Components of Ether-Insoluble Resin Glycoside (Convolvulin) from Seeds of *Quamoclit pennata*

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Alkaline hydrolysis of the ether-insoluble resin glycoside (convolvulin) fraction of the seeds of *Quamoclit pennata* Bojer (Convolvulaceae) provided five new glycosidic acids, quamoclinic acids B, C, D, E, and F, along with six organic acids, isobutyric, 2*S*-methylbutyric, tiglic, 2*R*,3*R*-nilic, 7*S*-hydroxydecanoic, and 7*S*-hydroxydodecanoic acids. These new compounds were characterized on the basis of spectroscopic data as well as chemical evidence. Quamoclinic acids E and F are the first examples of heptaglycosides of glycosidic acid.

Key words resin glycoside; convolvulin; *Quamoclit pennata*; Convolvulaceae; glycosidic acid; organic acid

The so-called resin glycosides are well known as purgative ingredients, which are characteristic of some crude drugs such as Mexican Scammony Root, Orizaba Root, Jalapae Tuber, Pharbitidis Semen, and Rhizoma Jalapae Braziliensis. These drugs all originate from Convolvulaceae plants and can be roughly divided into an ether-soluble resin glycoside called jalapin and an ether-insoluble resin glycoside called convolvulin.[1)] In a previous paper,[2)] we reported the isolation and structural elucidation of a new glycosidic acid called quamoclinic acid A that was obtained along with three organic acids, 2*S*-methylbutyric, *n*-decanoic, and *n*-dodecanoic acids, upon alkaline hydrolysis of the jalapin fraction of the seeds of *Quamoclit pennata* Bojer. Further, we isolated four genuine jalapins, quamoclins I, II, III, and IV, from the fraction.[2)] This paper deals with the component organic and glycosidic acids of the convolvulin fraction of the seeds of this plant.

The alkaline hydrolysis products of the convolvulin fraction previously obtained[2)] were fractionated into organic acid and glycosidic acid fractions. Gas chromatography (GC) of the former revealed the presence of isobutyric, 2-methylbutyric, and tiglic acids. Further, the organic acid fraction was methylated with diazomethane-ether and then examined using GC; it exhibited four peaks assignable to methyl tiglate, methyl nilate, methyl 7-hydroxydecanoate, and methyl 7-hydroxydodecanoate.

The organic acid fraction was acylated with *p*-bromophenacyl bromide followed by chromatographic separation to give *p*-bromophenacyl 2-methylbutyrate (**1**), *p*-bromophenacyl tiglate (**2**), *p*-bromophenacyl nilate (**3**), *p*-bromophenacyl 7-hydroxydecanoate (**4**), and *p*-bromophenacyl 7-hydroxydodecanoate (**5**) (Fig. 1). The absolute configuration of **1** was defined as *S* by comparison of the specific rotation with an authentic sample,[3)] and that of **3** was considered to be 2*R*,3*R* by comparisons of the specific rotation and the ^{1}H-NMR spectrum of **3** with those of an authentic sample.[3)] However, the absolute value of the specific rotation of **3** was approximately 6-fold greater than that of *p*-bromophenacyl nilate (**3′**) previously obtained in a similar process as that used for **3** from the convolvulin fraction of Pharbitidis Semen.[3)] Thus the optical purities of **3** and **3′** were examined using their ^{1}H-NMR spectra of (−)-α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) esters[4)] (**3a** from **3**; **3′a** from **3′**), and it was confirmed that **3** did not contain its enantiomer, while **3′** was a mixture of *p*-bromphenacyl esters of the 2*R*,3*R*- and the 2*S*,3*S*-nilic acid in the ratio of approximately 6 : 5 on the basis of the ratio of intensities of signals due to H_3-5 of the (2*R*,3*R*)-form and that of the (2*S*,3*S*)-form.

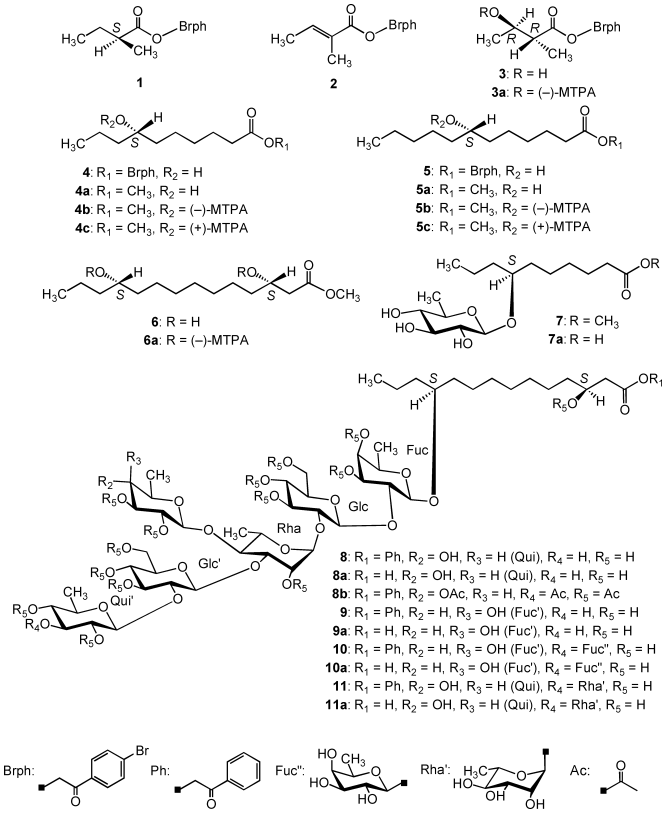

Fig. 1. Structures of **1**—**11**, **3a**—**11a**, **4b**, **4c**, **5b**, **5c**, and **8b**

The alkaline hydrolysis of **4** and of **5**, with subsequent diazomethane–ether treatment, gave methyl 7-hydroxydecanoate (**4a**) and methyl 7-hydroxydodecanoate (**5a**), respectively. The configurations at C-7 of **4a** and **5a** were determined using Mosher's method.[4)] Compounds **4a** and **5a** were converted into the corresponding (−)-MTPA esters (**4b** from **4a**; **5b** from **5a**) and (+)-MTPA esters (**4c** from **4a**; **5c** from **5a**).

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Comparison of the ^{1}H-NMR spectrum of **4b** with that of **4c** revealed chemical shift differences [$\Delta\delta(\delta$**4b**$-\delta$**4c**)] at the terminal methyl group and 2-methylene group of -0.067 and $+0.042$ ppm, respectively, and the differences [$\Delta\delta(\delta$**5b**$-\delta$**5c**)] were observed as -0.036 and $+0.042$ ppm in regard to H_3-12 and H_2-2, respectively; these results suggested that both configurations at C-7 of **4a** and **5a** were *S* (Fig. 1).[5]

Acidic hydrolysis of the glycosidic acid fraction gave aglycone and monosaccharide fractions. Methylation of the former with diazomethane–ether yielded methyl 7*S*-hydroxydecanoate (**4a**) and methyl 3*S*,11*S*-dihydroxytetradecanoate (methyl ipurolate) (**6**),[3] which were identified by their ^{13}C-NMR spectral data and ^{1}H-NMR spectral data of (−)-MTPA esters.[5] The sugar fraction was converted into trimethylsilyl ethers of diastereomeric thiazolidine derivatives and then analyzed using GC, according to the process reported by Hara *et al.*[6] Derivatives of D-glucose, D-fucose, D-quinovose, and L-rhamnose were detected.

The glycosidic acid fraction was roughly separated into two fractions (fr. 7 and 8) using silica gel column chromatography. Fr. 7 was derived into a methyl ester with diazomethane–ether, and subsequent chromatography separation afforded a methyl ester (**7**) of glycosidic acid. Acidic hydrolysis of **7** gave 7-hydroxydecanoic acid and D-quinovose. Saponification of **7** yielded a new glycosidic acid, quamoclinic acid B (**7a**), which showed an $[M-H]^-$ ion peak at *m*/*z* 333 ($C_{16}H_{29}O_7$) along with a fragment ion peak at *m*/*z* 187 [333−146 (6-deoxyhexose unit)]$^-$ in the negative-ion FAB-MS. The ^{13}C-NMR spectrum of **7a** indicated signals due to 16 carbons comprising one carbonyl carbon, one oxygenated methine carbon, and one terminal quinovopyranosyl unit.[7] Further, the ^{1}H-NMR spectrum of **7a** showed signals due to two equivalent methylene protons adjacent to a carbonyl group, and a primary methyl group ascribable to the 7-hydroxydecanoic acid moiety along with one β-D-quinovopyranosyl unit having the $^4C_1$ conformation. Consequently, the structure of **7a** was defined as 7*S*-hydroxydecanoic acid 7-*O*-β-D-quinovopyranoside (Fig. 1).

Fr. 8 was acylated with phenacyl bromide followed by separation to give four phenacyl esters (**8**—**11**) of glycosidic acids. On alkaline hydrolysis, **8**—**11** gave free glycosidic acids, quamoclinic acids C (**8a**), D (**9a**), E (**10a**), and F (**11a**), respectively.

On acidic hydrolysis, quamoclinic acid C (**8a**) gave ipurolic acid, D-glucose, D-fucose, D-quinovose, and L-rhamnose. The negative-ion FAB-MS of **8a** showed an $[M-H]^-$ ion peak at *m*/*z* 1167 along with fragment ion peaks at *m*/*z* 1021 [1167−146]$^-$, 859 [1021−162 (hexose unit)]$^-$, 713 [859−146]$^-$, 567 [859−2×146]$^-$, and 405 [567−162]$^-$ (Fig. 2). The ^{13}C-NMR spectrum of **8a** exhibited signals due to six anomeric carbons and one carbonyl carbon. In the ^{1}H-NMR spectrum of **8a**, signals due to six anomeric protons, four secondary methyl groups assignable to H_3-6 of 6-deoxyhexose units, as well as two nonequivalent methylene protons adjacent to a carbonyl group, and one primary methyl group ascribable to the ipurolic acid moiety were observed. The NMR signals due to the sugar moiety were assigned with the aid of ^{1}H–^{1}H correlation spectroscopy (COSY) and ^{1}H–^{13}C heteronuclear shift-correlated 2D-NMR (HETCOR) spectra (Tables 1 and 2); these data suggested that **8a** was composed of one mol each of ipurolic acid, D-fucose, and L-rhamnose,

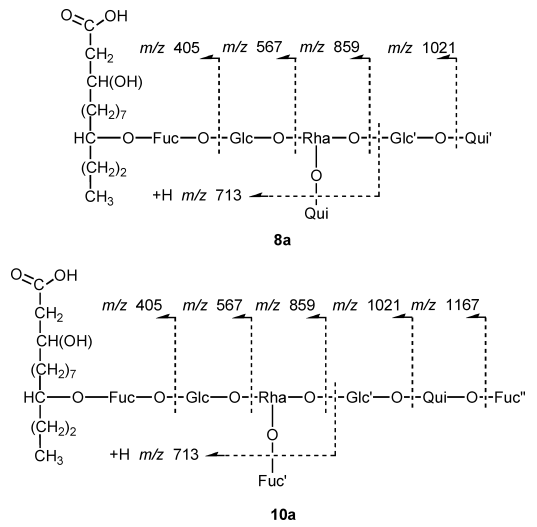

Fig. 2. Fragment Ions Observed in the Negative-Ion FAB-MS of **8a** and **10a**

and two mol each of D-glucose and D-quinovose. The coupling constants of signals due to anomeric and methine protons together with $J_{C\text{-}1\text{–}H\text{-}1}$ values due to the sugar moiety indicated that all the monosaccharide units were of the pyranose type, and further, that the mode of glycosidic linkage of the rhamnose unit was α in a $^1C_4$ conformation and those of the glucose, quinovose, and fucose units were β in $^4C_1$ conformations. The ^{13}C-NMR signals due to the sugar moiety of **8a** were compared with those of methyl pyranosides in the literature.[7,8] The glycosylation shifts[8,9] were observed at C-2 (+6.6 ppm) of the fucose unit (Fuc), C-2 (+2.8 ppm) of the first glucose unit (Glc), C-2 (+9.8 ppm) of the second glucose unit (Glc′), and C-3 (+6.5 ppm) and C-4 (+5.6 ppm) of the rhamnose unit (Rha). The ^{13}C-NMR signals assignable to C-11 of the aglycone moiety (Ag) showed a downfield shift of 9.4 ppm when compared with that of methyl ipurolate.[3] These data suggest that the sugar linkages of **8a** were located at OH-2 of Fuc, OH-2 of Glc, OH-2 of Glc′, OH-3 and OH-4 of Rha, and OH-11 of Ag. To determine the sequence of the sugar moiety, the nuclear Overhauser and exchange spectroscopy (NOESY) spectra of **8a** and peracetate (**8b**) of **8** were recorded. Five of the cross peaks observed in the NOESY spectrum of **8a** were assigned as those between H-1 of Glc and H-2 of Fuc, H-1 of Rha and H-2 of Glc, H-1 of Glc′ and H-3 of Rha, H-1 of Qui and H-4 of Rha, and H-1 of Qui′ and H-2 of Glc′, while the counterpart due to H-1 of Fuc could not be defined because the signals were overlapping. The NOESY spectrum of **8b** showed cross peaks that were assigned as in between H-1 of Fuc and H-11 of Ag, H-1 of Glc and H-2 of Fuc, and H-1 of Glc′ and H-3 of Rha.

Accordingly, the structure of **8a** was characterized as (3*S*,11*S*)-ipurolic acid 11-*O*-β-D-quinovopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→3)-[*O*-β-D-quinovopyranosyl-(1→4)]-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside (Fig. 1).

Acidic hydrolysis of quamoclinic acid D (**9a**) afforded ipurolic acid, D-glucose, D-fucose, D-quinovose, and L-rhamnose, which were the same products as derived from the acidic hydrolysis of **8a**. Further, the negative-ion FAB-MS of **9a** was superimposable on that of **8a**, in which an $[M-H]^-$

Table 1. ^{1}H-NMR Spectral Data for **8a**, **8b** and **9a** (in Pyridine-d_5, 600 MHz)

	8a	8b	9a
Fuc-1	4.78 d (7.0)	4.84 d (7.5)	4.71 d (6.5)
2	4.46 dd (7.0, 9.5)	4.45 dd (7.5, 9.5)	*ca.* 4.41
3	4.49 dd (3.5, 9.5)	5.45 dd (3.5, 9.5)	*ca.* 4.41
4	*ca.* 4.10	5.76 d (3.5)	4.06 d (3.0)
5	3.87 q (6.5)	*ca.* 4.53	3.72 q (6.5)
6	1.39 d (6.5)	1.50 d (6.5)	1.37 d (6.5)
Glc-1	5.60 d (7.5)	*ca.* 5.32	5.52 d (7.5)
2	4.19 dd (7.5, 9.0)	4.22 dd (8.0, 9.5)	4.17 dd (7.5, 9.0)
3	4.13 dd (9.0, 9.0)	5.69 dd (9.5, 9.5)	4.11 dd (9.0, 9.0)
4	4.03 dd (9.0, 9.0)	5.35 dd (9.5, 9.5)	4.03 dd (9.0, 9.0)
5	3.63 ddd (2.5, 5.5, 9.0)	3.97 m	3.63 ddd (3.5, 6.0, 9.0)
6	4.30 dd (2.5, 11.5)	*ca.* 4.53	4.31 dd (3.5, 11.5)
	4.17 dd (5.5, 11.5)	*ca.* 4.26	4.18 dd (6.0, 11.5)
Rha-1	6.31 d (2.0)	5.46 s	6.28 d (2.0)
2	4.93 dd (2.0, 3.0)	*ca.* 5.64	4.95 dd (2.0, 3.0)
3	5.18 dd (3.0, 9.5)	*ca.* 4.54	5.17 dd (3.0, 9.5)
4	4.69 dd (9.5, 9.5)	4.29 dd (9.5, 9.5)	4.70 dd (9.5, 9.5)
5	5.05 dq (9.5, 6.0)	4.71 dq (9.5, 6.0)	4.99 dq (9.5, 6.0)
6	1.92 d (6.0)	1.83 d (6.0)	1.90 d (6.0)
Glc′-1	5.99 d (7.5)	5.49 d (7.5)	5.99 d (8.0)
2	*ca.* 3.97	*ca.* 4.27	4.00 dd (8.0, 9.0)
3	4.38 dd (9.0, 9.0)	5.57 dd (9.5, 9.5)	*ca.* 4.41
4	*ca.* 4.10	5.29 dd (9.5, 9.5)	4.13 dd (9.0, 9.0)
5	*ca.* 3.98	*ca.* 4.29	3.98 ddd (2.5, 6.0, 9.0)
6	4.45 dd (2.5, 11.5)	4.49 dd (6.0, 11.5)	4.44 dd (2.5, 11.5)
	4.17 dd (5.5, 11.5)	4.43 dd (2.5, 11.5)	4.18 dd (6.0, 11.5)
Qui-1	5.76 d (7.5)	*ca.* 5.22	
2	3.94 dd (7.5, 9.0)	*ca.* 5.60	
3	4.26 dd (9.0, 9.0)	*ca.* 5.60	
4	3.67 dd (9.0, 9.0)	*ca.* 5.63	
5	*ca.* 4.00	*ca.* 3.94	
6	1.57 d (6.0)	1.46 d (6.0)	
Fuc′-1			5.66 d (7.5)
2			4.28 dd (7.5, 9.5)
3			4.25 dd (3.0, 9.5)
4			3.96 dd (1.0, 3.0)
5			*ca.* 4.08
6			1.50 d (6.5)
Qui′-1	5.09 d (8.0)	5.62 d (7.5)	5.11 d (7.5)
2	*ca.* 4.10	5.52 dd (7.5, 9.5)	4.09 dd (7.5, 9.0)
3	*ca.* 3.97	5.72 dd (9.5, 9.5)	4.01 dd (9.0, 9.0)
4	3.67 dd (9.0, 9.0)	5.19 dd (9.5, 9.5)	3.63 dd (9.0, 9.0)
5	3.70 dq (9.0, 6.0)	4.08 dq (9.5, 6.0)	3.71 dq (9.0, 6.0)
6	1.64 d (6.0)	1.38 d (6.0)	1.63 d (6.0)
Ag-2	2.88 dd (8.0, 15.0)	3.02 dd (7.5, 16.0)	2.89 dd (8.0, 15.0)
	2.85 dd (5.0, 15.0)	2.99 dd (5.0, 16.0)	2.86 dd (5.0, 15.0)
3	4.53 m	*ca.* 5.67	4.53 m
11	*ca.* 3.86	*ca.* 3.93	3.85 m
14	0.89 t (7.0)	0.92 t (7.0)	0.90 t (7.0)

δ in ppm from tetramethylsilane (TMS) (coupling constants (J) in Hz are given in parentheses). Fuc, fucopyranosyl; Glc, glucopyranosyl; Rha, rhamnopyranosyl; Qui, quinovopyranosyl; Ag, aglycone. **8b**: δ 2.38, 2.28, 2.27, 2.25, 2.23, 2.17, 2.15, 2.15, 2.11, 2.10, 2.09, 2.08, 2.06, 2.01, 2.01, 1.97 (all singlet, $COCH_3$).

and fragment ion peaks were seen at *m/z* 1167, 1021, 859, 713, 567, and 405. The ^{1}H- and ^{13}C-NMR spectral data of **9a** indicated that it was composed of one mol each of quinovopyranose, rhamnopyranose, and ipurolic acid, and two mol each of glucopyranose and fucopyranose. The data also indicated that the mode of glycosidic linkages of the glucose, quinovose, and fucose units are β in the $^4C_1$ conformations and that of the rhamnose unit is α in the $^1C_4$ conformation. Glycosylation shifts in the ^{13}C-NMR spectral data of **9a** were observed at C-11 (+9.3 ppm) of Ag, C-2 (+7.0 ppm) of Fuc, C-2 (+3.4 ppm) of Glc, C-3 (+6.7 ppm) and C-4 (+5.5 ppm) of Rha, and C-2 (+9.9 ppm) of Glc′. Moreover, the NOESY spectrum of **9a** showed six cross peaks between H-1 of Fuc and H-11 of Ag, H-1 of Glc and H-2 of Fuc, H-1 of Rha and H-2 of Glc, H-1 of Glc′ and H-3 of Rha, H-1 of the second fucose unit (Fuc′) and H-4 of Rha, and H-1 of Qui′ and H-2 of Glc′.

Consequently, the structure of **9a** was concluded to be (3*S*,11*S*)-ipurolic acid 11-*O*-β-D-quinovopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→3)-[*O*-β-D-fucopyranosyl-(1→4)]-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside (Fig. 1), which was an epimer of **8a** with replacement of the β-D-quinovopyranosyl group attached to OH-4 of Rha by the β-D-fucopyranosyl group.

On acidic hydrolysis, quamoclinic acid E (**10a**) gave the same products as those of **8a** and **9a**. In the negative-ion FAB-MS, **10a** exhibited an $[M-H]^-$ ion peak at *m/z* 1313, which was 146 mass units larger than that of **9a**, and fragment ion peaks at *m/z* 1167 $[1313-146]^-$, 1021 $[1167-146]^-$, 859 $[1021-162]^-$, 713 $[859-146]^-$, 567 $[713-146]^-$, and 405 $[567-162]^-$ (Fig. 2). The ^{1}H-NMR spectrum of **10a** indicated signals due to seven anomeric protons, five secondary methyl groups, two nonequivalent methylene protons, and one primary methyl group. The ^{13}C-NMR spectrum of **10a** showed signals due to seven anomeric carbons and one carbonyl carbon. These ^{1}H- and ^{13}C-NMR signals were assigned with the aid of techniques similar to those used for **8a**, and the data indicated that **10a** was composed of three mol of fucopyranose, two mol of glucopyranose, and one mol each of rhamnopyranose, quinovopyranose, and ipurolic acid. The mode of their glycosidic linkages was elucidated from the coupling constants of signals due to anomeric and methine protons as well as $J_{C\text{-}1\text{–}H\text{-}1}$ values due to the sugar moiety, as shown in Fig. 1. In the ^{13}C-NMR spectral data of **10a**, glycosylation shifts were observed at C-2 (+7.0 ppm) of Fuc, C-2 (+3.8 ppm) of Glc, C-3 (+6.5 ppm) and C-4 (+5.6 ppm) of Rha, C-2 (+10.2 ppm) of Glc′, C-3 (+9.4 ppm) of Qui′, and C-11 (+9.4 ppm) of Ag. From these data, it was assumed that on **10a** one additional β-D-fucopyranosyl unit may be attached to OH-3 of Qui′ of **9a**. This assumption was confirmed by the appearance of seven cross peaks between H-1 of Fuc and H-11 of Ag, H-1 of Glc and H-2 of Fuc, H-1 of Rha and H-2 of Glc, H-1 of Glc′ and H-3 of Rha, H-1 of Fuc′ and H-4 of Rha, H-1 of Qui′ and H-2 of Glc′, and H-1 of the third fucose (Fuc″) and H-3 of Qui′ in the NOESY spectrum of **10a**.

Thus the structure of **10a** was determined to be (3*S*,11*S*)-ipurolic acid 11-*O*-β-D-fucopyranosyl-(1→3)-*O*-β-D-quinovopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→3)-[*O*-β-D-fucopyranosyl-(1→4)]-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside.

On acidic hydrolysis, quamoclinic acid F (**11a**) liberated ipurolic acid, D-glucose, D-quinovose, D-fucose, and L-rhamnose. The negative-ion FAB-MS of **11a** was almost the same as that of **10a**, in which an $[M-H]^-$ and fragment ion peaks were observed at *m/z* 1313, 1167, 1021, 859, 567, and 405. The ^{1}H- and ^{13}C-NMR signals due to the sugar moiety of **11a** suggested that **11a** was composed of two mol each of glucose, quinovose, and rhamnose and one mol of fucose, which were all of the pyranose form, and further, the mode of glycosidic linkages of the glucose, quinovose, and fucose units

Table 2. ^{13}C-NMR Spectral Data for **8a**—**11a** (in Pyridine-d_5, 150 MHz)

	8a	**9a**	**10a**	**11a**		**8a**	**9a**	**10a**	**11a**
Fuc-1	102.4	102.4	102.4	102.4	Fuc′-1		103.4	103.4	
2	78.6	79.0	79.0	78.6	2		73.5	73.4	
3	76.0	75.8	75.9	76.1	3		75.7	75.6	
4	72.9	72.8	72.8	73.0	4		72.9	72.9	
5	70.9	70.9	70.9	71.0	5		71.0	71.0	
6	17.1	17.1	17.2	17.2	6		17.1	17.1	
Glc-1	102.6	102.9	102.7	102.5	Qui′-1	105.1	105.1	105.3	105.8
2	77.6	78.2	78.6	77.8	2	75.8	76.0	74.8	77.3
3	79.1	79.0	78.8	79.0	3	77.6	77.7	87.4	83.0
4	72.5	72.5	72.5	72.4	4	77.2	76.8	74.7	74.9
5	77.2	77.1	77.1	77.2	5	73.7	73.6	73.2	73.9
6	63.1	63.2	63.1	63.1	6	18.5	18.6	18.5	18.6
Rha-1	100.8	101.1	101.3	100.9	Fuc″-1			105.7	
2	71.7	71.6	71.8	72.0	2			72.5	
3	79.0	79.2	79.0	78.1	3			75.0	
4	79.2	79.1	79.2	79.7	4			72.4	
5	68.2	68.4	68.5	68.4	5			72.0	
6	19.1	19.2	19.2	19.3	6			17.0	
Glc′-1	101.2	101.1	101.5	101.6	Rha′-1				102.6
2	84.6	84.7	85.0	84.9	2				72.3
3	77.1	77.2	77.7	77.3	3				72.6
4	71.6	71.6	71.5	71.9	4				74.0
5	78.0	78.1	78.0	78.1	5				69.8
6	62.6	62.7	62.6	62.7	6				18.7
Qui-1	102.9			102.7	Ag-1	175.3	175.2	175.2	175.2
2	76.5			76.6	2	43.9	43.9	43.9	44.0
3	78.5			78.5	3	68.5	68.5	68.6	68.6
4	76.5			76.5	11	80.0	79.9	80.0	80.1
5	72.3			72.3	14	14.5	14.5	14.5	14.5
6	18.8			18.8					

δ in ppm from TMS. Fuc, fucopyranosyl; Glc, glucopyranosyl; Rha, rhamnopyranosyl; Qui, quinovopyranosyl; Ag, aglycone.

were β in the $^4C_1$ conformations and that of the rhamnose unit was α in the $^1C_4$ conformation. The ^{13}C-NMR spectral data indicated glycosylation shifts at C-2 (+6.6 ppm) of Fuc, C-2 (+3.0 ppm) of Glc, C-3 (+5.6 ppm) and C-4 (+6.1 ppm) of Rha, C-2 (+10.1 ppm) of Glc′, C-3 (+5.0 ppm) of Qui, and C-11 (+9.5 ppm) of Ag. The arrangement of sugar linkages was determined using the NOESY spectrum of **11a**, that is, seven cross peaks between H-1 of Fuc and H-11 of Ag, H-1 of Glc and H-2 of Fuc and/or H-1 of Glc and H-3 of Fuc, H-1 of Rha and H-2 of Glc, H-1 of Glc' and H-3 of Rha, H-1 of Qui and H-4 of Rha, H-1 of Qui′ and H-2 of Glc′, and H-1 of second rhamnose unit (Rha′) and H-3 of Qui′ were observed.

Consequently, the structure of **11a** was defined to be (3*S*,11*S*)-ipurolic acid 11-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-β-D-quinovopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→3)-[*O*-β-D-quinovopyranosyl-(1→4)]-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→2)-β-D-fucopyranoside, on which one mol of rhamnopyranose unit was bonded to OH-3 of Qui of **8a**.

As the components of the convolvulin fraction of *Q. pennata* Bojer, five new glycosidic acids, quamocilnic acids B, C, D, E, and F, and six organic acids, isobutyric, 2*S*-methylbutyric, tiglic, 2*R*,3*R*-nilic, 7*S*-hydroxydecanoic, and 7*S*-hydroxydodecanoic acids, were elucidated. These components were different from those of the jalapin fraction of this seed, except for 2*S*-methylbutyric acid. Further, quamoclinic acids E and F are the first examples of heptaglycosides of glycosidic acid.

Experimental

All instruments and materials used were as cited in the preceding report[10] unless otherwise specified.

Alkaline Hydrolysis of the Convolvulin Fraction The convolvulin fraction (5.01 g) previously obtained[2] was dissolved in 1 M KOH (30 ml) and heated at 95 °C for 1.5 h. After cooling, the reaction mixture was adjusted to pH 4.0 with 1 M HCl and shaken with ether (50 ml×3). The ether layer was dried over $MgSO_4$ and evaporated *in vacuo* to give an oil (organic acid fraction, 0.70 g). The H_2O layer was chromatographed over MCI gel CHP20 (solvent, H_2O→acetone). The acetone eluate was evaporated to dryness to afford a white powder (4.29 g, glycosidic acid fraction).

Identification of Organic Acids An aliquot of the organic acid fraction was analyzed using GC [column, 3.2 mm i.d.×2.0 m glass column packed with Unisole 30T (5%); carrier gas N_2, 1.5 kg/cm^2; column temperature, 120 °C; retention times (t_R) (min): 1.72 (isobutyric acid), 2.72 (2-methylbutyric acid), 6.10 (tiglic acid)]. A small portion of the organic acid fraction was methylated with diazomethane-ether and then analyzed using GC [column, 3.2 mm i.d.×2.0 m glass column packed with Unisole 30T (5%); carrier gas N_2, 1.0 kg/cm^2; column temperature, 60 °C for 3 min then elevated to 110 °C by 10 °C/min; t_R (min): 2.61 (methyl tiglate), 8.60 (methyl nilate); column, 3.2 mm i.d.×2.0 m glass column packed with Silicone OV-17 Uniport HP 80/100; carrier gas N_2, 1.25 kg/cm^2; column temperature, elevated from 140 °C to 190 °C by 2 °C/min; t_R (min): 4.39 (methyl 7-hydroxydecanoate), 8.99 (methyl 7-hydroxydodecanoate)].

The organic acid fraction (0.65 g) in dry acetone (30 ml) was neutralized with triethylamine. *p*-Bromophenacylbromide (1.12 g) was added and the mixture was left to stand at room temperature for 1 h and then concentrated *in vacuo* to give a residue. The residue was fractionated between H_2O (25 ml) and ether (25 ml×3). The ether layer was dried over $MgSO_4$ and evaporated *in vacuo* to give a residue. The residue was chromatographed over a silica gel column [solvent, *n*-hexane–AcOEt (9 : 1→5 : 1→3 : 1→2 : 1→1 : 1→0 : 1)→MeOH] to afford fr. 1 (538 mg), fr. 2 (20 mg), fr. 3 (15 mg), fr. 4 (64 mg), *p*-bromophenacyl nilate (**3**, 102 mg), fr. 5 (11 mg), and fr. 6 (344 mg). Fr. 1 (247 mg) was subjected to HPLC [column, Kusano C.I.G. Si, 22 mm i.d.×10 cm; solvent, *n*-hexane–AcOEt (60 : 1)] to give *p*-bromophenacyl 2-methylbutyrate (**1**, 12 mg) and *p*-bromophenacyl tiglate

(**2**, 133 mg). HPLC of fr. 3 (15 mg) and fr. 4 (64 mg) on the Kusano C.I.G. Si [column, 2.2 cm i.d.×10 cm; solvent, *n*-hexane–AcOEt (3 : 1)] furnished *p*-bromophenacyl 7-hydroxydodecanoate (**5**, 9 mg) from fr. 3 and *p*-bromophenacyl 7-hydroxydecanoate (**4**, 43 mg) from fr. 4, respectively.

1: Colorless needles (*n*-hexane–AcOEt), mp 52—53 °C, $[\alpha]_D^{20}$ +10.5° (*c*=1.5, $CHCl_3$). ^{1}H-NMR (in $CDCl_3$, 400 MHz) δ: 0.98 (3H, t, *J*=7.5 Hz, H_3-4), 1.24 (3H, d, *J*=7.0 Hz, H_3-5), 1.55, 1.79 (each 1H, ddq, *J*=14.0, 7.5, 7.0 Hz, H-3), 2.55 (1H, ddq, *J*=7.0, 7.0, 7.0 Hz, H-2), 5.27 (2H, s, OCH_2CO), 7.63 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H), 7.77 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H).

2: Colorless needles (*n*-hexane–AcOEt), mp 60—63 °C. ^{1}H-NMR (in $CDCl_3$, 400 MHz) δ: 1.82 (3H, dd-like, *J*=7.0, 1.0 Hz, H_3-4), 1.88 (3H, t-like, *J*=1.0 Hz, H_3-5), 5.33 (2H, s, OCH_2CO), 7.01 (1H, qq, *J*=7.0, 1.0 Hz, H-3), 7.60 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H), 7.78 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H).

3: Colorless needles (*n*-hexane–AcOEt), mp 98—99 °C, $[\alpha]_D^{20}$ −13.8° (*c*=12.6, $CHCl_3$). ^{1}H-NMR (in $CDCl_3$, 400 MHz) δ: 1.23 (3H, d, *J*=7.0 Hz, H_3-5), 1.28 (3H, d, *J*=6.0 Hz, H_3-4), 2.61 (1H, dq, *J*=7.0, 7.0 Hz, H-2), 3.97 (1H, dq, *J*=7.0, 6.0 Hz, H-3), 5.31, 5.41 (each 1H, d, *J*=16.5 Hz, OCH_2CO), 7.61 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H), 7.76 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H).

4: Colorless needles (*n*-hexane–AcOEt), mp 75—77 °C, $[\alpha]_D^{15}$ +0.3° (*c*=7.7, $CHCl_3$). ^{1}H-NMR (in $CDCl_3$, 400 MHz) δ: 0.92 (3H, t, *J*=7.0 Hz, H_3-10), 1.71 (2H, tt, *J*=7.5, 7.5 Hz, H_2-3), 1.33—1.47 (10H, H_2-4, H_2-5, H_2-6, H_2-8, H_2-9), 2.47 (2H, t, *J*=7.5 Hz, H_2-2), 3.60 (1H, m, H-7), 5.25 (2H, s, OCH_2CO), 7.62 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H), 7.76 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H). ^{13}C-NMR (in $CDCl_3$, 100 MHz) δ: 14.1 (C-10), 18.8, 24.8, 25.3, 29.1, 33.8, 37.2, 39.7, 65.7 (OCH_2CO), 71.5 (C-7), 129.1, 129.3, 132.2, 133.0, 173.1 (C-1), 191.5 (CO-aromatic). FD-MS *m/z* (%): 387 (24) $[M+2+H]^+$, 385 (24) $[M+H]^+$, 343 (77) $[M+2-C_3H_7]^+$, 341 (75) $[M-C_3H_7]^+$, 314 (22) $[M+2+H-C_3H_7CH(OH)]^+$, 312 (19) $[M+H-C_3H_7CH(OH)]^+$, 73 (100) $[C_3H_7CH(OH)]^+$.

5: White powder. ^{1}H-NMR (in $CDCl_3$, 400 MHz) δ: 0.89 (3H, t, *J*=7.0 Hz, H_3-12), 1.72 (2H, tt, *J*=7.5, 7.5 Hz, H_2-3), 1.25—1.49 (14H, H_2-4, H_2-5, H_2-6, H_2-8, H_2-9, H_2-10, H_2-11), 2.48 (2H, t, *J*=7.5 Hz, H_2-2), 3.59 (1H, m, H-7), 5.27 (2H, s, OCH_2CO), 7.63 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H), 7.77 (2H, ddd-like, *J*=8.5, 2.0, 2.0 Hz, aromatic H). ^{13}C-NMR (in $CDCl_3$, 100 MHz) δ: 14.0 (C-12), 22.7, 24.8, 25.3, 25.3, 29.1, 31.9, 33.8, 37.2, 37.5, 65.7 (OCH_2CO), 71.9 (C-7), 129.1 (aromatic), 129.3 (aromatic), 132.3 (aromatic), 133.1 (aromatic), 173.1 (C-1), 191.5 (CO-aromatic). FD-MS *m/z* (%): 415 (55) $[M+2+H]^+$, 413 (53) $[M+H]^+$, 343 (72) $[M+2-C_5H_{11}]^+$, 341 (70) $[M-C_5H_{11}]^+$.

Preparation of 4a and 5a Compounds **4** (10 mg) and **5** (9 mg) were each heated with 1 M KOH (1 ml) at 95 °C for 1 h. After cooling, the mixture was acidified (pH 4) with 1 M HCl, diluted by H_2O (10 ml), then extracted with ether (5 ml×4). The ether layer was methylated with diazomethane–ether, and then the residue was successively subjected to a silica gel column [solvent, *n*-hexane–AcOEt (4 : 1→3 : 1→0 : 1)] and HPLC [column, Kusano C.I.G. Si, 22 mm i.d.×10 cm; solvent, *n*-hexane–AcOEt (2 : 1)] to give methyl 7-hydroxydecanoate (**4a**, 3 mg) from **4** and methyl 7-hydroxydodecanoate (**5a**, 4 mg) from **5**, respectively.

4a: White powder. ^{13}C-NMR (in $CDCl_3$, 100 MHz) δ: 14.1 (C-10), 18.8, 24.9, 25.3, 29.2, 34.0, 37.2, 39.7, 51.5 (OCH_3), 71.5 (C-7), 174.3 (C-1).

5a: White powder. ^{13}C-NMR (in $CDCl_3$, 100 MHz) δ: 14.0 (C-12), 22.6, 24.9, 25.3, 25.3, 29.2, 31.9, 34.0, 37.2, 37.5, 51.5 (OCH_3), 71.9 (C-7), 174.2 (C-1).

Acidic Hydrolysis of the Glycosidic Acid Fraction The glycosidic acid fraction (0.86 g) in 2 M HCl (3 ml) was heated at 95 °C for 1 h. The reaction mixture was diluted with H_2O (5 ml) and then extracted with ether (5 ml×4). The ether extract was dried over $MgSO_4$ and concentrated *in vacuo* to give a residue (142 mg). Treatment of the residue with diazomethane–ether, followed by evaporation, gave a white powder, which was chromatographed over a silica gel column [solvent, *n*-hexane–AcOEt (10 : 1→5 : 1→2 : 1→0 : 1)] to afford methyl 7-hydroxydecanoate (**4a**, 35 mg) and methyl ipurolate (**6**, 53 mg).

6: Colorless needles (*n*-hexane–AcOEt), mp 67—69 °C, $[\alpha]_D^{15}$ +13.1° (*c*=3.8, $CHCl_3$). ^{13}C-NMR (in $CDCl_3$, 100 MHz) δ: 14.1 (C-14), 18.8, 25.5, 25.6, 29.5, 29.5, 29.6, 36.6, 37.5, 39.7, 41.3, 51.7 (OCH_3), 68.0 (C-3), 71.6 (C-11), 173.4 (C-1).

The aqueous layer was neutralized with 1 M KOH and the mixture was evaporated. Desalting of the residue by chromatography on a Sephadex LH-20 column (solvent, MeOH) followed by evaporation afforded a syrup (619 mg, sugar fraction) which was subjected to TLC analysis [condition 1: plate, Avicel SF (Funakoshi Pharm. Co.); solvent, *n*-BuOH–pyridine–H_2O (6 : 2 : 3) top layer+pyridine (1); rate of flow (*Rf*): 0.39 (glucose), 0.53 (fucose), 0.63 (rhamnose and/or quinovose)]. The sugar fraction (64 mg) was subjected to GC-analysis as the trimethylsilyl ethers of the thiazolidine derivatives, according to the process reported by Hara *et al.*[6] GC [condition 2: Hitachi G-3000 gas gaschromatograph equipped with 30 : 1 splitter and flame-ionizing detector; column, fused silica capillary column Bonded MPS-50 (Quadrex), 50 m×0.25 mm, 0.25 μm film thickness; carrier gas, He (30 ml/min); column temperature, 220 °C; t_R (min): 18.57 (D-quinovose derivative), 19.43 (L-rhamnose derivative), 21.10 (D-fucose derivative), 27.19 (D-glucose derivative)].

Preparation of (−)-MTPA Esters of 3, 3′, 4a, 5a, and 6 Freshly prepared (−)-MTPACl (15 mg) was added to individual solutions of **3** (3 mg), **3′** (4 mg), and **4a** (2 mg) obtained from the organic acid fraction, **4a** (2 mg) obtained from the glycosidic acid fraction, **5a** (1 mg), and **6** (3 mg) in pyridine (0.5 ml) and CCl_4 (5 drops) and left to stand at room temperature overnight. The solvent was removed under an N_2 stream to give a residue. The residue was purified by chromatography over a silica gel column [solvent, benzene–AcOEt (10 : 1→8 : 1→5 : 1→2 : 1)] to give (−)-MTPA ester of **3** (**3a**, 4 mg) from **3**, (−)-MTPA ester of **3′** (**3′a**, 4 mg) from **3′**, (−)-MTPA ester of **4a** (**4b**, 3 mg) from **4a** obtained from the organic acid fraction, **4b** (3 mg) from **4a** obtained from the glycosidic acid fraction, (−)-MTPA ester of **5a** (**5b**, 1 mg) from **5a**, and (−)-MTPA ester of **6** (**6a**, 5 mg) from **6**, respectively.

3a: Syrup. ^{1}H-NMR (in $CDCl_3$, 600 MHz) δ: 1.240 (3H, d, *J*=7.5 Hz, H_3-5), 1.434 (3H, d, *J*=6.0 Hz, H_3-4), 2.928 (1H, dq, *J*=7.5, 7.5 Hz, H-2), 3.555 (3H, d-like, *J*=1.0 Hz, OCH_3), 5.055 (1H, d, *J*=16.5 Hz, OCH_2CO), 5.121 (1H, d, *J*=16.5 Hz, OCH_2CO), 5.459 (1H, dq, *J*=7.5, 6.0 Hz, H-3).

3′a: Syrup. ^{1}H-NMR (in $CDCl_3$, 400 MHz) δ: 1.240 (d, *J*=7.5 Hz, H_3-5 of *R*,*R*-form), 1.302 (*J*=7.5 Hz, H_3-5 of *S*,*S*-form), 1.356 (d, *J*=7.5 Hz, H_3-4 of *S*,*S*-form), 1.434 (d, *J*=7.5 Hz, H_3-4 of *R*,*R*-form), 2.928 (1H, dq, *J*=7.5, 7.5 Hz, H-2 of *R*,*R*-form), 2.960 (1H, dq, *J*=7.5, 7.5 Hz, H-2 of *S*,*S*-form), 3.512 (d-like, *J*=1.0 Hz, OCH_3 of *S*,*S*-form), 3.555 (3H, d-like, *J*=1.0 Hz, OCH_3 of *R*,*R*-form), 5.055 (1H, d-like, *J*=16.5 Hz, OCH_2CO of *R*,*R*-form), 5.121 (1H, d, *J*=16.5 Hz, OCH_2CO of *R*,*R*-form), 5.180 (1H, d, *J*=16.5 Hz, OCH_2CO of *S*,*S*-form), 5.252 (d, *J*=16.5 Hz, OCH_2CO of *S*,*S*-form), 5.460 (m, H-3 of *R*,*R*- and *S*,*S*-form).

4b: Syrup. ^{1}H-NMR (in $CDCl_3$, 600 MHz) δ: 0.850 (3H, t, *J*=7.5 Hz, H_3-10), 2.285 (2H, t, *J*=7.5 Hz, H_2-2), 3.545 (3H, d-like, *J*=1.0 Hz, OCH_3), 3.664 (3H, s, $COOCH_3$), 5.092 (1H, m, H-7).

5b: Syrup. ^{1}H-NMR (in $CDCl_3$, 600 MHz) δ: 0.840 (3H, t, *J*=7.0 Hz, H_3-12), 2.287 (2H, t, *J*=7.5 Hz, H_2-2), 3.550 (3H, d-like, *J*=1.0 Hz, OCH_3), 3.666 (3H, s, $COOCH_3$), 5.077 (1H, m, H-7).

6a: Syrup. ^{1}H-NMR (in $CDCl_3$, 600 MHz) δ: 0.855 (3H, t, *J*=7.5 Hz, H_3-14), 2.602 (1H, dd, *J*=4.5, 16.0 Hz, Ha-2), 2.692 (1H, dd, *J*=8.0, 16.0 Hz, Hb-2), 3.540 (3H, q, *J*=1.0 Hz, OCH_3), 3.550 (3H, q, *J*=1.0 Hz, OCH_3), 3.659 (3H, s, $COOCH_3$), 5.093 (1H, m, H-11), 5.465 (1H, m, H-3).

Preparation of (+)-MTPA Esters of 4a and 5a (+)-MTPACl (15 mg) was added to individual solutions of **4a** (2 mg) and **5a** (1 mg) in pyridine (0.5 ml) and CCl_4 (5 drops), and treated in the same way as in the case of the preparation of (−)-MTPA esters to give the (+)-MTPA ester of **4a** (**4c**, 2 mg) from **4a** and (+)-MTPA ester of **5a** (**5c**, 1 mg) from **5a**, respectively.

4c: Syrup. ^{1}H-NMR (in $CDCl_3$, 600 MHz) δ: 0.917 (3H, t, *J*=7.5 Hz, H_3-10), 2.243 (2H, t, *J*=7.5 Hz, H_2-2), 3.560 (3H, s like, OCH_3), 3.663 (3H, s, $COOCH_3$), 5.089 (1H, m, H-7).

5c: Syrup. ^{1}H-NMR (in $CDCl_3$, 600 MHz) δ: 0.876 (3H, t, *J*=7.0 Hz, H_3-12), 2.245 (2H, t, *J*=7.5 Hz, H_2-2), 3.559 (3H, d-like, *J*=1.0 Hz, OCH_3), 3.664 (3H, s, $COOCH_3$), 5.076 (1H, m, H-7).

Isolation of 7—11 The glycosidic acid fraction (4.29 g) was chromatographed over silica gel column [solvent, $CHCl_3$–MeOH–H_2O (7 : 3 : 0.5→6 : 4 : 1→0 : 0 : 1)] to afford fr. 7 (0.66 g) and fr. 8 (2.50 g). Fr. 7 (0.66 g) in MeOH (3 ml) was methylated with diazomethane–ether. The concentrated reaction mixture was chromatographed over a silica gel column [solvent, $CHCl_3$–MeOH–H_2O (14 : 2 : 0.05→0 : 1 : 0)] to give fr. 9 (426 mg) and fr. 10 (180 mg). Fr. 9 was subjected to HPLC [column, Kusano C.I.G. Si, 22 mm i.d.×30 cm; solvent, *n*-hexane–AcOEt (1 : 4)] to furnish the methyl ester (**7**, 326 mg) of quamoclinic acid B and fr. 11 (38 mg). Fr. 8 was dissolved in 1,4-dioxane–H_2O (3 : 1, 40 ml) and neutralized with triethylamine, and then the solvent was removed. A mixture of the residue and phenacylbromide (0.8 g) in dimethylformamide (50 ml) was heated at 90 °C for 2.5 h. The mixture was concentrated to dryness, and the residue was chromatographed over a silica gel column [solvent, $CHCl_3$–MeOH–H_2O (8 : 2 : 0.2→7 : 3 : 0.5→6 : 4 : 1→0 : 1 : 0)] to afford fr. 12 (720 mg), fr. 13 (1878 mg), fr. 14 (261 mg), and fr. 15 (241 mg). Fr. 13 was subjected to HPLC [column, Kusano C.I.G. Si, 22 mm i.d.×30 cm; solvent,

Table 3. ^{1}H-NMR Spectral Data for **10a** and **11a** (in Pyridine-d_5, 600 MHz)

	10a	**11a**		**10a**	**11a**
Fuc-1	4.72 d (7.5)	4.82 d (7.5)	Fuc′-1	5.62 d (7.5)	
2	4.44 dd (7.5, 9.5)	*ca.* 4.50	2	4.25 dd (7.5, 9.5)	
3	4.39 dd (3.5, 9.5)	*ca.* 4.50	3	4.21 dd (3.5, 9.5)	
4	4.04 d (3.5)	*ca.* 4.08	4	3.98 d (3.5)	
5	3.78 q (6.0)	*ca.* 3.93	5	*ca.* 4.07	
6	1.41 d (6.0)	1.43 d (6.0)	6	1.52 d (6.0)	
Glc-1	5.52 d (7.0)	5.64 d (7.5)	Qui′-1	5.13 d (8.0)	5.00 d (7.5)
2	4.13 dd (7.0, 9.0)	*ca.* 4.20	2	*ca.* 4.09	*ca.* 4.05
3	*ca.* 4.11	4.15 dd (9.0, 9.0)	3	3.91 dd (9.0, 9.0)	*ca.* 4.08
4	4.04 dd (9.0, 9.0)	*ca.* 4.06	4	3.52 dd (9.0, 9.0)	3.59 dd (9.0, 9.0)
5	3.60 ddd (3.0, 5.5, 9.0)	3.63 ddd (3.0, 5.0, 9.0)	5	3.69 dd (9.0, 6.0)	3.74 dq (9.0, 6.0)
6	4.28 dd (3.0, 11.5)	4.30 dd (3.0, 11.0)	6	1.60 d (6.0)	1.71 d (6.0)
	4.17 dd (5.5, 11.5)	*ca.* 4.19	Fuc″-1	4.98 d (7.5)	
Rha-1	6.22 d (1.5)	6.30 d (2.0)	2	4.36 dd (7.5, 9.5)	
2	4.95 dd (1.5, 3.5)	4.92 dd (2.0, 3.0)	3	4.07 dd (3.0, 9.5)	
3	5.12 dd (3.5, 9.5)	5.19 dd (3.0, 9.5)	4	4.00 d (3.0)	
4	4.67 dd (9.5, 9.5)	4.73 dd (9.5, 9.5)	5	3.84 q (6.5)	
5	4.94 dq (9.5, 6.0)	5.02 dq (9.5, 6.0)	6	1.48 d (6.5)	
6	1.89 d (6.0)	1.94 d (6.0)	Rha′-1		6.05 d (1.5)
Glc′-1	5.93 d (7.5)	6.10 d (8.0)	2		4.64 dd (1.5, 3.5)
2	3.97 dd (7.5, 9.0)	*ca.* 3.93	3		4.47 dd (3.5, 9.5)
3	4.35 dd (9.0, 9.0)	4.40 dd (9.0, 9.0)	4		4.27 dd (9.5, 9.5)
4	*ca.* 4.11	4.10 dd (9.0, 9.0)	5		4.90 dq (9.5, 6.0)
5	3.94 ddd (2.0, 6.0, 9.0)	4.00 ddd (2.0, 6.0, 9.0)	6		1.65 d (6.0)
6	4.41 dd (2.0, 12.5)	*ca.* 4.49	Ag-2	2.89 dd (7.5, 15.0)	2.89 dd (8.0, 15.0)
	4.16 dd (6.0, 12.5)	*ca.* 4.18		2.86 dd (5.0, 15.0)	2.86 dd (5.0, 15.0)
Qui-1		5.81 d (7.5)	3	4.54 m	4.55 m
2		3.95 dd (7.5, 9.0)	11	3.84 m	3.87 m
3		4.25 dd (9.0, 9.0)	14	0.90 t (7.0)	0.89 t (7.0)
4		3.68 dd (9.0, 9.0)			
5		*ca.* 4.05			
6		1.60 d (6.0)			

δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses). Fuc, fucopyranosyl; Glc, glucopyranosyl; Rha, rhamnopyranosyl; Qui, quinovopyranosyl; Ag, aglycone.

$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5)] to give fr. 16 (40 mg), fr. 17 (92 mg), fr. 18 (449 mg), the phenacyl ester (**10**, 212 mg) of quamoclinic acid E, and fr. 19 (111 mg). Preparative HPLC (column, Inertsil ODS, 20 mm i.d.×25 cm; solvent, 75% MeOH) of fr. 18 (449 mg) yielded the phenacyl ester (**9**, 49 mg) of quamoclinic acid D, the phenacyl ester (**11**, 90 mg) of quamoclinic acid F, and the phenacyl ester (**8**, 209 mg) of quamoclinic acid C.

Preparation of 7a—11a Compounds **7** (30 mg), **8** (100 mg), **9** (49 mg), **10** (100 mg), and **11** (90 mg) were each heated with 1 M KOH (3 ml) at 95 °C for 1 h. After cooling, the mixture was acidified (pH 3) with 1 M HCl and then extracted with ether (3 ml×3). The aqueous layer was subjected to MCI gel CHP 20 (solvent, H_2O→acetone) to give quamoclinic acid B (**7a**, 26 mg) from **7**, quamoclinic acid C (**8a**, 80 mg) from **8**, quamoclinic acid D (**9a**, 39 mg) from **9**, quamoclinic acid E (**10a**, 87 mg) from **10**, and quamoclinic acid F (**11a**, 79 mg) from **11**, respectively.

7a: Syrup, $[\alpha]_D^{16}$ −40.5° (c=2.5, MeOH). Negative-ion FAB-MS m/z: 333 $[M-H]^-$, 187 $[333-146]^-$. HR-negative-ion FAB-MS m/z: 333.1909 (Calcd for $C_{16}H_{29}0_7$: 333.1914). ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 0.91 (3H, t, J=7.0 Hz, H_3-10 of Ag), 1.39 (2H, m, H_2-4 of Ag), 1.61 (3H, d, J=6.5 Hz, H_3-6 of Qui), 1.77 (2H, tt, J=7.5, 7.5 Hz, H_2-3 of Ag), 2.48 (2H, t, J=7.5 Hz, H_2-2 of Ag), 3.70 (1H, dd, J=9.0, 9.0 Hz, H-4 of Qui), 3.76 (1H, dq, J=9.0, 6.5 Hz, H-5 of Qui), 3.88 (1H, m, H-7 of Ag), 3.95 (1H, dd, J=7.5, 9.0 Hz, H-2 of Qui), 4.13 (1H, dd, J=9.0, 9.0 Hz, H-3 of Qui), 4.79 (1H, d, J=7.5 Hz, H-1 of Qui). ^{13}C-NMR (in pyridine-d_5, 125 MHz) δ: 14.3 (C-10 of Ag), 18.7 (C-6 of Qui), 18.8, 25.2, 25.6, 29.9, 34.7, 34.9, 37.7, 72.7 (C-5 of Qui), 75.6 (C-2 of Qui), 76.9 (C-4 of Qui), 78.3 (C-3 of Qui), 78.6 (C-7 of Ag), 103.4 (C-1 of Qui), 176.1 (C-1 of Ag).

8a: White powder, $[\alpha]_D^{22}$ −33.3° (c=1.0, MeOH). Negative-ion FAB-MS m/z: 1167 $[M-H]^-$, 1021 $[1167-146]^-$, 859 $[1021-162]^-$, 713 $[859-146]^-$, 567 $[859-2\times146]^-$, 405 $[567-162]^-$. ^{1}H-NMR δ: see Table 1. ^{13}C-NMR δ: see Table 2. $J_{C\text{-}1\text{–}H\text{-}1}$ (Hz): Fuc (156.7), Glc (166.8), Glc′ (166.8), Qui (164.8), Qui′ (156.7), Rha (172.9). *Anal*. Calcd for $C_{50}H_{88}O_{30}$: C, 51.36; H, 7.59. Found: C, 51.22; H, 7.78.

9a: White powder, $[\alpha]_D^{22}$ −29.5° (c=1.0, MeOH). Negative-ion FAB-MS m/z: 1167 $[M-H]^-$, 1021 $[1167-146]^-$, 859 $[1021-146]^-$, 713 $[859-146]^-$, 567 $[713-146]^-$, 405 $[567-162]^-$. ^{1}H-NMR δ: see Table 1. ^{13}C-NMR δ: see Table 2. $J_{C\text{-}1\text{–}H\text{-}1}$ (Hz): Fuc (159.0), Fuc′ (162.0), Glc (163.8), Glc′ (162.7), Qui′ (162.7), Rha (174.0). *Anal*. Calcd for $C_{50}H_{88}O_{30}\cdot H_2O$: C, 50.58; H, 7.44. Found: C, 50.55; H, 7.48.

10a: White powder, $[\alpha]_D^{22}$ −28.5° (c=1.0, MeOH). Negative-ion FAB-MS m/z: 1313 $[M-H]^-$, 1167 $[1313-146]^-$, 1021 $[1167-146]^-$, 859 $[1021-162]^-$, 713 $[859-146]^-$, 567 $[713-146]^-$, 405 $[567-162]^-$, 259 $[405-146]^-$. ^{1}H-NMR δ: see Table 3. ^{13}C-NMR δ: see Table 2. $J_{C\text{-}1\text{–}H\text{-}1}$ (Hz): Fuc (156.7), Fuc′ (158.7), Fuc″-1 (158.7), Glc (162.8), Glc′ (162.8), Qui′ (158.7), Rha (173.0). *Anal*. Calcd for $C_{56}H_{98}O_{34}\cdot 1/2H_2O$: C, 50.79; H, 7.46. Found: C, 50.83; H, 7.59.

11a: White powder, $[\alpha]_D^{17}$ −42.2° (c=1.0, MeOH). Negative-ion FAB-MS m/z: 1313 $[M-H]^-$, 1167 $[1313-146]^-$, 1021 $[1167-146]^-$, 859 $[1021-162]^-$, 567 $[859-146\times2]^-$, 405 $[567-162]^-$, 259 $[405-146]^-$. ^{1}H-NMR δ: see Table 3. ^{13}C-NMR δ: see Table 2. $J_{C\text{-}1\text{–}H\text{-}1}$ (Hz): Fuc (159.7), Glc (162.8), Glc′ (162.8), Qui (168.9), Qui′ (158.7), Rha (173.0), Rha′ (168.9). Calcd for $C_{56}H_{98}O_{34}$: C, 51.14; H, 7.51. Found: C, 51.11; H, 7.71.

Acidic Hydrolysis of 7 and 8a—11a Compounds **7** (8 mg), **8a** (10 mg), **9a** (11 mg), **10a** (10 mg), and **11a** (6 mg) were each heated with 1 M HCl (1 ml) at 95 °C for 1 h. The reaction mixture was diluted with H_2O (5 ml) and extracted with ether (3 ml×3). The extract was dried over $MgSO_4$ and concentrated *in vacuo* to give a residue. The residue was treated with diazomethane–ether and subjected to GC [column, 3.2 mm i.d.×2.0 m glass column packed with Silicone OV-17 Uniport HP 80/100; carrier gas N_2, 1.5 kg/cm^2; temperature, 140 °C; t_R (min): 4.95 (methyl 7-hydroxydecanoate) from **7**; temperature, 190 °C; t_R (min): 7.66 (methyl ipurolate) from **8a**—**11a**].

The aqueous layer was neutralized with 1 M KOH, and the mixture was evaporated. Desalting of the residue with chromatography on a Sephadex LH-20 column (solvent, MeOH) followed by evaporation gave a monosaccharide fraction (3—8 mg) that was analyzed using TLC (condition 1). The *Rf* value of the monosaccharide fraction of **7** was identical to that of D-

quinovose, and those of the monosaccharide fractions of **8a**—**11a** were each identical to those of D-glucose, D-fucose, L-rhamnose, and/or D-quinovose. The monosaccharide fraction (3—4 mg) was subjected to GC analysis (condition 2) as the trimethylsilyl ethers of the thiazolidine derivative, as reported by Hara *et al.*[6] The t_R of the product of **7** was identical to that of the D-quinovose derivative, and those of the products for **8a**—**11a** were each identical to those of the derivatives of L-rhamnose, D-fucose, D-glucose, and D-quinovose.

Acetylation of 8 Compound **8** (8 mg) was dissolved in Ac_2O–pyridine (1 : 1, 1 ml), and the solution was left to stand at room temperature overnight. After removal of the reagent under an N_2 stream, the residue was partitioned between ether (1 ml×5) and H_2O (0.5 ml). The ether layer was concentrated *in vacuo* to afford the acetate of **8** (**8b**, 9 mg).

8b: White powder, ^{1}H-NMR δ: see Table 1.

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