In the course of studies on Okinawan resource plants, the constituents of *Glochidion acuminatum* (Euphorbiaceae) have been investigated. In a previous communication, the isolation of a structurally rare dimeric butenolide, glochidiolide (1), was reported. Further studies on this plant led to the isolation of isoglochidiolide (2), a glucoside of a nitrogen-containing dimeric phenylethane which was designated acuminaminoside (3), and four glucosides with C₈ aglycones (4—7), along with one known glycoside (8). This paper deals with the structural elucidation of the new compounds.

**Results and Discussion**

The compounds were isolated using several chromatographic techniques and recrystallization. The details are given in the Experimental section.

A known compound (8) was identified as Z-hex-3-en-1-ol O-β-D-glucopyranoside, ([α]D²⁰ = −21.6° (c = 0.79, MeOH)²) based on spectroscopic evidence.

Glochidiolide (1) was isolated as colorless crystals and its structure was finally elucidated by X-ray crystallographic analysis to be that shown in Fig. 1 or its enantiomer.³ Isoglochidiolide (2) was isolated as an off-white syrup and its elemental composition was found to be the same as that of 1 by HR (high resolution)-FAB-MS. The ¹H- and ¹³C-NMR spectra including ¹H–¹H correlation (COSY) and heteronuclear single-quantum correlation (HSQC) spectroscopies revealed that the basic skeleton was the same as that of 1, and signals assignable to one (C-1’ to C-8’) of the halves were close to those of 1 (Table 1). This was also supported by the results of heteronuclear multiple-bond correlation (HMBC) spectroscopy, i.e., δH 2.62 and 2.69 (H-2) crossed δC 87.6 (C-8’), and δH 1.60 and 2.97 (H-7’) δC 49.9 (C-3) (see Fig. 2). This evidence indicated that isoglochidiolide (2) was a stereoisomer of the other part (C-1 to C-8) of the halves were close to those of 1 (Table 1). This was also supported by the results of heteronuclear multiple-bond correlation (HMBC) spectroscopy, i.e., δH 2.62 and 2.69 (H-2) crossed δC 87.6 (C-8’), and δH 1.60 and 2.97 (H-7’) δC 49.9 (C-3) (see Fig. 2). This evidence indicated that isoglochidiolide (2) was a stereoisomer of the other part (C-1 to C-8). The phase-sensitive nuclear Overhauser effect spectroscopy (PHNOESY) experiment (see Fig. 2) revealed that, since H-8 correlated with H-6, H-6 and H-8 were in axial positions and on the same...
face. This was also supported by the fact that H-8 was coupled with adjacent protons with coupling constants of 10 and 2 Hz. Such a correlation was not observed in 1. A significant correlation between H-8 and H-6 indicated that these protons were also on the same side. Finally, H-6 and H-7b also showed correlation. These results allowed us to establish the structure of 2 as an isomeric form of 1 regarding the stereochemistry of C-6, as shown in Fig. 1, or its enantiomer.

Acuminaminoside (3) was isolated as colorless needles, mp 212—215 °C (MeOH). On negative-ion FAB mass spectrometry, it exhibited a quasimolecular ion peak at m/z 428 ([M−H] ), which corresponded to C_{24}H_{22}O_{8}N on HR-FAB-MS. The IR and UV absorption maxima indicated the presence of an aromatic ring (s) (1595 and 1495 cm\(^{-1}\)) and a ketone functional group (1654 cm\(^{-1}\)). The IR absorption of the carbonyl double bond that appeared at 1654 cm\(^{-1}\).

The 1H-NMR spectrum of 3a in DMSO-\(d_6\) still showed the presence of D\(_2\)O exchangeable protons at \(\delta_{H} 8.20\) (2H, brs), which were expected to be an amino hydrogen signal. Although NMR spectra including two-dimensional ones were carefully inspected, only partial structures could be assigned, such as that one of the aromatic rings carried a \(\beta\)-glucopyranose moiety on the 2-hydroxyphenyl 1-(1-oxoethyl) skeleton and the other formed a fused ring system.

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Table 1. \(^{13}\)C-NMR Data for Glochidiolide (1) and Isoglobchiolide (2) (400 MHz, DMSO-\(d_6\))

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<td>2</td>
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a) Data taken from ref. 1.

Table 2. \(^{13}\)C-NMR Data for Acuminaminoside (3)

<table>
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Since the entire structure could not be elucidated using spectroscopic analysis, an X-ray crystallographic method was attempted. However, the crystals of the glucoside (3) were not suitable for such analysis, thus it was enzymatically hydrolyzed to give glucose and an aglycone (3b), which gave a suitable crystal from MeOH for X-ray analysis. Its structure was determined by means of the direct method with the teXsan crystallographic package. A computer-generated perspective drawing of 3b is shown in Fig. 3. The position of the sugar linkage has already been confirmed to be the hydroxy group at the 2-position, and the glucose is in the D-series. As a result, acuminaminoside (3) was found to be the \(\beta\)-
d-glucopyranoside of a novel dimeric phenylethanic compound containing a nitrogen atom, as shown in Fig. 1.

Alkaloidal glycosides are relatively rare in nature, with the exceptions being the conjugates of iridoid glucoside and tryptamine or tyramine, and nitrogen-containing steroidal compounds. Acuminaminoside (4) is an alkaloidal glucoside with an unusual aglycone moiety, i.e., a dimeric phenylethanes skeleton.

Glochidacuminoside A (4) was isolated as an amorphous powder and several molecular ion peaks were observed in positive-ion mode FAB-MS, such as 

\[
\text{m/z } 337 \ [\text{M} + \text{Na}]^+ , \quad 353 \ [\text{M} + \text{K}]^+ , \quad 359 \ [\text{M} - \text{H} + \text{Na} + \text{Na}]^+ , \quad \text{and} \quad 375 \ [\text{M} - \text{H} + \text{K} + \text{Na}]^+ .
\]

The \(^{13}\text{C}-\text{NMR} \) spectrum indicated the presence of six signals assignable to the aglycone moiety, six to the disubstituted aromatic ring, and a methylene carbon signal. However, the \(^{1}H\)-NMR spectrum showed four peculiar aromatic proton signals at \(\delta_{H} 6.95 \) (1H, m, split into more than eight peaks), \(7.15 \) (1H, br s), \(7.16 \) (1H, br s), and \(7.22 \) (1H, br d, \( J = 7 \) Hz). This is not a typical coupling pattern of a disubstituted aromatic ring. From these results, 4 was assumed to exist as a salt of several metal ions, and thus the carboxylic carbon signal collapsed and was not observed in the \(^{13}\text{C}-\text{NMR} \) spectrum. Therefore 4 was treated with Amberlite IR-120B (H\(^{+}\)) to give the metal-free compound 4a. The \(^{1}H\) and \(^{13}\text{C}-\text{NMR} \) spectra clearly demonstrated that the structure of 4a was 2-O-\(\beta\)-glucopyranosidase of 2-hydroxyphenylacetic acid (Experimental and Table 3). From the sign of the optical rotation value, glucose was presumed to be in the D-series. This was later confirmed by mild alkaline hydrolysis of 5 to give 4a.

Glochidacuminoside B (5) was isolated as an amorphous powder. An aliquot of 5 was treated with Amberlite IR-120B (H\(^{+}\)) prior to further spectroscopic analyses. Its elemental composition was determined to be \(C_{22}H_{28}O_{10}\) in negative-ion HR-FAB-MS. The IR spectrum indicated the presence of an ester linkage (1735 cm\(^{-1}\)). The \(^{1}H\)- and \(^{13}\text{C}-\text{NMR} \) spectra indicated that the aglycone moiety was the same as that of 4a (Table 3) with a further C\(_8\) moiety. The carbon skeleton of the C\(_8\) moiety consisted of four methylenes, one methine with a hydroxyl group, one trisubstituted double bond, and a carboxylic carbonyl functional group. The structure was elucidated to be 4-hydroxycyclohex-1-en-1-acetic acid by means of two-dimensional NMR spectroscopy. This part was assumed to be linked with the hydroxyl group on C-6’ of glucopyranose through an ester bond. This was supported by downfield shifts of the protons on C-6’ (\(\delta_{H} 4.22, 4.45 \)) and the cross peak between carbonyl carbon (\(\delta_{C} 173.6 \)) and methylene protons (\(\delta_{H} 4.22, 4.45 \)) in the HMBC spectrum. To determine the absolute configuration of the C-4’ position, 5 was hydrolyzed under mild alkaline conditions in MeOH to give methyl esters of 5a (=4a) and 5b. The ester 5b was further derivatized to its \((R)\)-(+) and \((S)\)-(−)\-\-\(\alpha\)-methoxy-\(\alpha\)-tri-fluoromethylphenylacetic acid (MTPA) esters (5d and 5e, respectively) to apply a modified Mosher’s method. Figure 4 shows the results. Although the protons on C-5’ of 5d and 5e were not resolved well, based on the chemical shift ranges of H-5’ the signs of their D\(\Delta\)-\(\Delta\) values are expected to be negative. From the signs of other protons, the absolute configuration of C-4’ was determined to be S. Glucoside 5a was hydrolyzed with emulsin to give 2-hydroxyphenylacetic acid (5b) as an aglycone and d-glucose. Therefore the structure of 5 was elucidated to be 2-hydroxyphenylacetic acid 2-O-\(\beta\)-d-glucopyranoside 6’-O-(4S)-4-hydroxycyclohex-1-en-1-acetate.

Glochidacuminoside C (6) was isolated as an amorphous powder and its elemental composition was determined to be \(C_{22}H_{26}O_{10}\) using HR-FAB mass spectrometry. The \(^{13}\text{C}-\text{NMR} \) spectrum showed 22 signals, of which eight exhibited essential the same chemical shifts as those of the ester moiety in 5. Eight other signals closely resembled the aforementioned eight signals except for the carbonyl carbon at \(\delta_{C} 172.0 \) (C-8’ at \(\delta_{C} 173.3 \), respectively). From the anumeric carbon signal appearing at \(\delta_{C} 95.6 \), the ester glucoside was presumed to be in the structure. This was confirmed by the HMBC spectrum, in which the anumeric proton (\(\delta_{H} 5.44 \)) crossed the carbonyl carbon at \(\delta_{C} 172.0 \). Since mild alkaline hydrolysis
of 5 furnished 5a and d-glucose, the structure of 6 was elucidated to be β-D-glucopyranose 1’-6’-bis-O-(4S)-4-hydroxy-cyclohex-1-en-1-yl acetate.

Glochidacuminoside D (7) was also isolated as an amorphous powder and its elemental composition was determined to be C_{23}H_{22}O_{11}N in negative-ion HR-FAB-MS. The IR spectrum showed an absorption maximum at 2255 cm^{-1}. These results indicate that 7 contains a nitrite moiety. The ^1H and ^13C-NMR spectra showed the presence of para-substituted [δ_{H} 125.5 (s) and 160.1 (s)] and tetrasubstituted symmetrical benzene rings, a substituted β-glucopyranoside, a methine with an oxygen atom, a nitrite [δ_{C} 118.7 (s)], and carboxyl functional groups. The structure of the tetrasubstituted symmetrical benzene was deduced to be gallic acid based on comparison of its ^13C-NMR chemical shifts with those reported.33 The acid was presumed to form an ester linkage (1704 cm^{-1}) with the hydroxyl group on C-2 of β-glucopyranoside. This was confirmed by H–H COSY and HMBC experiments, in which a significant downfield shift of H-2 was observed, and the H-2 signal crossed with the methine carbon at δ_{C} 167.7, respectively. Since the anomeric proton crossed the methine carbon (δ_{C} 68.6), the structure of 7 was elucidated to be 4-hydroxylprunasin 2’-O-gallate.

Experimental

General Experimental Procedures A highly porous synthetic resin (Diaion HP-20) was purchased from Mitsubishi Kagaku (Tokyo, Japan). Silica gel column chromatography (CC) was performed on silica gel 60 (E. Merck, Darmstadt, Germany) and redisolved (acetone). [octadecyl silicic acid (ODS)] open CC (RPCC) on Cosmosil 75C_{2}OPN (Nacalai Tesque, Kyoto, Japan) [Φ=50 mm, L=25 cm, linear gradient: MeOH–H2O (1 : 9, 1 l)] was equilibrated with 1-N-propanol (EtOAc) or water, respectively. The samples were collected and numbered according to their order of elution with increasing amounts of MeOH in H2O–EtOAc with 1-N-propanol. Fractions 2-1 were collected. Fractions 3-5 were combined (30.2 g) and then subjected to high performance liquid chromatography (HPLC) with MeOH–H2O (1 : 3) to give 10.1 mg of 7.

The residue (52.6 g) of fractions 5-9 was obtained on Diaion HP-20 CC and subjected to silica gel (1.20 kg) CC with increasing amounts of MeOH in H2O–EtOAc (1 : 9, 1 l). With 500-ml fractions collected. The residue of fractions 37–45 (217 mg) was purified by DCCC to give 50.0 mg of 7. The residue (52.6 g) of fractions 5-9 obtained on Diaion HP-20 CC was subjected to silica gel (1.20 kg) CC with increasing amounts of MeOH in H2O–EtOAc (1:9, 1l). The fractions were collected and numbered according to their order of elution. The residue of fractions 24-35 (1.17 g) was subjected to RPCC and then the residue of fractions 35-45 (217 mg) was purified by DCCC to give 50.0 mg of 7.

The residue of fractions 52-65 (4.42 g) obtained on silica gel CC was purified by RPCC (98 mg in fractions 81-92, DCCC (53 mg in fractions 18-24), followed by HPLC with MeOH–H2O (1 : 3) to give 10.1 mg of 7.

The residue of fractions 96-115 obtained on silica gel CC, 48.0 mg of 4 was isolated in a similar manner. From the residues of fractions 10-11 and 12 (12.5 g) of fractions 12 and 13 obtained on Diaion HP-20 CC, 147 mg of 5 was isolated as an amorphous powder and 216 mg of 3 as colorless needles, respectively.

Glochidiolide (1) Colorless rods, mp 210-213 °C. [α]_{D}^{25} = -69.8° (c=0.49, DMSO). IR ν_{max} (KBr): 3400, 3050, 1750, 1725, 1625, 1450, 1420, 1355, 1290, 1265, 1195, 1055, 1020, 1050, 975, 825, 800 cm^{-1}; UV λ_{max} (MeOH): 256 (4.17) nm (log ε). ^1H-NMR (DMSO-d_6, 400 MHz) δ: 1.60 (1H, dd, J=13, 10 Hz, H-7a), 1.77 (1H, dd, J=14, 9 Hz, H-7b), 2.26 (1H, d, J=17 Hz, H-2a), 2.39 (1H, dt, J=14, 5 Hz, H-7b), 2.48 (1H, d, J=17 Hz, H-2b), 2.93 (1H, dd, J=13, 6 Hz, H-7b), 4.09 (1H, t, J=17 Hz, H-6b), 4.53 (1H, d, J=17 Hz, H-6), 4.65 (1H, d, J=17 Hz, H-6), 4.87 (1H, dd, J=12, 10 Hz, H-4), 5.19 (1H, dd, J=10, 2 Hz, H-13), 6.19 (1H, s, H-10), 6.20 (1H, dd, J=10, 2 Hz, H-13), 6.79 (1H, dt, J=10, 1 Hz, H-12). ^13C-NMR (DMSO-d_6): Table 1. HR-FAB-MS (negative-ion mode) m/z: 303.0855 [M-H]^{-} (Calcd for C_{16}H_{16}O_{6}: C, 63.15%; H, 5.30%; Found: C, 62.97%; H, 5.35%).

Isoglochidiolide (2) Off-white syrup, [α]_{D}^{25} = +26.6° (c=2.33, MeOH). IR ν_{max} (film): 3350, 2952, 2929, 2856, 1734, 1721, 1667, 1514, 1457, 1172, 1006 cm^{-1}; UV λ_{max} (MeOH): 257 (3.87) nm (log ε). ^1H-NMR (DMSO-d_6, two drops of D_2O) δ: 1.60 (1H, dd, J=13, 9 Hz, H-7a), 1.62 (1H, td, J=13, 10 Hz, H-7a), 2.17 (1H, td, J=13, 5 Hz, H-7b), 2.62 (1H, d, J=18 Hz, H-2a), 2.69 (1H, dd, J=18 Hz, H-2b), 2.97 (1H, dd, J=14, 7 Hz, H-7b), 4.05 (1H, br dd d, J=10, 4, 2 Hz, H-6), 4.44 (1H, br dd, J=9, 7 Hz, H-14), 4.58 (1H, dd, J=10, 5 Hz, H-8), 5.51 (1H, dd, J=10, 2 Hz, H-13), 5.91 (1H, dd, J=10, 2 Hz, H-5), 6.14 (1H, s, H-10), 6.17 (1H, dd, J=10, 2 Hz, H-13), 6.72 (1H, dd, J=10, 2 Hz, H-13). ^12C-NMR (DMSO-d_6): Table 1. HR-FAB-MS (negative-ion mode) m/z: 303.0838 [M-H]^{-} (Calcd for C_{16}H_{16}O_{6}: C, 63.15%; H, 5.30%; Found: C, 62.97%; H, 5.35%).

Acuminaminoside (3) Colorless needles (MeOH), mp 212-215 °C. [α]_{D}^{25} = -33.0° (c=0.75, MeOH). IR ν_{max} (KBr): 3161, 1654, 1595, 1495, 1254, 1077, 999, 747 cm^{-1}. UV λ_{max} (MeOH): 214 (4.26), 236 (4.00), 256 (4.04), 296 (3.99), 310 (4.01) nm (log ε). ^1H-NMR (CD_{3}OD, 400 MHz) δ: 3.35 (1H, t, J=9 Hz, H-4), 3.41 (1H, dd, J=9, 7 Hz, H-2), 3.41 (1H, dd, J=10, 6 Hz, H-5), 3.46 (1H, dd, J=9 Hz, H-2), 3.70 (1H, dd, J=12, 6 Hz, H-6), 3.88 (1H, dd, J=12, 2 Hz, H-6b), 4.26 (2H, s, H-7), 4.94 (1H, d, J=8 Hz, H-12), 6.97 (1H, m, H-6), 7.06 (1H, td, J=8, 1 Hz, H-5s), 7.18 (1H, td, J=8, 2 Hz, H-6s), 7.22-7.25 (4H, m, H-3, 4, 6 and 7), 7.58 (1H, dd, J=8, 1 Hz, H-4). ^1H-NMR (DMSO-d_6, 400 MHz) δ: 8.33 (2H, brs,
exchangeable with \( \text{D_2O} \). \(^1^3\)C-NMR (CD\(_2\)OD, 100 MHz): Table 2. 2. HR-FAB-MS (negative-ion mode) \( m/z \): 428.1336 [M–H] (Caled for \( \text{C}_2\text{H}_4\text{O}_2 \)).

**Gliocladiumadox A** (4) Amorphous powder, \([\text{C}_6\text{H}_9\text{N}_2\text{O}]_2\text{KCl} \). HR \( ^{1}H \)-NMR (CD\(_3\)OD, 400 MHz): \( \delta \): 3.99–4.38 (3H, m, H-3'), 5.39 (1H, d, J = 9 Hz, H-2'), 3.86–3.88 (3H, m, H-2', 5'), 3.35 (1H, t, J = 15 Hz, H-2), 3.18 (2H, br, s, H-3 and 3a). 13C-NMR (CD\(_3\)OD, 100 MHz): Table 3. HR-FAB-MS (negative ion mode) \( m/z \): 313.9913 [M–H] (Caled for \( \text{C}_6\text{H}_8\text{O}_2 \)).

**Gliocladiumadox B** (5) Amorphous powder, \([\text{C}_6\text{H}_9\text{N}_2\text{O}]_2\text{KCl} \). IR \( v_{\max} \text{ (film-}) \): 3380, 2924, 2851, 1735, 1494, 1240, 1074 cm\(^{-1}\). \( \int \lambda_{\max} \text{ (MeOH)} \): 215 (3.78), 269 (3.11), 274 (0.06) nm (log e). 13C-NMR (CD\(_3\)OD, 100 MHz): \( \delta \): 15.77, 15.05, 10.72, 5.75 ppm (each 3H, each OMe).

**Enzymatic Hydrolysis of Gliocladiumadox (3) to Its Aglycone (3c)** 
Gliocladiumadox (3, 34 mg) was hydrolyzed with hesperidinase at 37°C for 24 h. The resulting hydrolysate was separated by silica gel column chromatography to give an aglycone (3c), which was crystallized from MeOH (6.7 mg, 33%), and 8.4 mg of n-glucose. Aglycone (3c): Colorless prisms (MeOH), mp 171–173°C. \( ^{1}H \)-NMR (CD\(_3\)OD, 400 MHz): \( \delta \): 4.12 (2H, s, H-7), 6.76 (1H, td, J = 8, 1.5 Hz, H-5), 6.83 (1H, dd, J = 8, 1.5 Hz, H-3), 7.06 (2H, s, H-2 and 6), 7.06 (2H, s, H-2' and 6'). 13C-NMR (CD\(_3\)OD, 100 MHz): \( \delta \): 134.9 (C-3 and 5), 118.8 (C-2), 25.8 (s, H-3 and 5), 120.7 (C-5), 122.8 (C-5'), 131.4 (C-2'), 149.3 (C-4), 155.1 (C-2), 165.2 (C-3), 169.1, 169.4, 170.2, 170.6 (CH\(_3\)C=O).

**X-Ray Analysis of 3** The crystal used for data collection was a colorless rod (0.3 mm × 0.3 mm × 0.4 mm). All data were obtained on a Rigaku AFC5-S5 automated four-circle diffractometer with graphite-monochromated MoK\(_\alpha\) radiation. Unit cell parameters were determined by least-squares refinement of the optimized setting of 21 reflections. The intensities were measured using a \( \omega \)-2\( \theta \) scan up to 45°. Three standard reflections were monitored for every 150 measurements. The data were corrected for Lorentz and polarization factors. Absorption was applied and decay correction was not applied. Of the 1407 reflections collected, 1161 unique reflections with \( I \geq 3.0 \sigma(I) \) were used for structure determination and refinement. The structure was solved using a direct method with the teXan crystallographic software package. All non-H atoms were found in a Fourier map. The refinement of atomic parameters was carried out by means of full-matrix least-squares refinement using anisotropic temperature factors for all non-H atoms. All H atoms, except for those attached to O atoms, were located geometrically and refined. The H atoms attached to the aglycone were assigned absolute configuration and refined isotropically. The minimum and maximum peaks in the final difference Fourier map were –0.19 and 0.25 e\(^{-}\text{A}^{-3}\). The final refinement converged with \( R_{1} = 0.049, R_{w} = 0.056 \) for 198 parameters. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.

**X-Ray Analysis of 3a** The crystal used for data collection was a colorless prism (0.2 mm × 0.2 mm × 0.2 mm). All data were obtained on a Rigaku AFC5-SS automated four-circle diffractometer with graphite-monochromated MoK\(_\alpha\) radiation. Unit cell parameters were determined by least-squares refinement of the optimized setting of 25 reflections in the range of 12.5° < \( \theta \) < 14.3°. The intensities were measured using an \( \omega \)-2\( \theta \) scan up to 55°. Three standard reflections were monitored for every 150 measurements. The data were corrected for Lorentz and polarization factors. Correction of secondary extinction was applied (coefficient = 0.75773×10\(^{-4}\)). Absorption (\( \psi \)-scan) transmission factor = 0.941–1.000 and decay (≤0.897%) corrections were also applied. Of the 6264 reflections collected, 6260 unique reflections were used for structure determination and refinement. The structure was solved using a direct method with the teXan crystallographic software package. All non-H atoms were found in a Fourier map. The refinement of atomic parameters was carried out by means of full-matrix least-squares refinement using anisotropic temperature factors for all non-H atoms. All H atoms, except for those attached to N and O atoms, were located geometrically and refined. The H atoms attached to N and O atoms were found in a difference Fourier map and refined isotropically. The
final refinement converged with \( R_r = 0.038 \), \( R_w = 0.186 \) for 386 parameters. Atomic scattering factors were taken from the "International Tables for X-ray Crystallography." Crystal data: \( \text{C}_{19}\text{H}_{22}\text{O}_3\text{N}, M_r = 267.28 \), triclinic, space group \( P_1_1_1_1 \), \( a = 12.1632(2) \AA, \quad b = 12.1632(2) \AA, \quad c = 10.625(1) \AA, \quad \alpha = 111.18(1)^\circ, \quad \beta = 99.20(1)^\circ, \quad \gamma = 70.33(9)^\circ, \quad V = 1299.1(3) \text{Å}^3, \quad Z = 4, \quad D_\text{C} = 1.366 \text{Mg/m}^3, \quad F(000) = 560, \mu(\text{MoK}\alpha) = 0.951 \text{ cm}^{-1}. \)

**Mild Alkaline Hydrolysis of Glycosidacinoside B (5)** Glycosidacinoside B (5) (39.4 mg) was treated with 1 ml of 0.1 M NaOH in MeOH at 25 °C for 30 min. The reaction mixture was diluted with 4 ml of H2O and then extracted with 4 ml of CHCl3 twice. The combined organic layer was washed with 1 ml of brine and then treated with Amberlite IR-120B (H+). After being dried over Na2SO4, the organic solvent was evaporated under reduced pressure. The residue was dissolved in H2O and then treated with a Sep-Pak C18 cartridge to give the methyl ester (5a) as a syrup (12.0 mg, 81%).

The aqueous layer was neutralized with Amberlite IR-120B (H+) to yield 5b (25.2 mg, 91%). Methyl ester (5a): Colorless syrup, \( [\alpha]_D^{25} + 23.8^\circ (c = 0.30, \text{CHCl}_3). \) IR: \( \gamma_{\text{vap}}: 3431, 3292, 2925, 2842, 1739, 1437, 1337, 1261, 1157, 1073, 1053 \text{ cm}^{-1}. \) NMR (CD3OD, 400 MHz): 3.66 (3H, s, –COOCH3), 3.96 (1H, dddd, \( J = 10, 8, 5, 3 \text{ Hz, H-4}), 6.75—6.79 (2H, m), 7.05—7.11 (2H, m) (aromatic protons). 13C-NMR (CD3OD, 100 MHz): 36.6 (C-7), 116.1 (C-3), 120.5 (C-5), 122.9 (C-2), 140.0 (C-1), 172.2 (C-8). HR-FAB-MS (negative-ion mode) \( m/z: 169.0683 [\text{M–H}]^- (\text{Calcld for C8H7O3}) \), 169.0685. All physical data were essentially the same as those for the natural 4a.

**Enzymatic Hydrolysis of 5b** The glucoside (5b, 25.2 mg) derived from 5 was hydrolyzed by emulsin (10 mg) in 3 ml of H2O at 37 °C for 4 h. The reaction mixture was then cooled to 25 °C and treated with Amberlite IR-120B (H+). After being dried over Na2SO4, the organic solvent was evaporated under reduced pressure. The residue was dissolved in H2O and then treated with 3 ml of 0.1 M NaOH as for the natural 4a.

(\text{R})- and (\text{S})-MTPA Esters of 5a A solution of 5a (3.0 mg) in 1 ml of dehydrated CH2Cl2 was reacted with (\text{R})- and (\text{S})-MTPA (45 mg) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (39 mg) and \( N,N'\)-dimethylaminopiridinol (DMAP) (21 mg), and the mixture was then stirred at 25 °C for 1 h. After the addition of 1 ml of CH2Cl2, the solution was successively washed with H2O (1 ml), 5% HCl (1 ml), NaHCO3-saturated H2O (1 ml), and brine (1 ml). The organic layer was dried over Na2SO4 and then evaporated under reduced pressure. The residue was purified by preparative TLC (silica gel 0.5 mm thickness, Merck), applied for 18 cm, developed with \( n\)-hexane–EtOAc (4:1) for 9 cm and eluted with CHCl3–MeOH (9:1) to furnish the \( \text{S} \)-MTPA ester, 5d (4.8 mg, 71%). Through a similar procedure, 5e (4.9 mg, 72%) was prepared from 5a (3.0 mg) using (\text{S})-MTPA (42 mg), EDC (39 mg), and DMAP (19 mg). (\text{R})-MTPA ester (5d): colorless syrup. \( {^1}\text{H-NMR (CDCl}_3, 400 \text{MHz}) \): 1.86—1.94 (1H, m, H-5a), 1.94—2.03 (1H, m, H-5b), 2.04 (1H, brd, \( J = 17\text{Hz, H-3a}), 2.17 (1H, v brd, \( J = 17\text{Hz, H-3a}), 2.19 (2H, t-like, \( J = 7\text{Hz, H-2}), 2.45 (1H, brd, \( J = 17\text{Hz, H-3b}), 2.96 (2H, s, H-7)), 3.54 (3H, brs, –OCH3), 3.66 (3H, s, –COOCH3), 5.28 (1H, ddd, \( J = 10, 8, 5, 3 \text{ Hz, H-4}).

5.44 (1H, br s, H-2), 7.26—7.41 (3H, m), 7.52—7.53 (2H, m) (aromatic protons). HR-FAB-MS (positive-ion mode) \( m/z: 409.1241 [\text{M}+\text{Na}]^+ (\text{Calcld for C19H24O4Na}) \).