Five New Resin Glycoside Derivatives Isolated from the Convolvulin Fraction of Seeds of *Quamoclit pennata* after Treatment with Indium(III) Chloride in Methanol

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Three new acetylated methyl glycosides and two new acetylated glycosidic acid methyl esters were isolated after treatment of the crude ether-insoluble resin glycoside (convolvulin) fraction from seeds of *Quamoclit pennata* Bojer (Convolvulaceae) with indium(III) chloride in methanol. Their structures were elucidated on the basis of spectroscopic data and chemical conversions.

Key words resin glycoside; convolvulin; *Quamoclit pennata*; Convolvulaceae; acetylated methyl glycoside; acetylated glycosidic acid methyl ester

Resin glycosides, well known as purgatives, are commonly found in plants of the Convolvulaceae family. These glycosides are characteristic ingredients of crude drugs such as *Pharbitis Semen*, Mexican Scammoniae Radix, Orizabae Tuber, Jalapae Tuber, and Rhizoma Jalapae Brazilianis. They can be roughly divided into an ether-soluble resin glycoside called jalapalin and an ether-insoluble one called convolvulin. Almost all jalapalins hitherto isolated and characterized are referred to tropical regions of South America and are primarily cultivated as Pharbitis Semen, Mexican Scammoniae Radix, Orizabae Tuber, Jalapae Tuber, and Rhizoma Jalapae Brazilianis. They can be roughly divided into an ether-soluble resin glycoside called jalapalin and an ether-insoluble one called convolvulin. Almost all jalapalins hitherto isolated and characterized have common macrolactone structures composed of an oligo-glycoside of a hydroxy fatty acid partially acylated by certain organic acids at the sugar moiety (acylated glycosidic acid); some examples are ester-type dimers. On the other hand, convolvulins are regarded as oligomers of various acylated glycosidic acids. However, no genuine convolvulin has thus far been isolated.

*Quamoclit pennata* Bojer is a Convolvulaceae plant native to tropical regions of South America and is primarily cultivated as an ornamental plant. We earlier reported the isolation and structural elucidation of a glycosidic acid called quamoclinic acid A along with 2S-methylbutyric, n-decanoic, and n-dodecanoic acids, upon alkaline hydrolysis of the crude jalapalin fraction of the seeds of the plant. Furthermore, we isolated six genuine jalapalins, quamoclins I, II, III, IV, V, and VI from the same fraction. On the other hand, we reported the structures of seven glycosidic acids, quamoclinic acids B, C, D, E, F, G, and H along with isobutyric, 2S-hydroxydodecanoic acids, upon alkaline hydrolysis of the crude jalapalin fraction of the seeds. Despite numerous attempts, isolation of pure resin glycosides from the crude convolvulin fraction of the seeds of *Q. pennata* has been unsuccessful, until now. Previous results suggested that resin glycosides in the crude convolvulin fraction possessed at least one carboxyl group. Hence, this fraction was treated with indium(III) chloride in methanol (MeOH), which has been reported by Mineno and Kansui to be a suitable catalyst for the mild methyl esterification of carboxylic acids. The fraction yielded a number of separate spots on TLC (silica gel) plate after treatment with InCl$_3$–MeOH. Previously, we reported the isolation and structural elucidation of three acylated glycosidic acid methyl esters, QM-1–QM-3, and two acetylated methyl glycosides, QM-4 and QM-5, from the above fraction. As part of an ongoing study of the resin glycoside of the seeds of *Q. pennata*, this report details the isolation and structural elucidation of three new acetylated methyl glycosides and two new acetylated glycosidic acid methyl esters from the above-mentioned treated fraction.

The crude convolvulin fraction after treatment with InCl$_3$–MeOH was successively subjected to Diaion HP20, Sephadex LH-20, silica gel, and Chromatorex octadecyl silica (ODS) column chromatography as well as HPLC on ODS and silica gel columns to afford five compounds, referred to as QM-6 (I)–QM-10 (5).

QM-6 (I) was obtained as an amorphous powder and exhibited an [M+H]$^+$ ion peak at m/z 1583 in negative-ion FAB-MS and an [M+Na]$^+$ ion peak at m/z 1607 in positive-ion FAB-MS. The molecular formula of I was determined as C$_{69}$H$_{116}$O$_{40}$ on the basis of high-resolution (HR)-positive-ion FAB-MS. The 1H-NMR spectrum of I indicated signals due to one H-2 of the niloyl residue [δ 2.96 (1H, dq, J = 7.0, 7.0 Hz)], one H-3 of the tigloyl residue [δ 7.09 (1H, qq, J = 1.5, 7.0 Hz)], one methoxy group [δ 3.29 (3H, s)], eight anomic protons [δ 6.14 (1H, s), 6.11 (1H, s), 6.01 (1H, d, J = 8.0 Hz), 5.93 (1H, d, J = 7.5 Hz), 5.31 (1H, d, J = 3.0 Hz), 5.20 (1H, d, J = 8.0 Hz), 4.91 (1H, d, J = 8.0 Hz), 4.79 (1H, d, J = 8.0 Hz)], two nonequivalent methylene protons [δ 2.46 (1H, ddd, J = 8.0, 8.0, 16.0 Hz), 2.40 (1H, ddd, J = 8.0, 8.0, 16.0 Hz)] adjacent to a carbonyl group, one tertiary methyl group [δ 2.00 (3H, br)] assigneable to H$_2$-5 of the tigloyl residue, nine secondary methyl groups [δ 1.80 (3H, d, J = 6.0 Hz), 1.75 (3H, d, J = 7.0 Hz), 1.62 (1H, d, J = 6.0 Hz), 1.60 (3H, d, J = 6.5 Hz), 1.60 (3H, d, J = 6.0 Hz), 1.55 (3H, d, J = 6.0 Hz), 1.45 (3H, d, J = 6.5 Hz), 1.39 (3H, d, J = 7.0 Hz), 1.38 (3H, d, J = 7.0 Hz), and one primary methyl group [δ 0.95 (3H, t, J = 7.0 Hz)]. The $^{13}$C-NMR spectrum exhibited signals due to three carboxyl...
carbons ($\delta$ 175.3, 173.4, 167.2), two olefinic carbons ($\delta$ 138.1, 128.9), and eight anomeric carbons ($\delta$ 106.6, 104.7, 103.3, 102.2, 101.8, 101.6, 100.8, 97.9). The $^1$H- and $^{13}$C-NMR signals were assigned on the basis of $^1$H–$^1$H correlation spectroscopy (COSY), heteronuclear multiple-quantum coherence (HMQC), and heteronuclear multiple-bond correlation (HMBC) spectra.

Table 1. $^1$H-NMR Spectral Data for 1, 7, and 9 (in Pyridine-$d_5$, 500 MHz)

| Position | 1          | 7          | 9          |
|----------|------------|------------|------------|
| Fuc-1    | 5.31 d (3.0)| 5.33 d (3.5)| 5.33 d (3.5)|
| 2        | 4.45$^{a}$  | 4.50 dd (3.5, 10.0)| 4.46 dd (3.5, 10.0)|
| 3        | 4.57 dd (3.0, 10.0)| 4.56 dd (3.0, 10.0)| 4.58$^{a}$  |
| 4        | 4.06 d (3.0) | 4.06$^{a}$  | 4.06$^{a}$  |
| 5        | 4.04$^{a}$  | 4.01 q (7.0) | 4.00$^{a}$  |
| 6        | 1.39 d (7.0) | 1.42 d (7.0) | 1.39 d (7.0) |
| Glc-1    | 4.91 d (8.0) | 4.99 d (7.5) | 4.93$^{a}$  |
| 2        | 4.14 dd (8.0, 9.5) | 4.10$^{a}$  | 4.16$^{a}$  |
| 3        | 4.03$^{a}$  | 4.09$^{a}$  | 4.03$^{a}$  |
| 4        | 4.05$^{a}$  | 4.09$^{a}$  | 4.06$^{a}$  |
| 5        | 3.56 m      | 3.63$^{a}$  | 3.58 ddd (3.5, 5.5, 9.0) |
| 6        | 4.33$^{a}$  | 4.36$^{a}$  | 4.35$^{a}$  |
| Glc'-1   | 5.93 d (7.5) | 5.96 d (8.0) | 6.06 d (8.0) |
| 2        | 3.96$^{a}$  | 3.92 dd (8.0, 9.0) | 3.99$^{a}$  |
| 3        | 4.29 dd (9.0, 9.0) | 4.35 dd (9.0, 9.0) | 4.36$^{a}$  |
| 4        | 4.05$^{a}$  | 4.11$^{a}$  | 4.06$^{a}$  |
| 5        | 3.81$^{a}$  | 3.88 ddd (2.5, 6.0, 9.0) | 3.91$^{a}$  |
| 6        | 4.32$^{a}$  | 4.36$^{a}$  | 4.36$^{a}$  |
| Rha-1    | 6.14 s      | 6.17 d (1.5) | 6.20 d (1.5) |
| 2        | 6.07 brs    | 4.92$^{a}$  | 6.03 dd (1.5, 3.5) |
| 3        | 5.34 dd (3.5, 9.0) | 5.16 dd (3.0, 9.0) | 5.43 dd (3.5, 9.0) |
| 4        | 5.00 dd (9.0, 9.0) | 4.70 dd (9.0, 9.0) | 4.56 dd (9.0, 9.0) |
| 5        | 4.94 dq (9.0, 6.0) | 4.90$^{a}$  | 4.93$^{a}$  |
| 6        | 1.80 d (6.0) | 1.87 d (6.5) | 1.85 d (6.0) |
| Rha'-1   | 6.11 s      | 6.07 d (1.0) | 6.09 d (1.0) |
| 2        | 4.39$^{a}$  | 4.65 dd (1.0, 3.5) | 4.56$^{a}$  |
| 3        | 4.30$^{a}$  | 4.48 dd (3.5, 9.0) | 4.33$^{a}$  |
| 4        | 4.16$^{a}$  | 4.28 dd (9.0, 9.0) | 4.19 dd (9.5, 9.5) |
| 5        | 4.13$^{a}$  | 4.92$^{a}$  | 4.16$^{a}$  |
| 6        | 1.55 d (6.0) | 1.66 d (6.0) | 1.57 d (6.0) |
| Qui-1    | 6.01 d (8.0) | 5.80 d (8.0) | 5.90 d (7.5) |
| 2        | 3.97$^{a}$  | 3.95 dd (8.0, 9.0) | 3.97$^{a}$  |
| 3        | 4.45$^{a}$  | 4.28 dd (9.0, 9.0) | 4.29 dd (9.0, 9.0) |
| 4        | 5.37 dd (9.5, 9.5) | 3.69 dd (9.0, 9.0) | 3.72$^{a}$  |
| 5        | 4.39$^{a}$  | 4.08$^{a}$  | 4.17$^{a}$  |
| 6        | 1.62 d (6.0) | 1.58 d (6.5) | 1.69 d (6.5) |
| Qui'-1   | 5.20 d (8.0) | 5.03 d (7.5) | 5.16 d (8.0) |
| 2        | 4.20 dd (8.0, 9.5) | 4.08$^{a}$  | 4.04$^{a}$  |
| 3        | 4.40 dd (9.5, 9.5) | 4.09$^{a}$  | 4.39 dd (9.0, 9.0) |
| 4        | 5.37 dd (9.5, 9.5) | 3.64 dd (9.0, 9.0) | 5.37 dd (9.0, 9.0) |
| 5        | 4.02$^{a}$  | 3.74 dq (9.0, 6.0) | 4.01$^{a}$  |
| 6        | 1.60 d (6.5) | 1.72 d (6.0) | 1.63 d (6.0) |
| Nia-2    | 2.96 dq (7.0, 7.0) | 2.97 dq (7.0, 7.0) | 2.97 dq (7.0, 7.0) |
| 4        | 4.38$^{a}$  | 4.38$^{a}$  | 4.38$^{a}$  |
| 5        | 1.38 d (7.0) | 1.38 d (7.0) | 1.38 d (7.0) |
| Tig-3    | 7.09 q (7.0) | 7.10 qq (1.5, 7.0) | 7.10 qq (1.5, 7.0) |
| 4        | 1.75 d (7.0) | 1.76 d (7.0) | 1.76 d (7.0) |
| 5        | 2.00 brs    | 2.02 brs    | 2.02 brs    |
| Hda-2    | 2.46 ddd (8.0, 8.0, 16.0) | 2.47 ddd (8.0, 8.0, 16.0) | 2.47 ddd (8.0, 8.0, 16.0) |
| 2        | 2.40 ddd (8.0, 8.0, 16.0) | 2.45$^{a}$  | 2.45$^{a}$  |
| 7        | 3.89 m      | 3.90$^{a}$  | 3.90$^{a}$  |
| 10       | 0.95 t (7.0) | 0.95 t (7.0) | 0.95 t (7.0) |
The spectral data indicated that 1 is a methyl heptaglycoside acylated by 1 mol each of nicic acid, tiglic acid, and quamocline acid B (6) (Tables 1, 2). The alkaline hydrolysis of 1 furnished a methyl heptaglycoside (7), temporarily referred to as methyl quamoside B, along with nicic acid, tiglic acid, and 6. The negative-ion FAB-MS of 7 exhibited an [M–H] − ion peak at \( m/z \) 1085 along with fragment ion peaks at \( m/z \) 939 [1085−46 (methylpentosyl unit)], 793 [939−162 (hexosyl unit)], and 339 [631−146×2]. Upon acidic hydrolysis, 7 afforded a monosaccharide fraction, which was converted into thiocarbamoyl-thiazolidine derivatives and then analyzed using HPLC, according to a procedure reported by Tanaka et al. Derivatives of D-glucose, D-fucose, D-qinovose, and L-rhamnose were detected. The 1H- and 13C-NMR spectra of 7 were quite similar to those of methyl quamoside A (8), except for the appearance of additional signals due to one

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### Table 1. 13C-NMR Spectral Data for 1–3, 7, and 9 (in Pyridine-\(d_5\), 125 MHz)

| Position | 1       | 7       | 9       |
|----------|---------|---------|---------|
| Fuc-1    | 100.8   | 100.8   | 100.9   |
| 2        | 79.2    | 79.2    | 79.5    |
| 3        | 70.0    | 70.0    | 70.0    |
| 4        | 73.0    | 73.0    | 73.2    |
| 5        | 66.5    | 66.5    | 66.5    |
| 6        | 16.8    | 16.9    | 16.9    |
| Glc-1    | 104.7   | 104.9   | 104.8   |
| 2        | 77.6    | 77.9    | 77.9    |
| 3        | 78.3    | 78.4    | 78.5    |
| 4        | 71.6    | 71.5    | 71.6    |
| 5        | 77.8    | 77.9    | 78.0    |
| 6        | 62.4    | 62.5    | 62.4    |
| Glc′-1   | 101.8   | 101.6   | 101.7   |
| 2        | 86.1    | 84.8    | 85.8    |
| 3        | 77.4    | 77.4    | 77.4    |
| 4        | 71.2    | 71.7    | 71.7    |
| 5        | 78.1    | 78.6    | 78.4    |
| 6        | 62.3    | 62.4    | 62.5    |
| Rha-1    | 97.9    | 101.4   | 97.8    |
| 2        | 73.8    | 71.6    | 73.8    |
| 3        | 75.9    | 78.4    | 75.6    |
| 4        | 78.5    | 79.1    | 79.0    |
| 5        | 67.9    | 68.8    | 68.3    |
| 6        | 18.7    | 18.8    | 18.7    |
| Rha′-1   | 102.2   | 102.6   | 102.3   |
| 2        | 72.2    | 72.2    | 72.3    |
| 3        | 73.6    | 73.8    | 73.8    |
| 5        | 69.8    | 69.8    | 70.1    |
| 6        | 18.6    | 18.5    | 18.7    |
| Qui-1    | 101.6   | 102.6   | 102.0   |
| 2        | 76.2    | 76.4    | 76.3    |
| 3        | 75.2    | 78.1    | 78.2    |
| 4        | 77.4    | 77.3    | 77.3    |
| 5        | 69.9    | 72.3    | 72.3    |
| 6        | 18.1    | 18.5    | 18.4    |

\( \delta \) in ppm from tetramethylsilane (TMS). Coupling constants (\( J \)) in Hz are given in parentheses. a) Signals were overlapped with other signals.

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### Table 2. 1H-NMR Spectral Data for 1–3, 7, and 9 (in Pyridine-\(d_5\), 500 MHz)

| Position | 1       | 7       | 9       |
|----------|---------|---------|---------|
| Qui-1    | 4.79 d (8.0) | 4.81 d (8.0) |
| 2        | 3.96 d   | 3.97 d   |
| 3        | 4.14 dd (9.0, 9.0) | 4.15 dd (9.0, 9.0) |
| 4        | 3.71 dd (9.0, 9.0) | 3.72 d   |
| 5        | 3.78 dq (9.0, 6.0) | 3.79 dq (9.0, 6.0) |
| 6        | 1.60 d (6.0) | 1.64 d (6.0) |
| OCH₃     | 3.29 s   | 3.29 s   | 3.29 s   |

\( \delta \) in ppm from tetramethylsilane (TMS).
terminal α-L-rhamnopyranosyl residue (Rha') and glycosylation shifts (Δδ = Δδ - δ8) of signals due to C-2 (Δδ = 0.5), C-3 (Δδ = 4.9), and C-4 (Δδ = -1.7) of the second quinovosyl residue (Qui'). In addition, the HMBC spectrum of 7 showed a key cross-peak between H-1 of Rha' and C-3 of Qui'. From these data, the structure of 7 was assigned as methyl α-L-rhamnopyranosyl-(1→3)-O-β-D-quinovopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranoside (Fig. 1).

Comparison of the 1H-NMR spectra of 1 and 7 indicated remarkable downfield shifts (Δδ = δ1 - δ7) of signals due to H-2 (Δδ = 1.15) of the first rhamnosyl residue (Rha), H-4 (Δδ = 1.68) of the first quinovosyl residue (Qui), and H-4 (Δδ = 1.73) of Qui' of 1, owing to acylation. In addition, the HMBC spectrum of 1 showed cross-peaks between the methoxy protons and C-1 of the first fucosyl residue (Fuc); H-1 of the first glucosyl residue (Glc) and C-2 of Fuc; H-1 of the second glucosyl residue (Glc') and C-3 of Rha; H-1 of Qui and C-4 of Rha; H-1 of Qui' and C-2 of Glc'; H-1 of Rha' and C-3 of Qui'; H-1 of the third quinovosyl residue (Qui'') and C-7 of 7S-hydroxydecanoyl residue (Hda; the aglycone moiety of quamoclinic acid B residue (QaB)) (22); H-4 of Qui or H-4 of Qui' and C-1 of the first niloyl residue (Nla); and H-4 of Qui' or H-4 of Qui and C-1 of the first tigloyl residue (Tig) (Fig. 2). However, the counterparts of C-1 of Nla and C-1 of Tig could not be defined because the 1H-NMR peaks due to H-4 of Qui and H-4 of Qui' heavily overlapped. Although no cross-peak between H-2 of Rha and C-1 of Hda was observed in the HMBC spectrum of 1, the above data suggested that QaB was attached to OH-2 of Rha.

To determine the sites of each ester linkage of nilic acid and tiglic acid, partial deacylation of 1 was conducted. Compound 1 was refluxed with 5% triethylamine–MeOH for 1 h, and the products were purified by HPLC to give 9. The positive-ion FAB-MS of 9 exhibited an [M+Na]+ ion peak at m/z 1507, 100 mass units (niloyl residue) less than that of 1. The 1H-NMR spectrum of 9 showed upfield shift (1.65 ppm) of the signal due to H-4 of Qui as compared to that of 1, along with disappearance of the signals due to the niloyl residue, whereas the signals owing to H-4 of Qui' and H-2 of Rha were observed at similar chemical shifts (Table 1). These data suggested that Nla and Tig of 1 were located at OH-4 of Qui and OH-4 of Qui', respectively. The absolute configuration of the nilic acid residue in this crude convolvulin fraction has been previously determined as 2R,3R (12). Accordingly, the structure of 1 was assigned as methyl α-L-rhamnopyranosyl-(1→3)-O-(4-O-tigloyl)-β-D-quinovopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→3)-[O-(4-O-2R,3R-niloyl)]-β-D-quinovopyranosyl-(1→4)]-O-(2-O-7S-hydroxydecanoyl)-7-O-β-D-quinovopyranoside)-α-L-rhamnopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→2)-α-D-fucopyranoside. The structure of 9 differs by the cleaved Nla.
residue (Fig. 1).

QM-7 (2) was obtained as an amorphous powder. Alkaline hydrolysis of 2 gave nalic acid, tiglic acid, and 7. Negative- and positive-ion FAB-MS of 2 revealed an [M−H]− ion peak at m/z 1267 and an [M+Na]+ ion peak at m/z 1291, respectively, which were 316 mass units (quamoclinic acid B residue) less than the corresponding peaks for 1. The molecular formula of 2 was determined as C53H88O34 by HR-positive-ion FAB-MS. The 1H- and 13C-NMR spectra of 2 and 1 were superimposable, apart from the absence of signals due to QaB in the spectrum of 2 (Tables 2, 3). When compared to 1H-NMR spectrum of 1, a remarkable upfield shift (1.17 ppm) of the signal assignable to H-2 of Rha was observed. On the other hand, the signals due to H-4 of Qui and H-4 of Qui/uni of 3 exhibited remarkable downfield shifts of 1.14, 1.70, and 1.77 ppm, respectively. In addition, the HMBC spectrum of 3 showed key cross-peaks between H-4 of Qui and C-1 of the second niloyl residue (Nla/uni). Consequently, the structure of 3 was assigned as methyl (3-O-2R,3R-niloyl)-β-D-quinovopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→3)-[O-(4-O-2R,3R-niloyl)-β-D-quinovopyranosyl-(1→4)]-O-α-L-rhamnopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→2)-α-D-fucopyranoside (Fig. 1).

QM-8 (3) was obtained as an amorphous powder and exhibited an [M−H]− ion peak at m/z 1455 in negative-ion FAB-MS and an [M+Na]+ ion peak at m/z 1479 in positive-ion FAB-MS. HR-positive-ion FAB-MS indicated C63H108O37 for the molecular formula of 3. Upon alkaline hydrolysis, 3 furnished nalic acid, 6, and 8. The 1H- and 13C-NMR spectra indicated that 3 is composed of 2 mol of nalic acid and 1 mol each of 6 and 8 (Tables 2, 3). Comparison of the chemical shifts of the 1H-NMR signals of the sugar moieties in 3 and 8 showed that the signals due to H-2 of Rha, H-4 of Qui, and H-3 of Qui’ of 3 exhibited remarkable downfield shifts of 1.14, 1.70, and 1.77 ppm, respectively. In addition, the HMBC spectrum of 3 showed key cross-peaks between H-4 of Qui and C-1 of Nla and H-3 of Qui’ of 3 exhibited remarkable downfield shifts of 1.14, 1.70, and 1.77 ppm, respectively. In addition, the HMBC spectrum of 3 showed key cross-peaks between H-4 of Qui and C-1 of Nla and H-3 of Qui’ and C-1 of the second niloyl residue (Nla’). Consequently, the structure of 3 was assigned as methyl (3-O-2R,3R-niloyl)-β-D-quinovopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→3)-[O-(4-O-2R,3R-niloyl)-β-D-quinovopyranosyl-(1→4)]-O-2-O-7S-hydroxydecanyl-7-O-β-D-quinovopyranoside)-α-L-rhamnopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→2)-α-D-fucopyranoside (Fig. 1).

QM-9 (4) was obtained as an amorphous powder and upon alkaline hydrolysis afforded tiglic acid, 6, and quamoclinic acid E (10). Negative- and positive-ion FAB-MS of 4 exhibited an [M−H]− ion peak at m/z 1807 and an [M+...
Table 3. 1H-NMR Spectral Data for 2 and 3 (in Pyridine-d$_2$, 500 MHz)

| Position | 2            | 3            |
|----------|--------------|--------------|
| Fuc-1    | 5.33 d (3.5) | 5.32 d (3.5) |
| 2        | 4.48 dd (3.5, 10.0) | 4.46 dd (3.5, 10.0) |
| 3        | 4.55 dd (3.0, 10.0) | 4.59 dd (3.0, 10.0) |
| 4        | 4.04 d (3.0)  | 4.08$^a$     |
| 5        | 4.03 q (6.5)  | 4.03$^a$     |
| 6        | 1.41 d (6.5)  | 1.39 d (7.0) |
| Glc-1    | 4.96$^a$     | 4.92 d (7.5) |
| 2        | 4.07$^a$     | 4.16 dd (7.5, 9.0) |
| 3        | 4.08$^a$     | 4.05$^a$     |
| 4        | 4.07$^a$     | 4.06$^a$     |
| 5        | 3.61 m       | 3.57 ddd (3.0, 5.0, 9.0) |
| 6        | 4.26 dd (4.5, 11.0) | 4.25$^a$    |
| Rha-1    | 6.02 d (7.5) | 5.94 d (7.5) |
| 2        | 3.92 dd (7.5, 9.0) | 3.96$^a$ |
| 3        | 4.37$^a$     | 4.31$^a$     |
| 4        | 4.12$^a$     | 4.05$^a$     |
| 5        | 3.87 dd (2.5, 6.0, 9.0) | 3.82$^a$  |
| 6        | 4.35$^a$     | 4.32$^a$     |
| 7        | 4.12$^a$     | 4.05$^a$     |
| Qui-1    | 5.90 d (7.5) | 6.00 d (8.0) |
| 2        | 3.97 dd (7.5, 9.5) | 3.99$^a$ |
| 3        | 4.38 dd (9.5, 9.5) | 4.49 dd (9.5, 9.5) |
| 4        | 5.34 dd (9.5, 9.5) | 5.38 dd (9.5, 9.5) |
| 5        | 4.23 dq (9.5, 6.5) | 4.37$^a$ |
| 6        | 1.53 d (6.5)  | 1.53 d (6.5) |
| Qui’-1   | 5.08 d (8.0) | 5.26 d (8.0) |
| 2        | 4.12$^a$     | 4.28$^a$     |
| 3        | 4.18 dd (9.5, 9.5) | 5.78 dd (9.5, 9.5) |
| 4        | 5.28 dd (9.5, 9.5) | 3.83$^a$ |
| 5        | 3.83 dq (9.5, 6.5) | 3.95$^a$ |
| 6        | 1.44 d (6.5)  | 1.79 d (6.0) |
| Nla-2    | 2.94 dq (7.0, 7.0) | 2.92 dq (7.0, 7.0) |
| 3        | 4.36$^a$     | 4.41 m       |
| 4        | 1.43 d (6.5)  | 1.45 d (7.0) |
| 5        | 1.36 d (7.0)  | 1.36 d (7.0) |
| Nla’-2   | 2.81 dq (7.0, 7.0) | 4.29$^a$ |
| 4        | 1.37 d (7.0)  | 1.37 d (7.0) |
| 5        | 1.18 d (7.0)  | 1.18 d (7.0) |
| Tig-3    | 7.04 qq (1.5, 7.0) | 7.03 d (7.0) |
| 4        | 1.73 d (7.0)  | 1.73 d (7.0) |
| 5        | 1.97 br s     | 2.43$^a$     |
| Hda-2    | 2.39$^a$     | 2.39$^a$     |
| 7        | 3.88 m       | 3.88 m       |
| 10       | 0.94 t (7.0)  | 0.94 t (7.0) |

Table 3. Continued

| Position | 2            | 3            |
|----------|--------------|--------------|
| Qui”-1   | 4.81 d (8.0) | 4.81 d (8.0) |
| 2        | 3.95$^b$        | 3.95$^b$        |
| 3        | 4.16 dd (9.0, 9.0) | 3.72 dd (9.0, 9.0) |
| 4        | 4.16 dd (9.0, 9.0) | 3.82$^b$     |
| 5        | 1.63 d (6.0)  | 1.63 d (6.0)  |

\( \Delta \delta = \delta_{\text{sample}} - \delta_{\text{reference}} \)

\( \delta \) in ppm from TMS. Coupling constants (\( J \)) in Hz are given in parentheses. $a$ Signals were overlapped with other signals.

The \( ^1H \)-NMR spectrum of 4 indicated signals due to one methoxy group, two tigloyl residues, two non-equivalent methylene protons assignable to H-2 of Hda, two nonequivalent methylene protons assignable to H-2 of 35,11S-dihydroxytetradecanoyl (puroloyl) residue (Ipu; the aglycone moiety of quamocitic acid C),\(^{12,19}\) eight anomic protons, and two primary methyl groups. The \( ^1C \)-NMR spectrum exhibited signals of four carboxyl carbons and eight anomic carbons. These \( ^1H \)- and \( ^1C \)-NMR spectra suggested that 4 is composed of 2 mol of tiglic acid and 1 mol each of 6 and 10. Comparison of the \( ^1H \)-NMR spectra\(^{12}\) due to the sugar moiety in 4 and 10 indicated acylation shifts (\( \Delta \delta \approx 0.10 \)) of signals due to H-2 (\( \Delta \delta = 1.12 \)) of Rha, H-4 (\( \Delta \delta = 1.71 \)) of the second fucosyl residue (Fuc), and H-4 (\( \Delta \delta = 1.81 \)) of Qui’. In addition, the HMBC spectrum of 4 showed cross-peaks between H-4 of Fuc’ and C-1 of the second tigloyl residue (Tig’) and H-4 of Qui’ and C-1 of Tig. Accordingly, the structure of 4 was assigned as methyl 35,11S-dihydroxytetradecanoate 11-O-\( ^\beta \)-D-glucopyranosyl-(1\( \rightarrow \)3)-O-[4-(4-O-tigloyl)-\( ^\beta \)-D-fuco pyranosyl-(1\( \rightarrow \)2)-\( ^\beta \)-D-glu copyranosyl-(1\( \rightarrow \)3)-[O-(4-O-tigl oyl)-\( ^\beta \)-D-fuco pyranosyl-(1\( \rightarrow \)4)]-O-(2-O-7S-hydroxydecanoyl-7-\( ^\beta \)-D-quinovopyranoside)-\( ^\alpha \)-L-rhamnopyranosyl-(1\( \rightarrow \)2)-\( ^\beta \)-D-glucopyranosyl-(1\( \rightarrow \)2)-\( ^\beta \)-D-fuco pyranoside (Fig. 1).

QM-10 (5) was obtained as an amorphous powder, and its molecular formula was determined as C$_{67}$H$_{118}$O$_{36}$ by HR-positive-ion FAB-MS. Upon alkaline hydrolysis, 5 furnished 6 and one quamocitic acid C (11).\(^{11,12}\) The \( ^1H \)- and \( ^1C \)-NMR spectra of 5 exhibited signals due to one methoxy group, one QaB, and one quamocitic acid C residue (Tables 4, 5). Comparison of the \( ^1H \)-NMR spectra\(^{12}\) of the sugar moieties in 5 and 11 indicated acylation shift (1.11 ppm) of the signal due to H-2 of Rha in 5. Accordingly, the structure of 5 was assigned as methyl 35,11S-dihydroxytetradecanoate 11-O-\( ^\beta \)-D-glucopyranosyl-(1\( \rightarrow \)2)-\( ^\beta \)-D-glucopyranosyl-(1\( \rightarrow \)3)-[O-(4-O-tigloyl)-\( ^\beta \)-D-fuco pyranosyl-(1\( \rightarrow \)4)]-O-(2-O-7S-hydroxydecanoyl-7-\( ^\beta \)-D-quinovopyranoside)-\( ^\alpha \)-L-rhamnopyranosyl-(1\( \rightarrow \)2)-\( ^\beta \)-D-glucopyranosyl-(1\( \rightarrow \)2)-\( ^\beta \)-D-fuco pyranoside (Fig. 1).

Mannich and Schumann\(^9\) have speculated that the convolvulin from Ipomoea purga is an oligomer of acylated glycosidic acid. However, herein we describe both QM-9 and QM-10 as methyl ester monomers of acylated glycosidic acid, as in the case of QM-1–QM-3. On the other hand, QM-6, QM-7, and QM-8 are all acylated methyl glycosides, as in the case of QM-4 and QM-5. Two acylated trisaccharides closely related to the resin glycosides were previously reported as...
Table 4. 1H-NMR Spectral Data for 4 and 5 (in Pyridine-d$_5$, 500 MHz)

| Position | 4          | 5          |
|----------|------------|------------|
| Fuc-1    | 4.81 d (7.5) | 4.82 d (7.5) |
| 2        | 4.49 (9)   | 4.49 (9)   |
| 3        | 4.51 (9)   | 4.56 dd (3.5, 9.5) |
| 4        | 4.11 (9)   | 4.15 (9)   |
| 5        | 3.98 (9)   | 3.96 (9)   |
| 6        | 1.43 d (6.5) | 1.39 d (6.5) |
| Fuc'1-1  | 5.87 d (8.0) |
| 2        | 4.25 dd (8.0, 9.5) |
| 3        | 4.40 dd (3.0, 9.5) |
| 4        | 5.69 d (3.0) |
| 5        | 4.31 (9)   |
| 6        | 1.43 d (6.5) |
| Fuc"1-1 | 4.96 d (7.5) |
| 2        | 4.22 dd (7.5, 8.5) |
| 3        | 3.03 (9)   |
| 4        | 3.96 (9)   |
| 5        | 3.77 (9)   |
| 6        | 1.45 d (6.5) |
| G1c-1    | 5.61 d (8.0) | 5.63 d (7.5) |
| 2        | 4.18 dd (8.0, 9.0) | 4.21 dd (7.5, 9.0) |
| 3        | 4.10 (9)   | 4.14 (9)   |
| 4        | 4.01 (9)   | 4.02 (9)   |
| 5        | 3.58 ddd (4.0, 5.0, 9.0) | 3.58 ddd (3.5, 5.0, 9.0) |
| 6        | 4.29 dd (4.0, 12.0) | 4.30 dd (3.5, 11.5) |
| 7        | 4.19 (9)   | 4.18 (9)   |
| G1c'1-1  | 6.10 d (8.0) | 6.06 (9)   |
| 2        | 3.98 (9)   | 4.01 (9)   |
| 3        | 4.37 dd (9.0, 9.0) | 4.39 dd (9.0, 9.0) |
| 4        | 4.04 (9)   | 4.04 dd (9.0, 9.0) |
| 5        | 3.96 (9)   | 3.94 (9)   |
| 6        | 4.45 br d (11.5) | 4.49 (9)   |
| 7        | 4.11 (9)   | 4.15 (9)   |
| Rha-1    | 6.27 d (2.0) | 6.32 s     |
| 2        | 6.07 dd (2.0, 3.5) | 6.04 (9)   |
| 3        | 5.35 dd (3.5, 9.0) | 5.39 dd (3.5, 9.5) |
| 4        | 4.51 dd (9.0, 9.0) | 4.62 dd (9.5, 9.5) |
| 5        | 5.03 dq (9.0, 6.5) | 5.12 (9)   |
| 6        | 1.89 d (6.5) | 1.96 d (6.0) |
| Qui-1    | 5.91 d (8.0) |
| 2        | 3.98 (9)   |
| 3        | 4.30 dd (9.0, 9.0) |
| 4        | 3.72 (9)   |
| 5        | 4.15 (9)   |
| 6        | 1.66 d (6.0) |
| Qui"1-1 | 5.24 d (7.5) | 5.13 (9)  |
| 2        | 4.08 (9)   | 4.10 (9)   |
| 3        | 4.32 dd (9.5, 9.5) | 4.13 (9)   |
| 4        | 5.33 dd (9.5, 9.5) | 3.73 (9)   |
| 5        | 4.03 (9)   | 3.84 (9)   |
| 6        | 1.63 d (6.0) | 1.76 d (6.0) |
| Tig-3    | 7.16 qq (1.0, 7.0) |
| 4        | 1.61 d (7.0) |
| 5        | 1.93 br s |
| Tig"3-3 | 7.11 qq (1.0, 7.0) |
| 4        | 1.73 d (7.0) |
| 5        | 1.97 br s |
| Hda-2    | 2.50 (9)   | 2.56 ddd (6.5, 8.5, 16.0) |
| 2        | 2.46 (9)   | 2.43 ddd (6.5, 8.5, 16.0) |
| 3        | 3.91 (9)   | 3.88 (9)   |
| 10       | 0.96 t (7.0) | 0.93 t (7.0) |
|          | 4          | 5          |
| Qui"-1  | 4.79 d (8.0) | 4.78 d (8.0) |
| 2        | 3.96 (9)   | 3.96 (9)   |
| 3        | 4.14 dd (9.0, 9.0) | 4.14 (9) |
| 4        | 3.72 dd (9.0, 9.0) | 3.72 (9)   |
| 5        | 3.79 (9)   | 3.78 dq (9.0, 6.0) |
| 6        | 1.63 d (6.0) | 1.62 d (6.0) |
| Ipu-2    | 2.73 dd (8.0, 15.0) | 2.73 dd (7.5, 15.0) |
| 2        | 2.69 dd (4.5, 15.0) | 2.69 dd (5.0, 15.0) |
| 3        | 4.41 (9)   | 4.40 (9)   |
| 11       | 3.91 (9)   | 3.87 (9)   |
| 14       | 0.93 t (7.0) | 0.89 t (7.0) |
|          | OCH$_3$    | 3.63 s     | 3.63 s     |

$d$ in ppm from TMS. Coupling constants ($J$) in Hz are given in parentheses. $a$ Signals were overlapped with other signals.

Table 4. Continued

natural constituents of the seeds of *Cuscuta chinensis* (Convolvulaceae). Therefore, QM-6–QM-8 are presumably formed from the corresponding acetylated saccharides with a reducing terminal during the treatment with InCl$_3$–MeOH. Although QM-6–QM-10 appear to be artifacts formed during the treatment, they present new information about the structures of genuine convolvulins of *Pennaria*. In addition, methyl quamoside B has the new carbohydrate chain; furthermore, QM-10 is the first representative of the quamoclinic acid C as the component glycosidic acid.

**Experimental**

All instruments and materials used were the same as cited in a previous report$^{(3)}$ unless otherwise specified.

**Treatment of the Convolutin Fraction with Indium(III) Chloride in MeOH, and Isolation of 1–5** The crude convolutin fraction (15.032 g) previously obtained$^{(3)}$ from the seeds of *Quamoclit pennata* was dissolved in MeOH (300 mL), and indium(III) chloride (7.500 g) was added to the solution at the room temperature. The mixture was heated at reflux for 27 d, while being monitored by TLC. The concentrated reaction mixture was chromatographed on a Diaion HP20 (Mitsubishi Chemical Industries) column, eluted with H$_2$O and MeOH. The MeOH eluate (11.162 g) was subjected to Sephadex LH-20 (Pharmacia Fine Chemicals) column chromatography (CC) eluted with MeOH to give fractions 1 (1.630 g) and 2 (8.113 g). CC of fraction 2 on silica gel eluted with a gradient of mixtures of CHCl$_3$–MeOH–H$_2$O (14:2:0.1, 10:2:0.1, 8:2:0.2, 7:3:0.5, 6:4:1:0, 1:0:0) afforded fractions 2–1 to 2–15. Fraction 2–9 (1.431 g) was chromatographed on a Chromatex ODS (Fuji Silysia Chemical, Ltd.) column using a gradient of mixtures of MeOH–H$_2$O (60% MeOH, 65% MeOH, 70% MeOH, 75% MeOH, 80% MeOH, 85% MeOH, 90% MeOH, 95% MeOH, 100% MeOH) as eluents to give fractions 2–9–1 to 2–9–52. Fraction 2–9–46 (68 mg) was subjected to HPLC [COSMOSIL 5C18-AR-II(Nacalai Tesque, Inc., 20 mm i.d.$	imes$250 mm, column 1)] using 90% MeOH as eluent to give fractions 2–9–46–1 to 2–9–46–5. HPLC [COSMOSIL 5S-L-II (Nacalai Tesque, Inc., 20 mm i.d.$	imes$250 mm, column 2)] of fractions 2–9–46–2 (22 mg) using CHCl$_3$–MeOH–H$_2$O (7:3:0.5) as eluent afforded 4 (8 mg). Fraction 2–10 (2.142 g) was chromatographed on a Chromatex ODS column using a gradient of mixtures of MeOH–H$_2$O (60% MeOH, 70%
MeOH, 80% MeOH, 85% MeOH, 90% MeOH, 100% MeOH) as eluents to give fractions 2-10-1-210-18. HPLC (column 1) of fraction 2-10-7 (53 mg) using 65% MeOH as eluent afforded 3 (10 mg). Fraction 2-10-12 (121 mg) was subjected to HPLC (column 1) using 80% MeOH as eluent to give 5 (10 mg) and fractions 2-10-12-1-210-12-5. Fraction 2-11 (2.666 g) was subjected to HPLC (column 1) using 65% MeOH as eluent to give 2 (12 mg). HPLC (column 2) of fraction 2-11-19 (156 mg) using CHCl3–MeOH–H2O (7:3:0.5) as eluent afforded 1 (73 mg).

QM-6 (1): Amorphous powder. $[\alpha]_D^{19} = 33.9^\circ$ ($c=1.2$, MeOH). Positive-ion FAB-MS $m/z$: 1607 [M+Na]+. HR-positive-ion FAB-MS $m/z$: 1607.6921 (Calcd for C63H108O37Na+). 1H-NMR spectral data: see Table 1. 13C-NMR spectral data: see Table 2. 1H-NMR spectral data: see Table 3. 13C-NMR spectral data: see Table 4. 13C-NMR spectral data: see Table 5. 1H-NMR spectral data: see Table 6.

QM-7 (2): Amorphous powder. $[\alpha]_D^{19} = 36.2^\circ$ ($c=0.6$, MeOH). Positive-ion FAB-MS $m/z$: 1291 [M+Na]+. HR-positive-ion FAB-MS $m/z$: 1291.5062 (Calcd for C63H108O37Na+, 1291.5055). Negative-ion FAB-MS $m/z$: 1267 [M–H]−. HR-negative-ion FAB-MS $m/z$: 1267.7054 (Calcd for C63H108O37Na–). 1H-NMR spectral data: see Table 1. 13C-NMR spectral data: see Table 2. 1H-NMR spectral data: see Table 3. 13C-NMR spectral data: see Table 4. 1H-NMR spectral data: see Table 5. 1H-NMR spectral data: see Table 6.

QM-8 (3): Amorphous powder. $[\alpha]_D^{24} = 23.7^\circ$ ($c=1.7$, MeOH). Positive-ion FAB-MS $m/z$: 1479 [M+Na]+. HR-positive-ion FAB-MS $m/z$: 1479.6495 (Calcd for C63H110O40Na+, 1479.6467). Negative-ion FAB-MS $m/z$: 1455 [M–H]−. HR-negative-ion FAB-MS $m/z$: 1455.1905 (Calcd for C63H110O40Na–). 1H-NMR spectral data: see Table 1. 13C-NMR spectral data: see Table 2. 1H-NMR spectral data: see Table 3. 13C-NMR spectral data: see Table 4. 1H-NMR spectral data: see Table 5. 1H-NMR spectral data: see Table 6.
rider gas, N₂ 1.2 kg/cm²; tᵣ (min): 4.20 (methyl nitrate) for 1-3].

The aqueous layers of 1-3 were each neutralized with 0.1 M NaOH. After removal of the solvent, the residues were each subjected to Sephadex LH-20 CC eluted with MeOH to give 7 (11 mg) and 6 (0.5 mg) from the residue derived from 1, 7 (4 mg) from the residue derived from 2, and 8 (1 mg) and 6 (0.1 mg) from the residue derived from 3. The aqueous layers of 4 and 5 were each desalted over Diaion HP20 CC using H₂O and acetone as eluents to give glycosidic acid fractions (3 mg from 4, 2 mg from 5) derived from 4 and 5. The glycosidic acid fractions derived from 4 and 5 were each chromatographed on Sephadex LH-20 column eluted with MeOH to afford 9 (1 mg) and 6 (0.1 mg) from the fraction derived from 4 as well as 10 (1 mg) and 6 (0.1 mg) from the fraction derived from 5. Compound 6 derived from 1 and 3-5 was identified by TLC analysis [plate, silica gel 60 F₂₅₄ (Merck Ltd., 1.05554.0009); solvent, CHCl₃–MeOH–H₂O (8:2:0.2); detection, 5% H₂SO₄–MeOH; Rf: 0.41]² and 7-10 derived from 2-5 were each identified by comparison of ¹H-NMR spectra with those of authentic samples.¹³

Quamoside B (7): Amorphous powder. [α]D²⁶ −27.3° (c=0.5, MeOH). Positive-ion FAB-MS m/z: 1109 [M+Na]^+ . HR-positive-ion FAB-MS m/z: 1109.4100 (Calcd for C₆₄H₉₀O₃₁Na⁺, 1109.4112). Negative-ion FAB-MS m/z: 1085 [M-H]^−, 939 [1085–146], 793 [939–146], 631 [793–162], 339 [631–146×2]. ¹H-NMR spectral data: see Table 1. ¹³C-NMR spectral data: see Table 2.

Sugar Analysis of 7 Compound 7 (1 mg) was heated in 1 ml HCl (0.2 mL) at 95°C for 1 h. The reaction mixture was neutralized with Amberlite MB-3 (Organo Co.) and then evaporated under reduced pressure to give a monosaccharide fraction. This fraction was dissolved in pyridine (0.2 mL) containing L-cysteine methyl ester hydrochloride (1 mg) and heated at 60°C for 1 h. A solution (0.01 mL) of o-tolylisothiocyanate (0.1 mL) in pyridine (1.0 mL) was added to the mixture, which was heated at 60°C for 1 h. The reaction mixture was analyzed by HPLC (detector, Shimadzu SPD-10A UV detector 250 nm), column, COSMOSIL 5C18-AR (Nacalai Tesque, Inc. 6.0 mm i.d.×250 mm, column 4); eluent 25% CH₃CN in 50 mM H₃PO₄; flow rate 0.8 mL/min; column temperature, 35°C; tᵣ (min): 28.65 (α-glucose deriv.), 38.57 (β-fucose deriv.), 44.07 (α-quinovose deriv.), 47.58 (α-rhamnose deriv.).

Partial Decaylation of 1 A solution of 1 (10 mg) in 5% triethylamine–MeOH (1 mL) was refluxed for 1 h. After removal of the solvent, the residue was subjected to HPLC (column 4) using 70% MeOH as eluent to give 9 (5 mg).

Compound 9: Amorphous powder. [α]D⁰ −55.7° (c=0.4, MeOH). Positive-ion FAB-MS m/z: 1507 [M+Na]^+ . HR-positive-ion FAB-MS m/z: 1507.6396 (Calcd for C₆₄H₁₀₉O₃₃Na⁺, 1507.6416). Negative-ion FAB-MS m/z: 1483 [M−H]^−, 1167, 1109, 947, 793, 631, 339, 333. ¹H-NMR spectral data: see Table 1. ¹³C-NMR spectral data: see Table 2.

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