Four New Acylated Glycosidic Acid Methyl Esters Isolated from the Convolvulin Fraction of Seeds of *Quamoclit pennata* after Treatment with Indium(III) Chloride in Methanol

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

**Key words** resin glycoside; convolvulin; *Quamoclit pennata*; Convolvulaceae; acylated glycosidic acid methyl ester; indium(III) chloride

Resin glycosides are well known as purgatives, and are characteristic ingredients of crude drugs such as Pharbitis Semen, Mexican Scammoniae Radix, Orizabae Tuber, and Rhizoma Jalapeae Braziliensis, all of which originate from Convolvulaceae plants.1) They can be divided into an ether-soluble resin glycoside called jalapin, and an ether-insoluble one called convolvulin.2) Almost all jalapins isolated hitherto and characterized had common macrolactone structures comprising an oligoglycoside of a hydroxy fatty acid partially acylated by a few organic acids at the sugar moiety (acylated glycosidic acid); ester-type dimers are an example.3–8) On the other hand, convolvulin is regarded as an oligomer of various acylated glycosidic acids.9) However, no genuine convolvulin has thus far been isolated.

*Quamoclit pennata* Bojer is a Convolvulaceae plant native to the tropical regions of the 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 three organic acids, 2S-methylbutyric, n-decanoic, and n-dodecanoic acids, obtained upon alkaline hydrolysis of the crude jalapin fraction of the seeds of the plant.10) Furthermore, we isolated six genuine jalapins, quamoclins I, II, III, IV, V, and VI from the same fraction.10,11) In addition, we reported the structures of seven glycosidic acids, quamoclinic acids B, C, D, E, F, G, and H, and six organic acids, isobutyric, 2S-methylbutyric, (E)-2-methylbut-2-enoic (tiglic), 2R-methyl-3R-hydroxybutyric (2R,3R-nilic), 7S-hydroxydecanoic, and 7S-hydroxydecanoic acids obtained upon alkaline hydrolysis of the crude jalapin fraction of the seeds.12,13) However, despite numerous attempts, isolation of pure resin glycosides from the crude convolvulin fraction14) of the seeds of *Q. pennata* had thus far been unsuccessful, because the crude convolvulin fraction show tailing or broad peaks in TLC and HPLC, 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), a reagent that has been reported by Mineno and Kansui to be a suitable catalyst for the mild methyl esterification of carboxylic acids.15) The convolvulin fraction yielded a number of separate spots on the TLC (silica gel) plate after treatment with InCl₃–MeOH. Previously, we reported the isolation and structural elucidation of five acylated glycosidic acid methyl esters, QM–1–QM–3, QM–9, and QM–10, and five acylated methyl glycosides, QM–4–QM–8, from the above fraction.15,16) As part of an ongoing study of the resin glycosides of this seed, this report deals with the isolation and structural elucidation of four new acylated glycosidic acid methyl esters from the above-mentioned treated fraction.

The treated crude convolvulin fraction15) after treatment with InCl₃–MeOH was successively subjected to Diaion HP20, Sephadex LH-20, silica gel, and Chromatorex octadecyl silica (ODS) column chromatographies as well as HPLC on ODS and silica gel to afford four new compounds, temporarily referred to as QM–11 (1)–QM–14 (4).

QM–11 (I) was obtained as an amorphous powder and exhibited an [M–H]⁻ ion peak at m/z 1597 in negative-ion FAB-MS and an [M+Na]⁺ ion peak at m/z 1621 in positive-ion FAB-MS. The ⁴H-NMR spectrum of I indicated signals due to one H-2 [δ 2.80 (1H, dq, J=7.0, 7.0Hz)] of niloyl residue, one methoxy group [δ 3.63 (3H, s), seven anomeric protons [δ 6.31 (1H, d, J=1.5Hz), 6.10 (1H, d, J=8.0Hz), 6.01 (1H, d, J=8.0Hz), 5.59 (1H, d, J=7.5Hz), 5.16 (1H, d, J=7.5Hz), 4.81 (1H, d, J=7.0Hz), 4.79 (1H, d, J=7.5Hz)], two nonequivalent methylene protons assignable to H₂-2 [δ 2.55 (1H, ddd, J=7.5, 7.5, 16.0Hz), 2.44 (1H, ddd, J=8.0, 8.0, 16.0Hz)] of 7S-hydroxydecanoyl residue12,15,16) (Hda, the aglycone moiety of quamoclinic acid B residue (QaB)), two nonequivalent methylene protons assignable to H₂-2 [δ 2.74 (1H, dd, J=7.5, 15.0Hz), 2.70 (1H, dd, J=5.0, 15.0Hz)] of 3S,15S-dihydroxytetradecanoyl (ipuroloyl) residue12,15,16) (Ipu, the aglycone moiety of quamoclinic acid C residue (QaC)), seven

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¹ The authors declare no conflict of interest.
Table 1. $^1$H-NMR Spectral Data for 1-4 (in Pyridine-d$_5$, 500 MHz)

| Position | 1 | 2 | 3 | 4 |
|----------|---|---|---|---|
| Fuc-1    | 4.81 d (7.0) | 4.83 d (8.0) | 4.81 d (7.5) | 4.80 d (8.0) |
| 2        | 4.47 dd (7.0, 9.0) | 4.49 dd (8.0, 9.5) | 4.48(1) | 4.47(1) |
| 3        | 4.53 dd (3.0, 9.0) | 4.57 dd (3.5, 9.5) | 4.51(1) | 4.48(1) |
| 4        | 4.13(1) | 4.15(1) | 4.11(1) | 4.10(1) |
| 5        | 3.94 q (7.0) | 3.98(1) | 3.96(1) | 3.93(1) |
| 6        | 1.36 d (7.0) | 1.38 d (6.5) | 1.36 d (6.5) | 1.36 d (6.5) |
| Glc-1    | 5.59 d (7.5) | 5.65 d (7.5) | 5.58 d (8.0) | 5.57 d (8.0) |
| 2        | 4.20 dd (7.5, 9.0) | 4.22 dd (7.5, 9.0) | 4.19(1) | 4.17(1) |
| 3        | 4.10 dd (9.0, 9.0) | 4.11(1) | 4.11(1) | 4.10(1) |
| 4        | 4.01(1) | 4.00(1) | 4.02(1) | 3.99(1) |
| 5        | 3.57 ddd (3.0, 5.0, 9.0) | 3.59 ddd (4.0, 5.5, 9.0) | 3.56 ddd (3.5, 5.5, 9.0) | 3.57 m |
| 6        | 4.29 dd (3.0, 11.5) | 4.30(1) | 4.29 dd (2.0, 11.0) | 4.29 dd (2.5, 12.0) |
| 6        | 4.18(1) | 4.18(1) | 4.17(1) | 4.17(1) |
| Glc'-1   | 6.10 d (8.0) | 6.16 d (8.0) | 6.09 d (8.0) | 6.07(1) |
| 2        | 3.98(1) | 4.02(1) | 4.02(1) | 3.99(1) |
| 3        | 4.40 dd (9.0, 9.0) | 4.41(1) | 4.38(1) | 4.37(1) |
| 4        | 4.05 dd (9.0, 9.0) | 4.02(1) | 4.05(1) | 4.04 dd (9.5, 9.5) |
| 5        | 3.98(1) | 3.98(1) | 3.98(1) | 3.95(1) |
| 6        | 4.48(1) | 4.50(1) | 4.46(1) | 4.47(1) |
| Glc''-1  | 5.16 d (7.5) | 5.15 d (8.0) | 5.20 d (7.5) | 5.20 d (7.0) |
| 2        | 4.17(1) | 4.11(1) | 4.20(1) | 4.20(1) |
| 3        | 4.15(1) | 4.19(1) | 4.21(1) | 4.21(1) |
| 4        | 3.77(1) | 5.32 dd (9.0, 9.0) | 5.35 dd (9.0, 9.0) | 5.34 dd (9.5, 9.5) |
| 5        | 3.88(1) | 3.98(1) | 4.02(1) | 3.99(1) |
| 6        | 1.80 d (6.5) | 1.67 d (6.5) | 1.69 d (6.5) | 1.67 d (6.5) |
| Nla-2    | 2.80 dq (7.0, 7.0) | 2.94 dq (7.0, 7.0) | 2.95 dq (7.0, 7.0) | 2.95 dq (7.0, 7.0) |
| 3        | 4.32(1) | 4.35(1) | 4.36(1) | 4.36(1) |
| 4        | 1.33 d (7.0) | 1.36 d (6.5) | 1.36 d (6.5) | 1.36 d (6.5) |
| 5        | 1.24 d (7.0) | 1.30 d (7.0) | 1.30 d (7.0) | 1.30 d (7.0) |
| Nla'-2   | 2.87 dq (7.0, 7.0) | 2.87 dq (7.0, 7.0) | 2.89 dq (7.0, 7.0) | 2.89 dq (7.0, 7.0) |
| 3        | 4.33(1) | 4.34(1) | 4.34(1) | 4.34(1) |
| 4        | 1.42 d (6.0) | 1.42 d (6.5) | 1.41 d (7.0) | 1.41 d (7.0) |
| 5        | 1.32 d (7.0) | 1.31 d (7.0) | 1.31 d (7.0) | 1.31 d (7.0) |
| Hda-2    | 2.55 ddd (7.5, 7.5, 16.0) | 2.54 ddd (7.0, 7.0, 16.5) | 2.51 ddd (8.0, 8.0, 16.0) | 2.50 m |
| 2        | 2.44 dd (8.0, 8.0, 16.0) | 2.44 dd (7.0, 7.0, 16.5) | 2.42 dd (8.0, 8.0, 16.0) | 2.41 m |
| 7        | 3.87(1) | 3.89(1) | 3.89(1) | 3.87(1) |
| 10       | 0.94 t (7.0) | 0.95 t (7.0) | 0.95 t (7.0) | 0.94 t (7.0) |
| Qui'-1   | 4.79 d (7.5) | 4.79 d (8.0) | 4.79 d (7.5) | 4.78 d (8.0) |
| 2        | 3.97(1) | 3.96(1) | 3.98(1) | 3.95(1) |
| 3        | 4.15(1) | 4.15(1) | 4.14(1) | 4.14 dd (9.0, 9.0) |
| 4        | 3.71 dd (9.0, 9.0) | 3.72(1) | 3.71 dd (9.0, 9.0) | 3.70 dd (9.0, 9.0) |
| 5        | 3.79 dq (9.0, 6.5) | 3.79 dq (9.0, 6.0) | 3.78 dq (9.0, 6.0) | 3.78 dq (9.0, 6.0) |
| 6        | 1.62 d (6.5) | 1.63 d (6.0) | 1.63 d (6.0) | 1.62 d (6.0) |
| Ipu-2    | 2.74 dd (7.5, 15.0) | 2.74 dd (7.5, 15.5) | 2.74 dd (8.0, 15.0) | 2.91 dd (6.5, 15.5) |
| 2        | 2.70 dd (5.0, 15.0) | 2.70 dd (5.0, 15.5) | 2.70 dd (5.0, 15.0) | 2.73 dd (5.0, 15.5) |
| 3        | 4.41(1) | 4.41(1) | 4.41(1) | 4.52(1) |
| 11       | 3.89(1) | 3.89(1) | 3.89(1) | 3.88(1) |
| 14       | 0.91 t (7.0) | 0.91 t (7.0) | 0.91 t (7.0) | 0.91 (7.0) |
| OCH$_3$  | 3.63 s | 3.63 s | 3.64 s | 3.66 s |

$^d$ in ppm from tetramethylsilane (TMS). Coupling constants (J) in Hz are given in parentheses. $^a$ Signals were overlapped with other signals.
J = 7.0 Hz), 1.24 (3H, t, \( J = 6.5 \) Hz), 1.80 (3H, q, \( J = 11 \) Hz), and 0.94 (3H, t, \( J = 6.5 \) Hz), indicate that the first niloyl residue (Nla) (Fig. 1). In addition, to deacylation of \( \text{I} \) was performed. The HMBC spectrum of \( \text{I} \) showed key cross peak between methoxy protons and C-1 of Ipu as well as that between H-4 of Qui and C-1 of the first niloyl residue (Nla) (Fig. 1). In addition, \( \text{I} \) was refluxed with 5% triethylamine-MeOH for 30 min, and the products were separated to obtain QM-10 (6).89 Although no cross-peak between H-2 of Rha and C-1 of Hda was observed in the HMBC spectrum of \( \text{I} \), the above data suggested that QaB and Nla were attached to OH-2 of Rha and OH-4 of Qui, respectively. The configuration of the component nilic acid of this crude convolvulin fraction had been previously determined as 2R,3R.12 Accordingly, the structure of \( \text{I} \) was defined as methyl 3,5,5,7,7-dihydroxytetradecan-11-O-β-D-quinovopyranosyl(1→2)-O-β-D-glucopyranosyl(1→4)-3-O-(4,2,3,5-R-4-niloyl)-β-D-quinovopyranosyl(1→4)-O-(2-O-75-hydroxydecanoxy)-7-O-β-D-quinovopyranosidol-α-L-rhamnopyranosyl(1→2)-O-β-D-glucopyranosyl(1→2)-β-D-fucopyranoside (Fig. 2).

QM-12 (2) was obtained as an amorphous powder. Its molecular formula was found to be the same as that of \( \text{I} \) by HR-positive-ion FAB-MS. The \( ^1\)H- and \( ^{13}\)C-NMR spectra of

### Table 2. \( ^{13}\)C-NMR Spectral Data for \( 1-4 \) (in Pyridine-\( d_6 \), 125 MHz)

| Position | \( ^{13}\)C-NMR Data | \( ^{13}\)C-NMR Data | \( ^{13}\)C-NMR Data | \( ^{13}\)C-NMR Data |
|----------|-------------------|-------------------|-------------------|-------------------|
| Fuc-1    | 102.4             | 102.4             | 102.4             | 102.3             |
| 2        | 78.5              | 78.4              | 78.7              | 78.5              |
| 3        | 76.0              | 76.1              | 75.9              | 75.9              |
| 4        | 75.0              | 73.0              | 73.1              | 73.0              |
| 5        | 71.0              | 71.0              | 71.0              | 71.0              |
| 6        | 71.1              | 71.1              | 71.1              | 71.1              |
| Glc-1    | 102.3             | 102.2             | 102.1             | 102.3             |
| 2        | 76.7              | 76.8              | 76.7              | 76.6              |
| 3        | 78.7              | 78.9              | 78.8              | 78.7              |
| 4        | 72.5              | 72.5              | 72.5              | 72.5              |
| 5        | 77.2              | 77.2              | 77.2              | 77.2              |
| 6        | 63.0              | 63.0              | 63.1              | 63.0              |
| Glc'-1   | 101.6             | 101.4             | 101.6             | 101.6             |
| 2        | 85.6              | 85.0              | 85.9              | 85.9              |
| 3        | 76.9              | 77.0              | 77.2              | 77.4              |
| 4        | 71.6              | 71.5              | 71.5              | 71.5              |
| 5        | 78.2              | 78.2              | 78.2              | 78.2              |
| 6        | 62.7              | 62.7              | 62.7              | 62.6              |
| Glc''-1  | 103.8             | 103.1             | 103.4             | 103.4             |
| 2        | 75.1              | 75.1              | 75.1              | 75.1              |
| 3        | 78.2              | 78.2              | 78.2              | 78.2              |
| 4        | 71.7              | 71.7              | 71.7              | 71.7              |
| 5        | 78.8              | 78.8              | 78.8              | 78.8              |
| 6        | 62.8              | 62.8              | 62.8              | 62.8              |
| Rha-1    | 97.5              | 97.3              | 97.5              | 97.5              |
| 2        | 73.8              | 73.7              | 73.9              | 73.9              |
| 3        | 75.8              | 75.6              | 75.8              | 75.8              |
| 4        | 79.2              | 79.3              | 79.1              | 79.1              |
| 5        | 67.6              | 67.8              | 67.6              | 67.6              |
| 6        | 19.0              | 19.1              | 19.0              | 19.0              |
| Qui-1    | 102.1             | 102.3             | 102.3             | 102.0             |
| 2        | 76.2              | 76.7              | 76.4              | 76.4              |
| 3        | 75.6              | 75.6              | 75.6              | 75.5              |
| 4        | 77.5              | 77.2              | 77.4              | 77.4              |
| 5        | 69.9              | 72.4              | 70.0              | 70.0              |
| 6        | 18.2              | 18.6              | 18.7              | 18.2              |

\( ^\delta \) in ppm from TMS.
2, which were similar to those of 1, indicated signals corresponding to the presence of one each of niloyl residue, QaB, QaC, and methoxy group (Tables 1, 2). Therefore, 2 was considered to be a positional isomer of 1 with respect to ester linkage. When compared with the $^1$H-NMR signals of 1, a downfield shift of 1.55 ppm for the signal assignable to H-4 of Qui along with an upfield shift of 1.63 ppm for the signal assignable to H-4 of Qui were observed, whereas H-2 of Rha resonated at a position similar to that in 1. The HMBC spectrum of 2 showed key cross-peaks between H-4 of Qui and C-1 of the second niloyl residue (Nla') and between methoxy protons and C-1 of Ipu (Fig. 1). Further, partial deacylation of 2 in a similar manner to that performed on 1 gave 6. Accordingly, 2 was concluded to be a positional isomer of 1, in which the niloyl residue of 2 was at the OH-4 of Qui rather than at the OH-4 of Qui (Fig. 2).
QM-13 (3) was obtained as an amorphous powder. Its positive-ion FAB-MS indicated an [M+Na]⁺ ion peak at \( m/z \) 1721, which was 100 mass units (niloyl residue) larger than those of 1 and 2. The \(^1\)H-NMR spectrum of 3 was analogous to those of 1 and 2, apart from the appearance of signals due to one more niloyl residue (Table 1). On comparing the chemical shifts of the \(^1\)H-NMR signals between 3 and 1, the signals due to H-4 of Qui of 3 showed a remarkable downfield shift of 1.58 ppm. On the other hand, the signals owing to H-2 of Rha, H-4 of Qui, and H-4 of Qui of 3 were observed at chemical shifts similar to those of 1. In addition, the HMBC spectrum of 3 showed key cross peaks between H-4 of Qui and C-1 of Nla and between methoxy protons and C-1 of Ipu (Fig. 1). These data suggest that 3 is a derivative of 1 with the nilic acid residue attached to OH-4 of Qui. This inference was supported by the partial deacylation of 3 in a manner similar to that performed on 1 to afford 6. Consequently, the structure of 3 was identified as methyl 35,11S-dihydroxytetradecanoate 11-O-(4-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-hydroxydecanoyl 7-O-β-D-quinovopyranoside)-α-L-rhamnopyranosyl-(1→2)-O-β-D-glucopyranoside-(1→2)-β-D-fucopyranoside (Fig. 2).

QM-14 (4) was obtained as an amorphous powder. The positive-ion FAB-MS of 4 exhibited an [M+Na]⁺ ion peak at \( m/z \) 1883, which was 162 mass units (hexosyl residue) larger than that of 3. The molecular formula of 4 was analyzed to be C\(_{48}\)H\(_{144}\)O\(_{45}\) by HR-positive-ion FAB-MS. The \(^1\)H- and \(^13\)C-NMR spectra of 4 were quite similar to those of 3, apart from the appearance of additional signals due to one terminal β-D-glucopyranosyl residue\(^{13,17}\), the absolute configuration of the glucose component of the glycosidic acid fraction of the above-mentioned crude convolvulin fraction had previously been determined as \( \alpha \)-form.\(^{12}\) Comparison of the NMR signals of 4 and 3 indicated glycosilation shift\(^{18,19}\) (\( \Delta \delta = 0.5 - 3.0 \)) of signal owing to C-3 (\( \Delta \delta = 8.0 \)) of Ipu, whereas the signals owing to H-2 of Rha, H-4 of Qui, and H-4 of Qui resonated at chemical shifts quite similar to those of 3. In addition, the HMBC spectrum of 4 showed cross peaks between the following: H-4 of Qui and C-1 of Nla; methoxy protons and C-1 of Ipu; and H-1 of the third glucosyl unit (Glc") and C-3 of Ipu (Fig. 1). From these data, 1 was presumed to be a derivative of 3, in which QaC was replaced by quamaclinic acid G\(^{13}\) residue. This assumption was confirmed by the enzymatic hydrolysis of 4 with \( \beta \)-glucosidase from sweet almonds to give 3. Accordingly, the structure of 4 was identified as 11-O-(4-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-hydroxydecanoyl 7-O-β-D-quinovopyranoside)-α-L-rhamnopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→2)-β-D-fucopyranosyl-methyl 35,11S-dihydroxytetradecanoate 3-O-β-D-glucopyranoside (Fig. 2).

Although QM-11–QM-14 were all considered to be artifacts formed during the treatment of the crude convolvulin fraction with \( \text{InCl}_3 \)-MeOH, they gave new information on the structures of genuine convolvulins of \( Q. \) pennata. Further, QM-14 is the first representative of acylated glycosidic acid methyl ester having sugar linkages at C-3 of Ipu as well as at its C-11.

**Experimental**

All instruments and materials used were the same as cited in a previous report\(^{19}\) unless otherwise specified.

**Treatment of the Convolvulin Fraction with Indium(III) Chloride in MeOH, and Isolation of 1–4**

The crude convolvulin fraction (15.032 g) previously obtained\(^{10}\) from the seeds of \( Q. \) 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 column, eluted with H\(_2\)O and MeOH. The MeOH eluate (11.162 g) was subjected to Sephadex LH-20 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) afforded fractions 2-1–2-15. Fraction 2-10 (2.142 g) was chromatographed on a Chromatorex 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 frac-
tions 2-10-1–2-10-18. Fraction 2-10-12 (121 mg) was subjected to HPLC [COSMOSIL 5C18-AR-II (Nacalai Tesque, Inc., 20 mm i.d.×250 mm, column 1)] using 80% MeOH as eluent to give 6 (10 mg), 2 (11 mg), and 1 (17 mg). HPLC (column 1) of fraction 2-10-13 (272 mg) using 85% MeOH as eluent afforded fractions 2-10-13-1–2-10-13-3. Fraction 2-10-13-1 (52 mg) was subjected to HPLC [COSMOSIL SSL-II (Nacalai Tesque, Inc., 20 mm i.d.×250 mm)] using CHCl₃–MeOH–H₂O (8:2:0.2) as eluent afforded 3 (12 mg). Fraction 2-11 (2.666 g) was chromatographed on a Chromatorex ODS column using a gradient of mixtures of MeOH–H₂O (60% MeOH, 65% MeOH, 70% MeOH, 75% MeOH, 80% MeOH, 85% MeOH, 90% MeOH, 95% MeOH, 100% MeOH) as eluents to give fractions 2-11-1–2-11-38. Fraction 2-11-26 (75 mg) was subjected to HPLC (column 1) using 80% MeOH as eluent to give 4 (32 mg).

**QM-11 (1):** Amorphous powder. [a]_D25^26 +33.9° (c=1.3, MeOH).
Positive-ion FAB-MS m/z: 1621 [M+Na]+. HR-positive-ion FAB-MS m/z: 1621.7848 (Calcd for C_{77}H_{134}O_{40}Na^+, 1621.7819).
Negative-ion FAB-MS m/z: 1597 [M−H]^−, 333 [quamoclinic acid B−H]^−. ¹H-NMR spectral data: see Table 1. ¹³C-NMR spectral data: see Table 2.

**QM-12 (2):** Amorphous powder. [a]_D25^25 +37.6° (c=0.9, MeOH).
Positive-ion FAB-MS m/z: 1621 [M+Na]+. HR-positive-ion FAB-MS m/z: 1621.7841 (Calcd for C_{77}H_{134}O_{40}Na^+, 1621.7819).
Negative-ion FAB-MS m/z: 1597 [M−H]^−, 333. ¹H-NMR spectral data: see Table 1. ¹³C-NMR spectral data: see Table 2.

**QM-13 (3):** Amorphous powder. [a]_D19^26 +40.9° (c=1.0, MeOH).
Positive-ion FAB-MS m/z: 1721 [M+Na]+. HR-positive-ion FAB-MS m/z: 1721.8365 (Calcd for C_{77}H_{134}O_{40}Na^+, 1721.8344).
Negative-ion FAB-MS m/z: 1697 [M−H]^−, 333. ¹H-NMR spectral data: see Table 1. ¹³C-NMR spectral data: see Table 2.

**QM-14 (4):** Amorphous powder. [a]_D19^19 +40.4° (c=0.6, MeOH).
Positive-ion FAB-MS m/z: 1883 [M+Na]^+. HR-positive-ion FAB-MS m/z: 1883.8883 (Calcd for C_{77}H_{134}O_{40}Na^+, 1883.8877).
¹H-NMR spectral data: see Table 1. ¹³C-NMR spectral data: see Table 2.

**Partial Deacylation of 1–3** Solutions of 1 (3 mg), 2 (3 mg), and 3 (5 mg) in 5% triethylamine–MeOH (1 mL) were each refluxed for 30 min. The reaction mixture was adjusted to pH 3 with 1 M HCl and then diluted with H₂O (5 mL) and extracted with ether (2×3 mL). The aqueous layer was subjected to Diaion HP20 CC using H₂O and MeOH as eluents to elute 6 (2 mg from 1, 2 mg from 2, 4 mg from 3), which was identified by comparison of ¹H-NMR spectrum with that of authentic sample.

**Enzymatic Hydrolysis of 4** Compound 4 (5 mg) was suspended in CH₃COOH–CH₃COONa buffer solution (pH 5.5, 1 mL), and β-glucosidase (from sweet almonds, 12.6 U/mg, Lot. No. 81241, Toyobo Co., Ltd., 10 mg) was added. The mixture was left to stand at 37°C for 7 d. After removal of solvent in vacuo, the residue was extracted with MeOH, and the MeOH extract was subjected to HPLC [COSMOSIL 5C18-AR-II (Nacalai Tesque, Inc., 4.6 mm i.d.×250 mm)] using 85% MeOH as eluent to give 3 (2 mg), which was identified by comparison of ¹H-NMR spectrum with that of authentic sample.

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