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Resin Glycosides. II.[1] Identification and Characterization of the Component Organic and Glycosidic Acids of the Crude Resin Glycoside from the Seeds of *Ipomoea muricata*

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Contrary to the work of Khanna and Gupta [*Phytochemistry*, **6**, 735 (1967)], alkaline hydrolysis of the glycoside fraction obtained from the seeds of *Ipomoea muricata* (L) JACQ. (Convolvulaceae) gave three glycosidic acids, muricatic acids A (**5**), B (**6**) and C (trace), together with isobutyric, 2*S*-methylbutyric and (2*R*,3*R*)-nilic (3-hydroxy-2-methylbutyric) acids. Muricatic acids A and B were characterized 11*R*-jalapinolic acid 11-*O*-β-D-fucopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl-(1→2)-β-D-quinovopyranoside and 11*R*-jalapinolic acid 11-*O*-β-D-quinovopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl-(1→2)-β-D-quinovopyranoside, respectively, on the basis of chemical and spectroscopic data.

The similarity of the component organic and glycosidic acids to those of resin glycoside from *I. orizabensis* suggests the glycoside fraction to be a mixture of so-called resin glycosides.

Keywords——*Ipomoea muricata*; Convolvulaceae; resin glycoside; glycosidic acid; (11*R*)-jalapinolic acid tetraglycoside; muricatic acid A; muricatic acid B; 2*S*-methylbutyric acid; 2*R*,3*R*-nilic acid

The seeds of *Ipomoea muricata* (L) JACQ. (Convolvulaceae) are used as a laxative and carminative folk medicine in India, in addition to the seeds of *I. hederacea* JACQ.[2] As for the glycosidic constituents of the seeds, Misra and Tewari[3] reported a glycoside, muricatin A (ethyl 4,14-dihydroxystearate 14-*O*-diglucoside) and its alkaline hydrolysis product, muricatin B (4,14-dihydroxystearic acid lactone 14-*O*-diglucoside). Later, Khanna and Gupta[4] re-examined the constituents and found that muricatin A, on alkaline hydrolysis, afforded *n*-caproic, palmitic and stearic acids together with muricatin B (mp 108—109 °C, $[\alpha]_D$ −44.5 °), for which they proposed the structure jalapinolic acid (11-hydroxypalmitic acid)[5a] 11-*O*-β-L-rhamnopyranosyl-(1→4)-β-L-rhamnopyranoside. However, both the rhamnopyranosyl linkages were revised, on the basis of synthetic studies, to α-configuration by Wagner *et al.*[6] These findings suggested that muricatins A and B correspond, respectively, to a so-called resin glycoside and its component glycosidic acid.

In the course of our studies on the resin glycosides, which are characteristic of Convolvulaceae plants,[1] we searched for organic and glycosidic acids in the alkaline hydrolysis products of the glycoside fraction from the seeds in the hope of confirming the above suggestion. This paper deals with the detailed structural studies on the component organic and glycosidic acids.

The crude glycoside fraction, pale yellow powder, mp 106—110 °C (yield; 6.8%), was saponified and fractionated into organic and glycosidic acid fractions. The former was

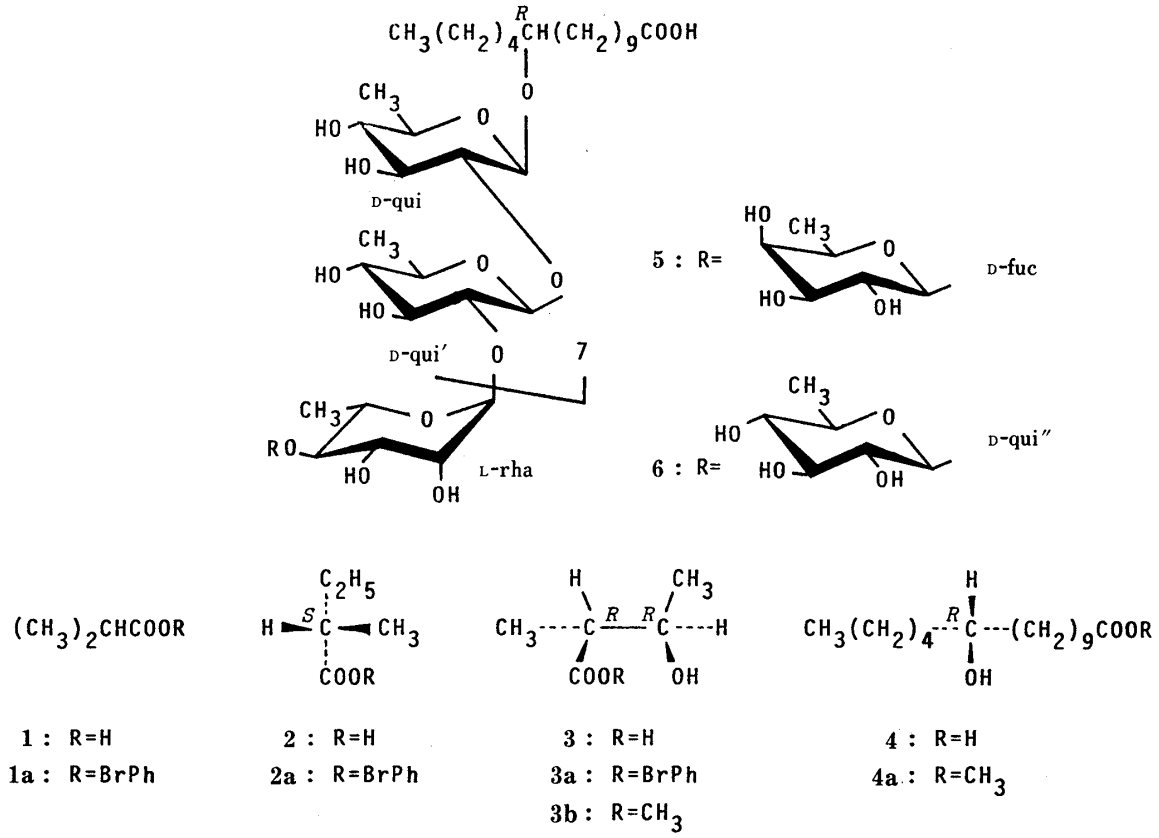

Fig. 1. Structures of the Compounds
qui, quinovose; rha, rhamnose; fuc, fucose; BrPh, *p*-bromophenacyl

methylated with diazomethane and then examined by gas chromatography (GC). It exhibited three peaks (ratio, *ca.* 3:2:1), which were identical with those of authentic methyl esters of isobutyric (**1**), 2-methylbutyric (**2**) and nilic (3-hydroxy-2-methylbutyric)[7] (**3**) acids, respectively. The organic acid fraction was treated with *p*-bromophenacyl bromide, followed by chromatographic separation, to give the esters **1a** (mp 77.5 °C), **2a** (mp 53.0 °C) and **3a** (mp 97—98 °C) which were identical with those of authentic **1**, **2** and **3**, respectively, as judged from infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) comparisons.

Fractional distillation of the organic acid fraction furnished a compound (**2**), oil, bp 70 °C/20 mmHg, $[\alpha]_D$ +17.2 °, which was identical with authentic 2*S*-methylbutyric acid ($[\alpha]_D$ +17.0 °), previously isolated from the root of *I. orizabensis*.[1]

The residue of the above distillation was treated with diazomethane and then distilled to afford **3b**, bp 85 °C/18 mmHg, $[\alpha]_D$ −30.8°, the ^{1}H-NMR and IR spectra of which were superimposable on those of authentic methyl (2*S*, 3*S*)-nilate, bp 85 °C/18 mmHg, $[\alpha]_D$ +27.8 ° previously obtained.[1] The specific rotation of **3b** was similar in value but opposite in sign to that of an authentic sample. According to Tai and Imaida,[8] **3** was defined as (2*R*, 3*R*)-nilic acid.

The glycosidic acid fraction gave, on acid hydrolysis, an aglycone **4**, mp 62—63 °C, electron impact-mass spectra (EI-MS) *m/z*: 272 $(M)^+$, and a monosaccharide mixture. Methylation of **4** provided a methyl ester **4a**, mp 42.5—43.3 °C, $[\alpha]_D$ +1.2 °, which was identical with an authentic sample of methyl 11*R*-jalapinolate (methyl 11-hydroxypalmitic acid).[1]

Chromatography of the sugar fraction on an Avicel SF column gave L-rhamnose ($[\alpha]_D$ +12.5 °), D-fucose ($[\alpha]_D$ +58.7 °) and D-quinovose ($[\alpha]_D$ +32.9 °).

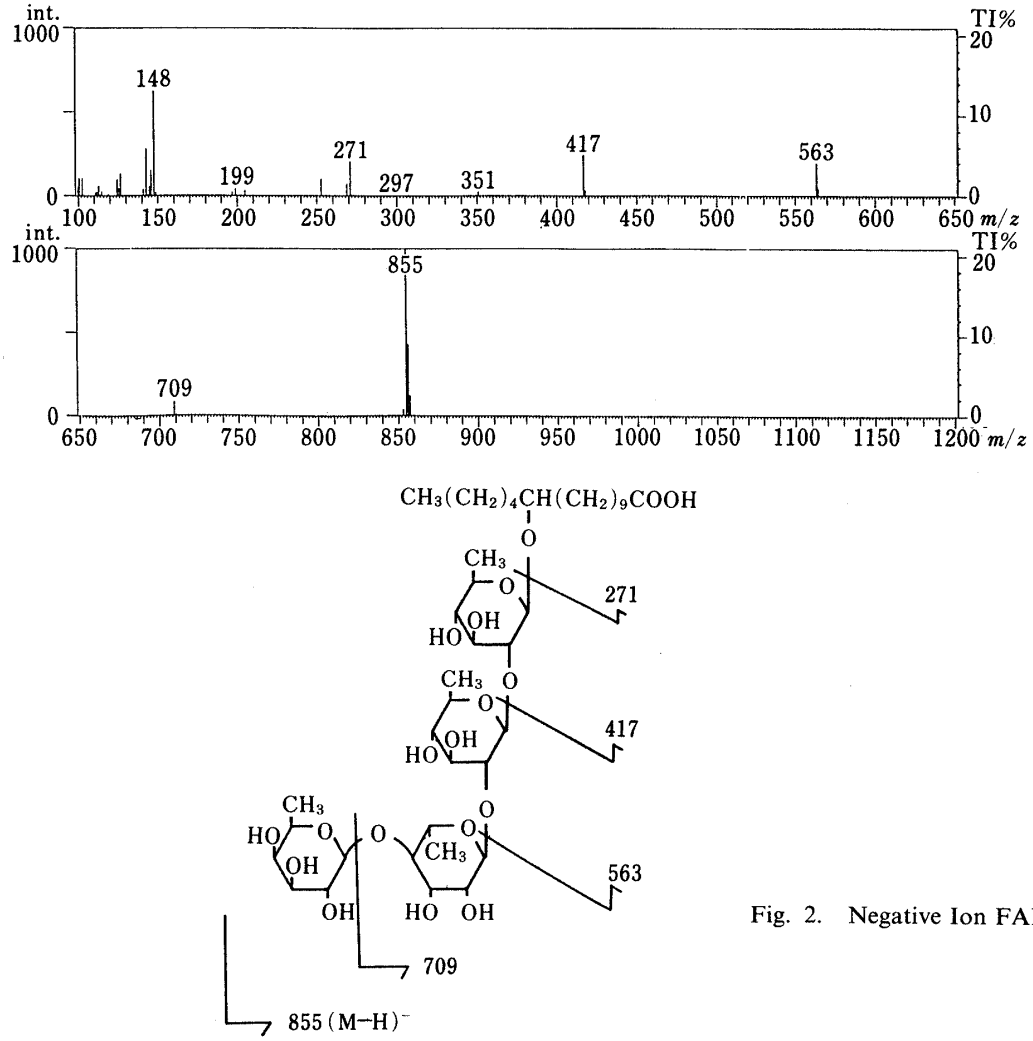

Fig. 2. Negative Ion FAB-MS of **5**

Silica gel chromatography of the glycosidic acid fraction provided three homogeneous (^{1}H-NMR) glycosidic acids named muricatic acids A (**5**), B (**6**) and C.

Muricatic acid A (**5**), mp 104—110 °C, $[\alpha]_D$ −54.5°, exhibited the $(M-H)^-$ peak at *m/z* 855 along with the fragment peaks at *m/z* 709 $(855-146$ (methylpentose unit)$)^-$, 563 $(709-146)^-$, 417 $(563-146)^-$ and 271 $(417-146$, jalapinolic acid $-H)^-$ in the negative ion fast atom bombardment mass spectrum (FAB-MS)[9] (Fig. 2), suggesting that **5** is a tetraglycoside composed of jalapinolic acid and four methylpentose units.

On complete hydrolysis, **5** gave jalapinolic acid (**4**) and a monosaccharide mixture. The latter was trimethylsilylated and examined by GC, exhibiting the presence of quinovose, rhamnose and fucose in the ratio of *ca.* 2 : 1 : 1. Permethylation and methanolysis of **5** yielded methyl 2,3,4-tri-*O*-methylfucopyranoside, methyl 2,3-di-*O*-methylrhamnopyranoside and methyl 3,4-di-*O*-methylquinovopyranoside together with methyl jalapinolate (**4a**) (GC). Partial hydrolysis of **5** with 40% formic acid yielded a diglycoside **7**, mp 144—146 °C, which showed two anomeric carbon signals at 101.6 and 105.9 in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum. Permethylation and methanolysis of **7** liberated methyl 3,4-di-*O*-methylquinovopyranoside and methyl 2,3,4-tri-*O*-methylquinovopyranoside (GC).

All the proton and carbon signals arising from the sugar moieties of **5** were assigned with the aid of ^{1}H–^{1}H and ^{13}C–^{1}H shift correlated two-dimensional NMR (2D-NMR) analyses (Tables I and II). The coupling constants of the anomeric and methine proton signals due to the sugar moiety indicated that the mode of glycosidic linkage of rhamnopyranose unit is α in $^1C_4$ conformation and those of fucopyranose as well as the two quinovopyranose units are β

TABLE I. Proton Chemical Shifts and Coupling Constants of Sugar Moieties of **5** and **6**

Proton	**5**	**6**
qui-1	4.85 (d, J=8.0 Hz)	4.88 (d, J=7.0 Hz)
2	4.31 (dd, J=8.0, 8.0 Hz)	4.26 (dd, J=7.0, 8.0 Hz)
3	4.47 (dd, J=8.0, 9.0 Hz)	4.47 (dd, J=8.0, 8.0 Hz)
4	3.69 (dd, J=9.0, 9.0 Hz)	3.58 (dd, J=8.0, 8.0 Hz)
5	3.70 (dq, J=9.0, 6.0 Hz)	3.6[a]
6	1.59 (d, J=5.5 Hz)	1.51 (d, J=6.0 Hz)
qui′-1	5.82 (d, J=8.0 Hz)	5.77 (d, J=7.2 Hz)
2	4.22 (dd, J=8.0, 8.8 Hz)	4.19 (dd, J=7.2, 8.0 Hz)
3	4.13 (dd, J=8.8, 8.8 Hz)	4.10 (dd, J=8.0, 8.0 Hz)
4	3.65 (dd, J=8.8, 9.0 Hz)	3.6[a]
5	3.71 (dq, J=9.0, 6.0 Hz)	3.73 (dq, J=9.0, 6.0 Hz)
6	1.47 (d, J=6.0 Hz)	1.52 (d, J=6.0 Hz)
rha-1	6.33 (d, J=1.2 Hz)	6.31 (d, J=1.2 Hz)
2	4.75 (dd, J=1.2, 3.0 Hz)	4.67 (dd, J=1.2, 3.0 Hz)
3	4.83 (dd, J=3.0, 9.0 Hz)	4.82 (dd, J=3.0, 9.0 Hz)
4	4.46 (dd, J=9.0, 9.0 Hz)	4.41 (dd, J=9.0, 9.0 Hz)
5	5.05 (dq, J=9.0, 6.2 Hz)	5.06 (dq, J=9.0, 6.0 Hz)
6	1.47 (d, J=6.2 Hz)	1.51 (d, J=6.0 Hz)
fuc-1	5.19 (d, J=7.9 Hz)	
2	4.38 dd, J=7.9, 9.8 Hz)	
3	4.12 (dd, J=9.8, 3.5 Hz)	
4	3.97 (d, J=3.5 Hz)	
5	3.70 (q, J=5.5 Hz)	
6	1.55 (d, J=5.5 Hz)	
qui″-1		5.24 (d, J=7.2 Hz)
2		4.00 (dd, J=7.2, 8.0 Hz)
3		4.08 (dd, J=8.0, 8.0 Hz)
4		3.6[a]
5		3.6[a]
6		1.51 (d, J=6.0 Hz)

δ in ppm from tetramethylsilane (TMS); 2% solution in pyridine-d_5. *a*) Signals were overlapping; qui, qui′, qui″-, quinovopyranosyl. rha, rhamnopyranosyl; fuc, fucopyranosyl. The signals of qui and qui′ may be reversed.

in $^4C_1$.

On the basis of all the above data the structure of muricatic acid A (**5**) was concluded to be (11*R*)-jalapinolic acid 11-*O*-β-D-fucopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl-(1→2)-β-D-quinovopyranoside.

Muricatic acid B (**6**), mp 115—121 °C, $[\alpha]_D$ −45.0 °, which afforded a negative ion FAB-MS almost identical to that of **5**, furnished jalapinolic acid and a monosaccharide mixture on complete acid hydrolysis. GC analysis of the latter in the same manner as for **5** revealed the presence of quinovose and rhamnose (ratio, *ca.* 3 : 1). Comparisons of the ^{1}H- and ^{13}C-NMR spectra suggested that **6** and **5** differ only in the terminal sugar unit where fucose of **5** is replaced by quinovose in **6**. This view was supported by analyses of the permethylation-methanolysis products as well as the partial hydrolysis product which was identified as **7** (^{1}H-NMR). The ^{1}H-NMR data of **6** indicated that the linkage of the rhamnopyranose unit is α in $^1C_4$ conformation and those of the three quinovopyranose units are β in $^4C_1$.

Consequently, **6** was assigned the structure (11*R*)-jalapinolic acid 11-*O*-β-D-quinovopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-quinovopyranosyl-(1→2)-β-D-quinovopyranoside.

TABLE II. Carbon-13 Chemical Shifts of Sugar Moieties of **5** and **6**

Carbon	**5**	**6**	Carbon	**5**	**6**
qui-1	102.2	102.3	fuc-1	106.0	
2	79.9	80.0	2	73.2	
3	79.0	79.0	3	75.3	
4	77.0	77.0	4	72.6	
5	72.5	72.3	5	71.5	
6	18.5	18.6	6	17.1	
qui′-1	101.8	101.6	qui″-1		105.4
2	79.1	78.5	2		76.2
3	79.0	79.0	3		78.0
4	77.0	77.1	4		76.7
5	72.3	72.5	5		72.9
6	18.5	17.1	6		18.5
rha-1	101.6	101.5			
2	72.0	71.9			
3	72.2	72.3			
4	84.1	83.8			
5	67.8	67.7			
6	18.7	18.8			

δ in ppm from TMS; 10% solution in pyridine-d_5. The signals of qui and qui′ may be reversed.

Khanna and Gupta reported that muricatin B formed by saponification of muricatin A is a jalapinolic acid dirhamnoside (M.W. 564) on the basis of the found M.W. 545 determined by titration and the consumption of 3.2 mol of periodate per mol in oxidation. On the other hand, the calculated consumption of periodate by **5** and **6** (each M.W. 856) is 5 mol. If the molecular weight of muricatin B is assumed to be 856, the found periodate value should be not 3.2 but 4.9 mol, in good accordance with that of **5** and **6**.

Therefore, it seems likely that muricatin B is actually nothing but a mixture of **5** and **6** or either of them. The close similarities of the melting points and rotation values of these compounds may support this supposition.

It should be noted that the chirality of nilic acid (2*R*, 3*R*) found in this study was enantiomeric to that from *I. orizabensis*, while 2*S*-methylbutyric and 11*R*-jalapinolic acid coexist in both plants. Taking into account the component organic acids and glycosidic acids obtained here, the crude glycoside is considered to be a mixture of so-called resin glycosides.

The structure of muricatic acid C will be reported elsewhere.

Experimental

Melting points (mp) were determined on Yanaco MP-S3 apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL FX-100 and JEOL JNM GX-400 spectrometers. Spectra were taken as 1—2% w/v solutions at 26 °C with tetramethylsilane as an internal reference. The abbreviations used are as follows: s, singlet; d, doublet; dd, double-doublet; dq, double-quartet; ddd, double-double-doublet; ddq; double-double-quartet; t, triplet; tq, triple-quartet; m, multiplet. COSY spectra were obtained by the use of a ^{1}H–^{1}H shift correlation sequence with a 45° mixing pulse and N-type peak selection (1—2% w/v solution). The ^{1}H–^{13}C shift-correlated spectra were measured for 10—16% solution in pyridine-d_5 using the usual sequence. Data processing was performed with the standard JEOL software with a 512 × 2048 data point matrix. Mass spectrum (MS) were produced on a JEOL JMS DX-300 spectrometer equipped with a JMA 3500 data system (EI-MS: ionization voltage, 30 eV; accelerating voltage, 3 kV. Negative ion FAB-MS: accelerating voltage, 3 kV; matrix, triethanolamine; collision gas, Xe). The analytical GC was carried out with a Shimadzu GC-8A gas chromatograph. IR spectra were taken on a JASCO A302 spectrometer, and optical rotations were determined with a JASCO DIP-140 polarimeter. Thin layer chromatographies (TLCs) were carried out on silica gel-precoated Al sheets (Merck, Art 5554), while for analysis of saccharides, Silica gel 60 HPTLC (Merck, Art 5556) was used. For column chromatography, Silica gel 60 (230—400 mesh, Merck), Avicel SF

(Funakosi Pharmaceutical Co., Ltd.) and Sephadex LH-20 (Pharmacia Fine Chemicals) were used.

Extraction and Preparation of Crude Glycoside——The powdered seeds of *I. muricata* (2.2 kg) cultivated in the garden of this university were percolated with MeOH (5 l) at room temperature and the extract was evaporated under reduced pressure. The extractive (370 g) was partitioned with *n*-hexane–MeOH (1 : 1) mixture (1.5 l). The MeOH phase was concentrated to afford a brown solid (310 g). The solid was treated with ether (1.5 l) and the extract was evaporated to yield a yellow syrup (205 g), which was defatted repeatedly by treatment with *n*-hexane to give a pale yellow powder, mp 106—110 °C (150 g, crude glycoside).

Alkaline Hydrolysis of Crude Glycoside——The crude glycoside (40 g) was dissolved in 5% KOH (H_2O–dioxane, 3 : 1) (100 ml) and heated at 90 °C for 3 h. The reaction mixture was adjusted to pH 4.0 with 2 N HCl and shaken with ether (50 ml). The ether layer was dried over $MgSO_4$ and evaporated under reduced pressure to give an oil (organic acid fraction, 2.6 g). A part of this fraction was methylated with diazomethane in the usual way and examined by GC, exhibiting three peaks at retention times t_R (min) of 1.6, 3.0, 24.4, which were identical with those of the methyl esters of isobutyric acid,[1] 2-methylbutyric acid[1] and nilic acid,[1] respectively (GC conditions: Unisol F-200, 4 mm i.d. × 2 m glass column; column temp. 50—120°C (3 °C/min); N_2, 1.5 kg/cm^2).

The aqueous layer was extracted with *n*-BuOH (50 ml) and the solvent was distilled off *in vacuo* to afford a white powder (glycosidic acid fraction, 35 g).

Preparation of *p*-Bromophenacyl Esters, 1a, 2a and 3a——The organic acid fraction (1.5 g) was dissolved in dry acetone (30 ml) and neutralized with triethylamine, then *p*-bromophenacylbromide (500 mg) was added. The mixture was left standing at room temperature for 1 h. Precipitates were filtered off, and the filtrate was concentrated to about 1.5 ml then diluted with water (20 ml). The solution was extracted with ether (20 ml) and the ether layer was dried over $MgSO_4$. After removal of the solvent, the reaction mixture was column-chromatographed over silica gel (*n*-hexane–AcOEt, 1 : 3) followed by crystallization from *n*-hexane–acetone (3 : 1) to give **1a** (110 mg), colorless needles, mp 77.5 °C, **2a** (85 mg), colorless needles, mp 53.0 °C, $[\alpha]_D$ +11.0° (c=2.0, $CHCl_3$) and **3a** (40 mg), colorless needles, mp 97—98 °C, $[\alpha]_D$ −2.2° (c=2.0, $CHCl_3$). IR (KBr): 3340, 2920, 1740, 1170 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, d, J=7.0 Hz, 2-CH_3), 1.30 (3H, d, J=6.5 Hz, 3-CH_3), 2.62 (1H, dq, J=7.0, 7.0 Hz, 2-H), 3.97 (1H, dq, J=7.0, 6.5 Hz, 3-H), 5.33, 5.43 (each 1H, d, J=16.5 Hz, 2-H), 7.63 (2H, ddd, J=8.6, 2.3, 2.3 Hz, arom. H), 7.79 (2H, ddd, J=8.6, 2.3, 2.3 Hz, arom. H). The IR spectra of **1a** and **2a** were superimposable on those of the *p*-bromophenacyl esters of authentic isobutyric and 2-methylbutyric acids,[1] respectively.

Isolation of 2-Methylbutyric Acid (2) and Methyl 2*R*, 3*R*-Nilate (3b)——The organic acid fraction (880 mg) was subjected to fractional distillation to afford **2** (100 mg), colorless liquid, bp 70 °C/20 mmHg, $[\alpha]_D$ +17.2° (c=4.3, MeOH). IR (neat): 2970 (OH), 1710 cm^{-1} (carbonyl). ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3H, t, J=7.2 Hz, 3-CH_3), 1.18 (3H, d, J=7.0 Hz, 2-CH_3), 1.51 (1H, ddq, J=7.0, 7.0, 7.2 Hz, 3-H), 1.72 (1H, ddq, J=7.0, 7.0, 7.2 Hz, 3-H), 2.40 (1H, tq, J=7.0, 7.0 Hz, 2-H).

The residue of the above distillation (175 mg) was methylated with diazomethane in the usual manner followed by fractional distillation to give **3b** (22 mg), colorless liquid, bp 85 °C/18 mmHg, $[\alpha]_D$ −30.8° (c=2.0, MeOH). IR (KBr): 2990, 2960, 1732, 1045 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.18 (3H, d, J=7.2 Hz, 2-CH_3), 1.22 (3H, d, J=6.3, 3-CH_3), 2.47 (1H, dq, J=7.2, 2-H), 3.71 (3H, s, $COOCH_3$), 3.88 (1H, m, 3-H).

Acid Hydrolysis of Glycosidic Acid Fraction——The crude resin glycoside (8 g) was dissolved in 2 N H_2SO_4 (100 ml) and heated at 90 °C for 3 h. The reaction mixture was extracted with ether and the ether layer was evaporated to afford a solid, which was chromatographed over silica gel (*n*-hexane–AcOEt, 3 : 1) followed by crystallization from MeOH to furnish **4** (1.0 g), colorless needles, mp 62—63 °C, EI-MS m/z: 272 $(M)^+$. Compound **4** was shown to be identical with jalapinolic acid[5b] by means of the mixed fusion test and by TLCs (*n*-hexane–AcOEt, 1 : 1; $CHCl_3$–MeOH, 10 : 1). Compound **4** (520 mg) was treated with diazomethane in ether and the solvent was removed. Crystallization of the residue from petroleum ether gave **4a** (538 mg), yellowish plates, mp 42.5—43.3 °C, $[\alpha]_D$ +1.2°, (c=10.0, $CHCl_3$). EI-MS m/z: 286 $(M)^+$, 255 $(M-OCH_3)^+$, 215 $(CH(OH)(CH_2)_9COOCH_3)^+$, 101 $(CH_3(CH_2)_4CH(OH))^+$. IR (KBr): 3360 (OH), 1745 (carbonyl), 1170 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, t, J=7.0 Hz, 16-H_3), 2.30 (2H, d, J=7.0 Hz, 2-H_2), 3.66 (3H, s, $COOCH_3$).

The aqueous layer was neutralized with 10% $Ba(OH)_2$ and precipitates were filtered off. The filtrate was concentrated *in vacuo* to yield a syrup (4.3 g). The syrup (2 g) was subjected to chromatography on Avicel SF (H_2O-saturated *n*-BuOH) and silica gel (AcOEt–$CHCl_3$–MeOH–H_2O, 12 : 8 : 5 : 1 containing AcOH (trace) (solv. 1)) to give three syrupy compounds, L-rhamnose (24 mg), $[\alpha]_D$ +12.5° (c=2.0, H_2O), *Rf* 0.49 (HPTLC, $CHCl_3$–MeOH–H_2O, 6 : 4 : 1), D-quinovose (180 mg), $[\alpha]_D$ +32.9° (c=1.0, H_2O), *Rf* 0.48 and D-fucose (250 mg), $[\alpha]_D$ +58.7° (c=1.0, H_2O), *Rf* 0.47.

Isolation of Muricatic Acids A (5), B (6) and C——The glycosidic acid (10 g) was subjected to repeated column chromatographies over silica gel ($CHCl_3$–MeOH–H_2O, 6 : 4 : 1) to afford **5** (3.5 g), **6** (620 mg) and muricatic acid C. **5**: white powder, mp 104—110 °C (dec.), $[\alpha]_D$ −54.5° (c=1.3, MeOH). Negative ion FAB-MS: see Fig. 2. ^{1}H-NMR δ: see Table I. ^{13}C-NMR δ: see Table II. *Anal.* Calcd for $C_{40}H_{72}O_{19}$: C, 56.06; H, 8.46. Found: C, 56.11; H, 8.65. **6**: white powder, mp 115—121 °C (dec.), $[\alpha]_D$ −45.0° (c=1.0, MeOH). Negative ion FAB-MS m/z: 855 $(M-H)^-$, 709 (855−(methylpentose unit))$^-$, 563 (709−(methylpentose unit))$^-$, 417 (563−(methylpentose unit))$^-$, 271 (jalapinolic acid−H)$^-$. ^{1}H-NMR δ: see Table I, ^{13}C-NMR δ: see Table II. *Anal.* Calcd for $C_{40}H_{72}O_{19}$: C, 56.06; H,

8.46. Found: C, 56.17; H, 8.61. Muricatic acid C: white powder, mp 105—109 °C. (dec.), $[\alpha]_D$ −51.2° (c=1.0, MeOH).

Acid Hydrolysis of 5——A solution of **5** (20 mg) in 1,4-dioxane–H_2O (1 : 1) (10 ml) was treated with 2 N H_2SO_4 (50 ml) and heated at 90 °C for 3 h. The reaction mixture was extracted with ether (100 ml) and the ether layer was dried ($MgSO_4$) and evaporated to afford **4** (4 mg), colorless needles, mp 62 °C. The aqueous layer was neutralized with 10% $Ba(OH)_2$ and precipitates were filtered off. The filtrate was evaporated under reduced pressure to give a syrup (10 mg). The syrup exhibited three spots identical with those of authentic samples of D-rhamnose, D-fucose and D-quinovose on HPTLC ($CHCl_3$–MeOH–H_2O, 6 : 4 : 1).

A solution of the above syrup (9 mg) in pyridine (0.1 ml) was treated with *N*-trimethylsilylimidazole (0.1 ml) and the mixture was heated on a boiling water bath for 1 h. The products were subjected to GC (10% SE-30 on Chromosorb W (80—100 mesh), 7 mm i.d. × 1.5 m glass column; column temp. 175 °C; N_2, 0.7 kg/cm^2), t_R (min) 6.5, 8.6 (rhamnose-$(OTMS)_4$), 6.6, 7.9, 9.2 (fucose-$(OTMS)_4$), 10.2, 12.9 (quinovose-$(OTMS)_4$).

Acid Hydrolysis of 6——Compound **6** (20 mg) was treated in the same manner as described above and was examined by GC under the same conditions as for **5**, t_R (min) 6.5, 8.6 (rhamnose-$(OTMS)_4$), 10.2, 12.9 (quinovose-$(OTMS)_4$).

Permethylation and Methanolysis of 5 and 6——Compounds **5** (50 mg) and **6** (15 mg) were separately methylated according to Hakomori[10] and the products were separated by chromatography on silica gel to afford **5a** (41 mg) and **6a** (11 mg). **5a:** EI-MS m/z: 965 $(M-OCH_3)^+$, IR (KBr): no OH absorption band, ^{1}H-NMR ($CDCl_3$) δ: 4.14 (1H, d, J=7.0 Hz, 1-H of qui), 4.70 (1H, d, J=7.0 Hz, 1-H of qui′), 4.59 (d, J=7.0 Hz, 1-H of fuc), 5.31 (s, 1-H of rha). **6a**: EI-MS m/z: 965 $(M-OCH_3)^+$. IR (KBr): no OH absorption band. ^{1}H-NMR ($CDCl_3$) δ: 4.14 (1 H, d, J=7.0 Hz, 1-H of qui), 4.61 (1H, d, J=7.0 Hz, 1-H of qui′), 4.70 (1H, d, J=7 Hz, 1-H of qui″), 5.31 (1H, s, 1-H of rha). Compounds **5a** and **6a** were each dissolved in 0.5 N HCl–MeOH and the solution was refluxed for 3 h. Each solution was neutralized with 0.5 N KOH–MeOH and then extracted with $CHCl_3$. The $CHCl_3$ layer was dried ($MgSO_4$) and examined by GC (10% 1,4-butanediol succinate on Chromosorb W (60—80 mesh), 4 mm i.d. × 1.2 m glass column; column temp. 125 °C; N_2, 1.1 kg/cm^2). **5a**: t_R (min) 1.9, 2.6 (methyl 2,3,4-tri-*O*-methylfucopyranoside), 3.3, 4.2 (3,4-di-*O*-methylquinovopyranoside), 5.9 (methyl 2,3-di-*O*-methylrhamnopyranoside), **6a**: t_R (min) 1.0, 1.5 (methyl 2,3,4-tri-*O*-methylquinovopyranoside), 3.3, 4.2 (methyl 3,4-di-*O*-methylquinovopyranoside), 5.9 (methyl 2,3-di-*O*-methylrhamnopyranoside).

Partial Hydrolysis of 5 and 6——Compounds **5** (200 mg) and **6** (130 mg) were each dissolved in 40% formic acid solution (10 ml) and heated at 60 °C for 5 h, then extracted with AcOEt and washed with water. The extracts were evaporated *in vacuo*. Silica gel column chromatographies ($CHCl_3$–MeOH–H_2O, 8 : 2 : 0.1) of the residues yielded the same diglycoside (**7**) (19 and 16 mg), fine needles (acetone–H_2O), mp 144—146 °C, $[\alpha]_D$ −22.5° (c=2.9, MeOH), negative ion FD-MS m/z: 563 $(M-H)^-$, 417 $(M-146)^-$, 297, 271 (jalapinolic acid − H)$^-$ ^{13}C-NMR (pyridine-d_5) δ: 101.6 (d), 79.6 (d), 77.6 (d), 76.8 (d), 72.4 (d), 18.7 (q), (C_1–C_6 of qui), 105.9 (d), 76.6 (d), 77.6, (d), 76.3 (d), 73.4 (d), 18.5 (q) (C_1–C_6 of qui′), 175.8 (C_1 of jalapinolic acid). *Anal.* Calcd for $C_{28}H_{52}O_{11}$: C, 59.55; H, 9.28. Found: C, 59.45; H, 9.22.

Permethylation and Methanolysis of 7——Compound **7** (15 mg) was permethylated and methanolyzed in the same manner as described for **5** and **6**, then the product was examined by GC under the same conditions as for **5a** except for column temperature, 110 °C: same as for **5a** t_R (min) 1.6, 2.6 (methyl 2,3,4-tri-*O*-methylquinovopyranoside), 6.0, 7.8 (methyl 3,4-di-*O*-methylquinovopyranoside).

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