fig. 2. ^{1}H-NMR Spectra of **1**, **5** and **11** (400 MHz, in Pyridine-d_5)

^{1}H-NMR spectrum, compound **11** showed, besides the almost unshifted 3-H of quinovose, an upfield shift (1.17 ppm) of 2-H of rhamnose and loss of the signals due to a 2-methylbutyric acid residue. Accordingly, the second 2-methylbutyric acid and jalapinolic acid residues of **1** are concluded to be attached, respectively, to 2-OH of rhamnose and 3-OH of one of two quinovoses (Fig. 2).

In the negative ion FAB-MS spectra of **1** and its glycosidic acid (**7**), along with the fragment peaks observed at *m/z* 271 and 417, **1** showed a strong fragment peak at *m/z* 545 in place of that at *m/z* 563 $[M-2\times(\text{methylpentose unit})]^-$ of **7** (Fig. 3). The diference of 18 mass units suggests that the ester linkage of jalapinolic acid might be located at the second quinovose (qui′).

To confirm the above suggestion, **1** was converted to an acetonide (**12**) and its negative ion FAB-MS was compared with that of **1**. Compound **12** showed the $(M-H)^-$ peak at *m/z* 1085 and, in contrast to **1**, the fragment peaks at *m/z* 585 and 457 which are, respectively, 40 mass units higher than those of *m/z* 545 and 417 in **1**, but no fragment peak at *m/z* 399 (expected for the introduction of isopropylidene into the second quinovose) was observed (Fig. 3). These data suggested that **12** is a diacetonide in which one isopropylidene group is

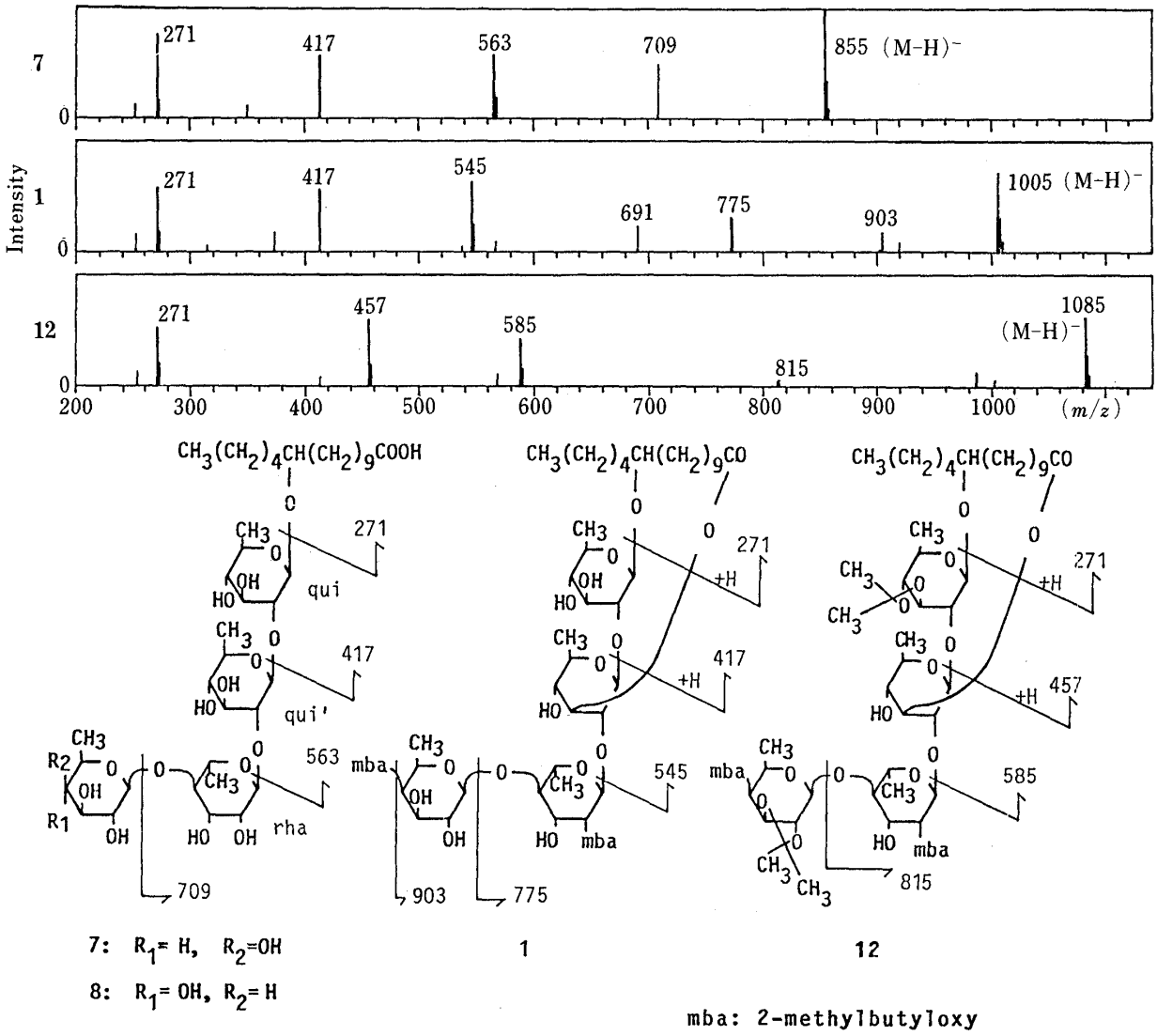


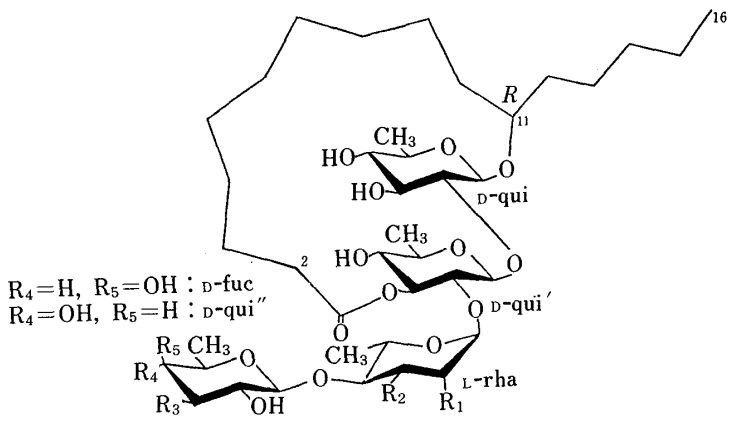
Fig. 3. Negative Ion FAB-MS of **7**, **1** and **12**

combined with 3,4-diOH of the first quinovose (qui) and hence the ester linkage of jalapinolic acid is located in the second quinovose (qui′). The ^{1}H-NMR of the acetate (**13**) derived from **12** revealed, compared with that of **1**, downfield shifts of 4-H of quinovose (1.32 ppm) and 3-H of rhamnose (1.16 ppm) together with two acetoxy methyl signals at δ 2.19 and 2.04 (each 3H, s) as well as four singlet methyl signals due to isopropylidene groups at δ 1.48, 1.46, 1.52 and 1.78, indicating that the isopropylidene moieties have been introduced into 3,4-diOH of the first quinovose and 2,3-diOH of fucose. Consequently, the ester linkage of jalapinolic acid at 3-OH of the second quinovose was confirmed.

Taking the J values of anomeric and methine proton signals due to the sugar moiety into account, the linkage of the rhamnose unit of **1** is concluded to be α in $^1C_4$ conformation, while those of the other three sugar units are β in $^4C_1$.

On the basis of all the above data and the previous study[1] on the absolute configurations of 2-methylbutyric acid and jalapinolic acid, the full structure of **1** is defined as 11*R*-jalapinolic acid 11-*O*-(4-*O*-(2*S*-methylbutyryl))-β-D-fucopyranosyl-(1→4)-(2-*O*-(2*S*-methylbutyryl))-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl(qui′)-(1→2)-β-D-quinovopyranosy-1,3(qui′)-olide (Fig. 4).

Compounds **3**, **9** and **10**, formed by partial deacylation of **1**, were characterized by comparing their ^{1}H-NMR spectra with that of **1** as follows. The spectrum of **3** showed an



1: $R_1=R_5=$mba, $R_2=R_3=OH$, $R_4=H$
2: $R_1=$mba, $R_2=R_3=OH$, $R_4=H$, $R_5=$iba
3: $R_1=R_3=OH$, $R_2=R_5=$mba, $R_4=H$
4: $R_1=R_3=OH$, $R_2=$mba, $R_4=H$, $R_5=$iba
5: $R_1=$mba, $R_2=R_3=R_5=OH$, $R_4=H$
6: $R_1=$mba, $R_2=R_3=R_4=OH$, $R_5=H$
9: $R_1=R_3=$mba, $R_2=R_5=OH$, $R_4=H$
10: $R_1=R_3=R_5=OH$, $R_2=$mba, $R_4=H$
11: $R_1=R_2=R_3=R_5=OH$, $R_4=H$
14: $R_1=$mba, $R_2=R_5=OH$, $R_3=$iba, $R_4=H$
15: $R_1=R_3=R_4=OH$, $R_2=$mba, $R_5=H$
16: $R_1=R_2=R_3=R_4=OH$, $R_5=H$

mba: $CH_3CH_2-\underset{S}{\overset{CH_3}{\underset{|}{C}}}HCOO$ iba: $(CH_3)_2CHCOO$

Fig. 4

upfield shift (1.09 ppm) of 2-H of rhamnose along with a downfield shift (1.43 ppm) of 3-H of rhamnose, while the other proton signals due to the sugar moieties remain almost unshifted. Therefore, **3** is an acyl migration product of **1** in which the 2-methylbutyric acid group had shifted from 2- to 3-OH of rhamnose. On the other hand, compound **9** showed, in contrast to **1**, an upfield shift (1.28 ppm) of 4-H and a downfield shift (1.18 ppm) of 3-H of fucose, indicating that the 2-methylbutyric acid moiety originally linked with 4-OH of fucose had migrated to 3-OH. The ^{1}H-NMR spectrum of **10**, in comparison with that of **5**, showed 1.17 ppm upfield and 1.48 ppm downfield shifts, respectively, of the 2- and 3-H signals of rhamnose. Therefore, **10** should have been produced by migration of 2-methylbutyric acid group from 2- to 3-OH of rhamnose.

Muricatin II (**2**), colorless needles, mp 117—120 °C (dec.), $[\alpha]_D$ −22.8°, afforded, on alkaline hydrolysis, 2-methylbutyric acid, isobutyric acid and muricatic acid A. Compound **2** showed an $(M-H)^-$ ion peak at *m/z* 991 together with the same fragment peaks as those of **1** at *m/z* 547, 417 and 271 in the negative ion FAB-MS and provided a ^{1}H-NMR spectrum quite similar to that of **1** except that the signals due to one mole each of isobutyric acid and 2-methylbutyric acid were observed in place of those of two 2-methylbutyric acid groups in **1**. These data suggested that the structure of **2** is analogous to that of **1** and differs only in the fact that the 2-methylbutyric acid group at 4-OH of fucose in **1** is replaced by isobutyric acid in **2**.

Treatment of **2** with mild alkali in the same way as for **1** gave three compounds, **4** (1.9%), **5** (1.8%) and **14** (3.8%). The ^{1}H-NMR spectrum of **5** was just the same as that of **5** formed by release of 2-methylbutyric acid from 4-OH of fucose of **1**. Therefore, the presumption was confirmed and **2** is assigned the structure as shown in Fig. 4.

Compound **4** showed upfield (1.1 ppm) and downfield (1.41 ppm) shifts of the 2- and 3-H signals of rhamnose, respectively, on comparison of its ^{1}H-NMR spectra with that of **2**. Therefore, **4** was defined as an isomer of **2** formed by the migration of 2-methylbutyric acid from 2- to 3-OH of rhamnose (Fig. 4). Similarly, compound **14** was proved to be another isomer in which isobutyric acid had shifted from 4- to 3-OH of fucose of **2** (Fig. 4).

Muricatin III (**3**), colorless needles, mp 121—124 °C (dec.), $[\alpha]_D$ −41.0° and muricatin IV (**4**), colorless needles, mp 123—127 °C (dec.), $[\alpha]_D$ −50.5° afforded ^{1}H-NMR spectra identical to those of **3** and **4** which were produced by alkaline treatment of **1** and **2** (*vide supra*) respectively. Therefore, muricatins III and IV are simply **3** and **4**, respectively (Fig. 4).

Muricatin V (**5**), powder, mp 119—127 °C (dec.), $[\alpha]_D$ −31.1°, gave a ^{1}H-NMR spectrum superimposable on that of compound **5** formed from **1** and **2** by mild alkaline hydrolysis (*vide supra*). Accordingly, **5** was assigned the structure shown in Fig. 4.

Muricatin VI (**6**), powder, mp 114—118 °C (dec.), $[\alpha]_D$ −41.0°, afforded 2-methylbutyric acid and, contrary to **1**—**5**, muricatic acid B (**8**) as a glycosidic acid. Its negative ion FAB-MS exhibited, besides the $(M-H)^-$ ion peak at *m/z* 921, the same fragment peaks as those of **1**—**5** at *m/z* 775 $[M-146$ (methylpentose unit)$]^-$, 545 $(775-146)^-$, 417 and 271 (jalapinolic acid $-H)^-$, suggesting **6** to be also a monomer in which the jalapinolic acid group of the glycosidic acid combines intramolecularly with the second quinovose (qui′) to form a macrocyclic ester ring. The ^{1}H-NMR spectrum of **6** exhibited, in comparison with that of its glycosidic acid (**8**), marked acylation shifts of the signals due to 2-H of rhamnose (1.08 ppm) and 3-H of quinovose (1.59 ppm). Further, compound **6** gave, on alkaline treatment as described for **1**, **15** (1.9%) and **16** (3.6%). Compound **16** afforded a spectrum in which an upfield shift (1.16 ppm) of 2-H or rhamnose was observed and the signals attributable to 2-methylbutyric acid had disappeared. Therefore, 2-methylbutyric acid should be attached at 2-OH of rhamnose, while the ester linkage of jalapinolic acid is located at 3-OH of the second quinovose (qui′). Consequently, **6** is characterized as shown in Fig. 4.

Compound **15** was determined to be an acyl-migration product in which the 2-methylbutyric acid group at 2-OH of rhamnose of **6** had migrated to 3-OH by comparing the ^{1}H-NMR spectra of **6** and **15**.

Compounds **3**, **4** and **5** could be artifacts produced from **1**, **2** and **1** (or **2**), respectively. However, this possibility seems to be excluded by the fact that these compounds were detected by high performance thin-layer chromatography (HPTLC) in the ether-soluble fraction prepared from the MeOH extract of fresh seeds.

It should be noted that all the resin glycosides isolated in this study are similar to the resin glycosides previously isolated from *I. orizabensis* (monomers having an intramolecular macrocyclic ester structure).

Experimental

The instruments and materials generally used are cited in the preceding report.[1] Specific rotations were measured at 26 °C.

Isolation of the Resin Glycosides, Muricatins I (1)—VI (6)——The crushed powder of the seeds of *I. muricata* (2.2 kg) was percolated with MeOH at room temperature. The extract was evaporated *in vacuo* to afford a brown syrup (370 g), which was partitioned between MeOH and *n*-hexane (2 : 1) (1.5 l). The MeOH layer was evaporated and the brown residue (310 g) was separated by treatment with ether (1.5 l) into ether-soluble (205 g) and insoluble (95 g) portions. The former was column-chromatographed on silica gel ($CHCl_3$–MeOH–H_2O, 9 : 1 : 0.1) to give three fractions, fr-1 (5 g), fr-2 (170 g) and fr-3 (21 g). Fr-2 was subjected to column chromatography on Sephadex LH-20 (MeOH) to give a white powder (150 g). It was column-chromatographed on a silica gel Lobar column to provide five fractions, fr-5 (12 g), fr-6 (96 g), fr-7 (2.7 g), fr-8 (21 g) and fr-9 (14.5 g). Fr-5 (1 g) was subjected to preparative HPLC on a Kusano C.I.G. prepacked silica gel column ($CHCl_3$–MeOH–H_2O, 9 : 1 : 0.1) to give **3** (0.6 g) and **4** (0.2 g). Preparative HPLC with $CHCl_3$–MeOH–H_2O (9 : 1 : 0.1) of the fr-6 (6 g) yielded **1** (2.8 g) and **2** (2.2 g). Similar HPLC ($CHCl_3$–MeOH–H_2O, 8 : 2 : 0.1) fo fr-8 (5.5 g) afforded **5** (2.2 g) and **6** (2.3 g).

Muricatin I (**1**): Colorless needles (acetone–*n*-hexane), mp 119—123 °C (dec.), $[\alpha]_D$ −18.2° (*c* = 1.1, MeOH). IR (KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS *m/z*: Fig. 3. ^{1}H-NMR δ: Table I. ^{13}C-NMR (pyridine-d_5) δ: 102.6, 76.4, 78.9, 77.2, 72.5, 18.5 (C_1—C_6 of qui), 99.6, 81.1, 79.1, 75.2, 71.8, 18.1 (C_1—C_6 of qui′), 99.2, 73.0, 69.7, 84.7, 68.0, 18.7 (C_1—C_6 of rha), 106.1, 73.1, 73.0, 73.7, 70.0, 17.1 (C_1—C_6 of fuc), 80.6 (C_{11} of jla), 176.6, 176.0, 172.4 (carbonyl C). *Anal.* Calcd for $C_{50}H_{86}O_{20}\cdot H_2O$: C, 58.58; H, 8.65. Found: C, 58.34; H, 8.72. Muricatin II (**2**): Colorless needles (acetone–*n*-hexane), mp 117—120 °C (dec.), $[\alpha]_D$ −22.8° (*c* = 1.3, MeOH). IR

(KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS *m/z*: 991 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR δ: Table I. *Anal.* Calcd for $C_{49}H_{84}O_{20}$: C, 59.25; H, 8.52. Found: C, 59.31; H, 8.51. Muricatin III (**3**): Colorless needles (acetone–*n*-hexane), mp 121—124 °C (dec.), $[\alpha]_D$ −41.0° (*c*=1.0, MeOH). IR (KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS *m/z*: 1005 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR δ: Table I. *Anal.* Calcd for $C_{50}H_{86}O_{20}$: C, 57.26; H, 8.60. Found: C, 57.39; H, 8.66. Muricatin IV (**4**): Colorless needles (acetone–*n*-hexane), mp 123—127 °C (dec.), $[\alpha]_D$ −50.5° (*c*=1.1, MeOH). IR (KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS *m/z*: 991 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR δ: Table I. *Anal.* Calcd for $C_{49}H_{84}O_{20}\cdot 2H_2O$: C, 57.18; H, 8.62. Found: C, 57.25; H, 8.58. Muricatin V (**5**): White powder ($CHCl_3$–MeOH), mp 119—127 °C (dec.), $[\alpha]_D$ −31.1° (*c*=1.1, MeOH). IR (KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS *m/z*: 921 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR δ: Table I. *Anal.* Calcd for $C_{45}H_{78}O_{19}$: C, 58.55; H, 8.51. Found: C, 58.70; H, 8.70. Muricatin VI (**6**): White powder ($CHCl_3$–MeOH), mp 114—118 °C (dec.), $[\alpha]_D$ −41.0° (*c*=1.1, MeOH). IR (KBr): 3400 (OH), 1720 (carbonyl) cm^{-1}. Negative ion FAB-MS *m/z*: 921 $(M-H)^-$, 775, 545, 417, 271. ^{1}H-NMR δ: Table I. *Anal.* Calcd for $C_{45}H_{78}O_{19}$: C, 58.55; H, 8.51. Found: C, 58.46; H, 8.57.

Saponification of 1—6——Solutions of **1—6** (each 25 mg) in 5% KOH (H_2O–1,4-dioxane, 3 : 1) (10 ml) were each refluxed for 1 h. The reaction mixture was made acidic (pH 4.0) and then extracted with ether (10 ml). The ether layer was treated with diazomethane in ether and the product was subjected to gas chromatography (GC) (Unisol F-200, 4 mm i.d. × 2 m glass column; column temp. 70 °C; N_2 2 kg/cm^2). **1**: t_R 2.0 (methyl 2-methylbutyrate). **2**: t_R 0.9 (methyl isobutyrate), 2.0 (methyl 2-methylbutyrate). **3**: t_R 1.9 (methyl 2-methylbutyrate). **4**: t_R 0.9 (methyl isobutyrate), 2.0 (methyl 2-methylbutyrate). **5**: t_R 2.0 (methyl 2-methylbutyrate). **6**: t_R 2.0 (methyl 2-methylbutyrate).

The aqueous phase was extracted with *n*-BuOH (5 ml) and the organic layer was evaporated *in vacuo* to give a white powder (glycosidic acid) (each *ca.* 15 mg). The glycosidic acids derived from **1**, **2**, **3**, **4** and **5** were each shown to be identical to muricatic acid A (**7**) and that from **6** to be identical with muricatic acid B (**8**) by comparison of the ^{1}H-NMR spectra.

Mild Alkaline Treatment of 1——A solution of **1** (407 mg) in 7% NH_3–MeOH (1 : 6) (10 ml) was left to stand at room temperature for 1.5 h. The mixture was acidified (pH 4.0) and added to H_2O (20 ml) and then extracted with ether (20 ml × 2). After removal of the solvent, the residue was subjected to preparative HPLC on a Kusano C.I.G. prepacked silica gel column ($CHCl_3$–MeOH–H_2O, 9 : 1 : 0.1) to give **3** (12 mg, 2.9%), **9** (15 mg, 3.7%) and **5** (8 mg, 2.2%) together with unreacted **1** (360 mg). **9**: Colorless needles (acetone–*n*-hexane), mp 121—132 °C (dec.), $[\alpha]_D$ −22.7° (*c*=1.1, MeOH). *Anal.* Calcd for $C_{50}H_{86}O_{20}\cdot H_2O$: C, 58.58; H, 8.65. Found: C, 58.53; H, 8.69. ^{1}H-NMR δ: Table I.

Preparation of Acetonide (12) of 1——A small amount of molecular sieve (4 Å, Merck) (*ca.* 300 mg) was added to a solution of **1** (30 mg) and a trace of *p*-toluenesulfonic acid monohydrate in 2,2-dimethoxypropane (2 ml), and then the mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water and extracted with ether (20 ml). The ether layer was washed with water, then evaporated, and the residue was purified by column chromatography on silica gel to afford **12** (4 mg), white powder ($CHCl_3$–MeOH), mp 85—87 °C (dec.), $[\alpha]_D$ −21.2° (*c*=0.2, MeOH). *Anal.* Calcd for $C_{56}H_{94}O_{20}\cdot 2H_2O$: C, 59.87; H, 8.79. Found: C, 59.93; H, 8.59. Negative ion FAB-MS (Fig. 3). Compound **12** (3 mg) was acetylated in a usual manner to yield **13** (4 mg), white powder ($CHCl_3$–MeOH), mp 91—95 °C (dec.). ^{1}H-NMR δ: Table I. *Anal.* Calcd for $C_{60}H_{98}O_{22}$: C, 61.52; H, 8.43. Found: C, 61.39; H, 8.52.

Mild Alkaline Treatment of 2, 5 and 6——Compounds **2**, **5** and **6** were each treated with 7% NH_3–MeOH (1 : 6) mixture and fractionated in the same manner as for **1**.

Compound **2** (370 mg) afforded **4** (7 mg, 1.9%), **14** (14 mg, 3.8%) and **5** (6 mg, 1.8%) along with **2** (330 mg). **14**: Colorless needles (acetone–*n*-hexane), mp 140—145 °C (dec.), $[\alpha]_D$ −24.7° (*c*=0.8, MeOH). ^{1}H-NMR δ: Table I.

Compound **5** (320 mg) yielded **10** (14 mg, 4.4%), **11** (5 mg, 1.7%) and unreacted **5** (298 mg). **10**: Colorless needles (acetone–*n*-hexane), mp 113—118 °C (dec.), $[\alpha]_D$ −46.3° (*c*=1.6, MeOH). ^{1}H-NMR δ: Table I. *Anal.* Calcd for $C_{45}H_{78}O_{19}$: C, 58.55; H, 8.51. Found: C, 58.79; H, 8.64. **11**: White powder (acetone–*n*-hexane), mp 176—185 °C (dec.). ^{1}H-NMR δ: Table I.

Compound **6** (362 mg) gave **15** (7 mg, 1.9%) and **16** (12 mg, 3.6%) together with **6** (340 mg). **15**: White powder ($CHCl_3$–MeOH), mp 114—119 °C (dec.). **16**: White powder ($CHCl_3$–MeOH), mp 123—126 °C (dec.), $[\alpha]_D$ −51.0° (*c*=0.7, MeOH). ^{1}H-NMR spectral data of **15** and **16** are summarized in Table I.

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