Five New Phenylethanoid Glycosides from the Whole Plants of *Lamium purpureum* L.

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Five new phenylethanoid glycosides, lamiusides A (1), B (2), C (3), D (4) and E (5), were isolated from the whole plants of *Lamium purpureum* L. (Labiatae) together with seven known compounds (6—12). On the basis of chemical and spectral analyses, the structures of the new compounds were elucidated to be 2-(3,4-dihydroxyphenyl)ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(4-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (1), 2-(3,4-dihydroxyphenyl)ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(4-*O*-*trans*-feruloyl)-β-D-glucopyranoside (2), 2-(3,4-dihydroxyphenyl)ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(6-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (3), 2-(3,4-dihydroxyphenyl)-*R*,*S*-methoxy-ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(4-*O*-*trans*-caffeoyl)-β-D-glucopyranoside (4) and 2-(3-hydroxy-4-methoxyphenyl)ethyl-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-glucopyranosyl-(1→6)-(4-*O*-*cis*-feruloyl)-β-D-glucopyranoside (5). In addition, the radical-scavenging activities of compounds 1—4 on 1,1-diphenyl-2-picrylhydrazyl radical were examined.

Key words *Lamiun purpureum*; Labiatae; phenylethanoid glycoside; radical-scavenging activity

The genus *Lamium* (Labiatae) comprises about 40 species, distributed in Europe, Asia and Africa. Some *Lamium* plants have been used in official and folk medicine. The most popular is *L. album* L. with uterytonic, astringent, antispasmodic and anti-inflammatory activities.[1] In previous paper, we reported on the components of essential oil of the whole plants of *L. purpureum* L. (*hime-odorikoso* in Japanese).[2] In the course of further studies on the constituents of the above plant, five new phenylethanoid glycosides, lamiusides A (**1**), B (**2**), C (**3**), D (**4**) and E (**5**), along with seven known compounds (**6**—**12**) have been isolated. This paper deals with the structural elucidation of these compounds. Additionally, we describe the radical-scavenging activities of compounds **1**—**4** on 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical. The known compounds were identified as acteoside (**6**),[3] leucosceptoside A (**7**),[4] isoacteoside (**8**),[5] 6″-*O*-β-D-glucopyranosylmartynoside (**9**),[6] shanzhiside methyl ester (**10**),[7] caryoptoside (**11**)[8] and lamalbide (**12**),[9] respectively, by comparison of their spectroscopic data with those previously described in the literature. This is the first time that compounds **7**—**12** have been isolated from *L. purpureum.*

Lamiuside A (**1**) was isolated as an amorphous powder. The molecular formula was determined to be $C_{35}H_{46}O_{20}$ by high-resolution (HR)-FAB-MS. Acid hydrolysis of **1** gave D-galactose, D-gulcose and L-rhamnose, which were identified by these retention times and optical rotations using chiral detection by HPLC analysis. The ^{1}H-NMR spectrum showed the presence of a 2-(3,4-dihydroxyphenyl)ethyl moiety [δ_H 2.79 (2H, br t, J=7.0 Hz, H-β), 3.75 (1H, m, Ha-α), 4.05 (1H, dt, J=9.8, 7.6 Hz, Hb-α), 6.56 (1H, dd, J=8.1, 2.0 Hz, H-6), 6.68 (1H, d, J=8.1 Hz, H-5) and 6.71 (1H, d, J=2.0 Hz, H-2)] and a *trans*-caffeoyl moiety [δ_H 6.27 (1H, d, J=16.0 Hz, H-8′), 6.78 (1H, d, J=8.3 Hz, H-5′), 6.96 (1H, dd, J=8.3, 2.0 Hz, H-6′), 7.06 (1H, d, J=2.0 Hz, H-2′) and 7.60 (1H, d, J=16.0 Hz, H-7′)]. Furthermore, three anomeric proton signals [δ_H 4.35 (1H, d, J=8.1 Hz, H-1‴), 4.37 (1H, d, J=8.3 Hz, H-1″), 5.57 (1H, d, J=1.5 Hz, H-1‴)] were recognized. The ^{13}C-NMR spectrum showed close similarity to that of **6**. However, a set of additional signals, corresponding to a D-galactopyranosyl group, appeared at δ 62.9 (C-6‴), 70.5 (C-4‴), 72.9 (C-2‴), 74.9 (C-3‴), 77.0 (C-5‴), and 107.6 (C-1‴) in the ^{13}C-NMR spectrum of **1**. The relatively large $^3J_{1'''-2'''}$ value of the anomeric proton of this D-galactopyranosyl group (8.1 Hz) indicated a β anomeric orientation. In comparing the ^{13}C-NMR spectra of **1** and **6**, the signals due to C-2‴ of α-L-rhamnopyranosyl group showed the glycosylation shift[10] by 10.6 ppm. Interpretation of the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) spectrum revealed correlations from H-1‴ of the β-D-galactopyranosyl group to C-2‴ of the α-L-rhamnopyranosyl group; H-1‴ of the α-L-rhamnopyranosyl group to C-3″ of the β-D-glucopyranosyl group; H-4″ of the β-D-glucopyranosyl group to C-9′ of the *trans*-caffeoyl group; and H-1″ of the β-D-glucopyranosyl group to C-α of the 2-(3,4-dihydroxyphenyl)ethyl group. Therefore, the structure of **1** was determined to be 2-(3,4-dihydroxyphenyl)ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(4-*O*-*trans*-caffeoyl)-β-D-glucopyranoside.

Lamiuside B (**2**) was isolated as an amorphous powder whose molecular formula was determined to be $C_{36}H_{48}O_{20}$ by HR-FAB-MS. Acid hydrolysis of **2** gave D-galactose, D-gulcose and L-rhamnose in the above manner. The ^{1}H- and ^{13}C-NMR spectral data were closely similar to those of **1**, except for the presence of a phenolic methoxyl group [δ_H 3.89 (3H, s); δ_C 56.5] arising from the acyl moiety. The location of the methoxyl group on C-3′ was deduced from spectral comparison of the acyl moiety of **2** with that of the *trans*-feruloyl moiety of compound **7**. Consequently, the structure of **2** was determined to be 2-(3,4-dihydroxyphenyl)ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(4-*O*-*trans*-feruloyl)-β-D-glucopyranoside.

Lamiuside C (**3**) was isolated as an amorphous powder, and its molecular formula, $C_{35}H_{46}O_{20}$, was determined by HR-FAB-MS. Acid hydrolysis of **3** gave D-galactose, D-gulcose and L-rhamnose in the above manner. The ^{1}H- and ^{13}C-NMR spectra of **3** resembled those of **8**, except for the pres-

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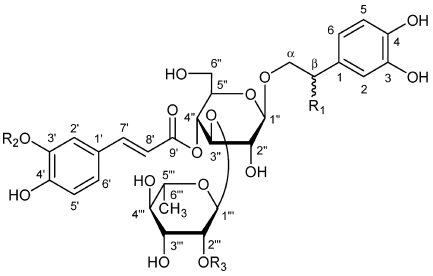
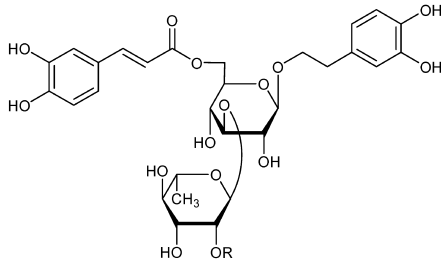
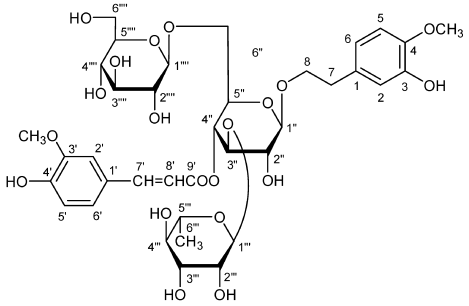


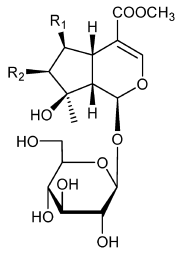
1 $R_1 = R_2 = H$, $R_3 = \beta$-D-Gal*p*
2 $R_1 = H$, $R_2 = CH_3$, $R_3 = \beta$-D-Gal*p*
4 $R_1 = OCH_3$, $R_2 = H$, $R_3 = \beta$-D-Gal*p*
6 $R_1 = R_2 = R_3 = H$
7 $R_1 = R_3 = H$, $R_2 = CH_3$
13 $R_1 = OCH_3$, $R_2 = R_3 = H$



3 R = β-D-Gal*p*
8 R = H



5 7',8' - *cis*
9 7',8' - *trans*



10 $R_1 = OH$, $R_2 = H$
11 $R_1 = H$, $R_2 = OH$
12 $R_1 = OH$, $R_2 = OH$

Chart 1

ence of an additional β-D-galactopyranosyl group [δ_H 4.38 (1H, d, J=7.6 Hz, H-1‴); δ_C 62.8 (C-6‴), 70.5 (C-4‴), 73.0 (C-2‴), 75.0 (C-3‴), 77.0 (C-5‴), 107.6 (C-1‴)] and a difference in the chemical shift at C-2‴ [δ 82.8 (+10.4 ppm)] due to glycosylation. Therefore, compound **3** was determined to be 2-(3,4-dihydroxyphenyl)ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(6-*O*-*trans*-caffeoy)-β-D-glucopyranoside.

Lamiuside D (**4**) was isolated as an amorphous powder, $C_{36}H_{48}O_{21}$ (HR-FAB-MS). Acid hydrolysis gave D-galactose, D-gulcose and L-rhamnose in the above manner. The ^{1}H- and ^{13}C-NMR spectra of **4** were closely related to those of campneoside I (**13**),[11] except for the presence of an additional β-D-galactopyranosyl group [δ_H 4.41 (1H, d, J=7.8 Hz, H-1‴); δ_C 62.8 (C-6‴), 70.4 (C-4‴), 72.9 (C-2‴), 75.0 (C-3‴), 77.0 (C-5‴), 107.7 (C-1‴)] and a difference in the chemical shift at C-2‴ [δ 83.1 (+10.8 ppm)] due to glycosylation. The ^{13}C-NMR spectral data of **4** showed two kinds of chemical shift for each carbon in the vicinity of the asymmetric C-7, such as C-2, C-1″, C-2″, C-6″, C-α and C-β. These findings indicated that **4** existed as epimers at the C-β position of the phenethyl alcohol moiety like campneoside I (**13**). Accordingly, **4** was determined to be 2-(3,4-dihydroxyphenyl)-*R*,*S*-methoxy-ethyl-*O*-β-D-galactopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(4-*O*-*trans*-caffeoyl)-β-D-glucopyranoside. Compound **4** might be an artifact produced during the extraction and isolation procedure.

Lamiuside E (**5**) was isolated as an amorphous powder, $C_{37}H_{50}O_{20}$ (HR-FAB-MS). Acid hydrolysis gave D-gulcose and L-rhamnose in the above manner. Its ^{1}H-NMR spectrum closely resembled that of **9**, except that the olefin proton signals at δ 5.80 (H-8′) and 6.94 (H-7′) shifted upfield and their coupling constant (J=12.7 Hz) was smaller than that of **9** [δ_H 6.37 (1H, d, J=15.9 Hz, H-8′), 7.67 (1H, d, J=15.9 Hz, H-7′)]. This indicates that the geometry of the olefin in the feruloyl moiety in **5** is in the *cis*-form. The structure of **5** was therefore determined as 2-(3-hydroxy-4-methoxyphenyl)-ethyl-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-glucopyranosyl-(1→6)-(4-*O*-*cis*-feruloyl)-β-D-glucopyranoside.

Phenylethanoid glycosides are water soluble natural products widely distributed in the plant kingdom, most of which are isolated from traditional medicinal plants. Their significant biological activities such as enzyme inhibition, immunomodulatory, antibacterial and cytotoxic activities have been reported.[12] Recently, some *in vitro* antioxidative assay models were demonstrated antioxidative and free radical scavenging activities for phenylethanoid glycosides.[13—16] We determined the antioxidative activities of compounds **1**—**4** by using a DPPH free radical scavenging system by comparing *dl*-α-tocopherol, commonly used natural antioxidant. Among them, **1** (Reducing %: 84.7%), **3** (Reducing %: 66.5%) and **4** (Reducing %: 45.1%) showed potent activities

at 4.0×10^{-5} M comparable to that of *dl*-α-tocopherol (Reducing %: 38.5%), while **2** (Reducing %: 9.2%) was found to be almost inactive at 4.0×10^{-5} M. In a comparison of compounds **1**, **3** and **4** with **2**, the antioxidative effects of these compounds was potentiated by an increase in the number of phenolic hydroxyl group in the molecule.

Experimental

General Procedures Optical rotations were determined using a JASCO DIP-360 digital polarimeter. UV spectra were recorded with a Beckman DU-64 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL JNM-LA 400 (400 and 100 MHz, respectively) spectrometer. Chemical shifts are given on a δ (ppm) scale, with tetramethylsilane as internal standard. The HR-FAB-MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on a Kieselgel 60 (230—400 mesh, Merck). HPLC was performed by using a system comprised of CCPS pump (Tosoh), an RI-8020 detector (Tosoh), and a JASCO OR-2090 plus chiral detector.

Plant Material The whole plants of *Lamium purpureum* were collected in Sendai City, Miyagi Prefecture, Japan, in April of 2004.

Extraction and Isolation The whole plants of *L. purpureum* (4.1 kg) were extracted with MeOH at room temperature. The MeOH extract was concentrated under reduced pressure. The MeOH extract (164 g) was suspended in water, and this suspension was extracted with *n*-hexane, $CHCl_3$, AcOEt, *n*-BuOH and H_2O. The *n*-BuOH extract (27 g) was chromatographed on a silica gel column using $CHCl_3$–MeOH–H_2O (30 : 10 : 1) to afford 102 fractions. Fraction 42 was purified by preparative HPLC [column, TSKgel ODS-120T (7.8 mm i.d.×30 cm, Tosoh), column temperature, 40 °C; mobile phase, MeOH–H_2O (1 : 3); flow rate, 1.0 ml/min] to give **7** (2.0 mg), **8** (1.0 mg), **9** (1.4 mg) and **10** (1.0 mg). Fraction 56 was purified by preparative HPLC [column, TSKgel Amide-80 (7.8 mm i.d.×30 cm, Tosoh), column temperature, 40 °C; mobile phase, CH_3CN–H_2O (3 : 1); flow rate, 1.5 ml/min] to give **2** (1.5 mg) and **6** (1.0 mg). Fraction 79 was purified by preparative HPLC [column, TSKgel Amide-80 (7.8 mm i.d.×30 cm, Tosoh), column temperature, 40 °C; mobile phase, CH_3CN–H_2O (3 : 1); flow rate, 1.5 ml/min] to give **1** (3.5 mg), **3** (1.5 mg) and **4** (10.0 mg). The H_2O extract (12 g) was chromatographed on a silica gel column using $CHCl_3$–MeOH–H_2O (30 : 10 : 1) to afford 80 fractions. Fraction 30 was purified by preparative HPLC [column, TSKgel ODS-120T (7.8 mm i.d.×30 cm, Tosoh), column temperature, 40 °C; mobile phase, MeOH–H_2O (1 : 3); flow rate, 1.0 ml/min] to give **5** (0.5 mg), **11** (1.0 mg) and **12** (1.5 mg).

Lamiuside A (**1**): Amorphous powder. $[\alpha]_D^{26}$ −45.1° (c=2.38, MeOH). UV λ_{max} (MeOH) nm (log ε): 217 (4.3), 290 (4.2), 329 (4.3). HR-FAB-MS m/z: 809.2491 ($[M+Na]^+$, Calcd for $C_{35}H_{46}O_{20}Na$: 809.2480). ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.05 (3H, d, J=6.1 Hz, H-6‴), 2.79 (2H, br t, J=7.0 Hz, H-β), 3.75 (1H, m, Ha-α), 3.99 (1H, dd, J=3.4, 1.5 Hz, H-2‴), 4.04 (1H, dt, J=9.8, 7.6 Hz, Hb-α), 4.35 (1H, d, J=8.1 Hz, H-1⁗), 4.37 (1H, d, J=8.3 Hz, H-1″), 4.93 (1H, dd, J=9.5, 9.3 Hz, H-4″), 5.57 (1H, d, J=1.5 Hz, H-1‴), 6.27 (1H, d, J=16.0 Hz, H-8′), 6.56 (1H, dd, J=8.1, 2.0 Hz, H-6), 6.68 (1H, d, J=8.1 Hz, H-5), 6.71 (1H, d, J=2.0 Hz, H-2), 6.78 (1H, d, J=8.3 Hz, H-5′), 6.96 (1H, dd, J=8.3, 2.0 Hz, H-6′), 7.06 (1H, d, J=2.0 Hz, H-2′), 7.60 (1H, d, J=16.0 Hz, H-7′). ^{13}C-NMR (100 MHz, CD_3OD) δ: 131.6 (C-1), 117.2 (C-2), 144.7 (C-3), 146.1 (C-4), 116.4 (C-5), 121.3 (C-6), 72.3 (C-α), 36.6 (C-β), 127.7 (C-1′), 115.3 (C-2′), 149.8 (C-3′), 146.9 (C-4′), 116.6 (C-5′), 123.3 (C-6′), 148.1 (C-7′), 114.7 (C-8′), 168.3 (C-9′), 104.2 (C-1″), 76.2 (C-2″), 83.0 (C-3″), 70.4 (C-4″), 76.0 (C-5″), 62.4 (C-6″), 102.4 (C-1‴), 83.0 (C-2‴), 71.9 (C-3‴), 74.2 (C-4‴), 70.5 (C-5‴), 18.5 (C-6‴), 107.6 (C-1⁗), 72.9 (C-2⁗), 74.9 (C-3⁗), 70.5 (C-4⁗), 77.0 (C-5⁗), 62.9 (C-6⁗).

Lamiuside B (**2**): Amorphous powder. $[\alpha]_D^{24}$ −27.8° (c=0.09, MeOH). UV λ_{max} (MeOH) nm (log ε): 216 (4.3), 290 (4.1), 326 (4.3). HR-FAB-MS m/z: 823.2625 ($[M+Na]^+$, Calcd for $C_{36}H_{48}O_{20}Na$: 823.2637). ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.06 (3H, d, J=6.1 Hz, H-6‴), 2.79 (2H, br t, J=7.0 Hz, H-β), 3.75 (1H, m, Ha-α), 3.89 (3H, s, CH_3O-3′), 4.05 (1H, dt, J=9.8, 7.6 Hz, Hb-α), 4.35 (1H, d, J=7.8 Hz, H-1⁗), 4.37 (1H, d, J=7.8 Hz, H-1″), 4.93 (1H, dd, J=9.5, 9.3 Hz, H-4″), 5.57 (1H, d, J=1.5 Hz, H-1‴), 6.37 (1H, d, J=16.0 Hz, H-8′), 6.57 (1H, dd, J=8.1, 2.0 Hz, H-6), 6.67 (1H, d, J=8.1 Hz, H-5), 6.70 (1H, d, J=2.0 Hz, H-2), 6.81 (1H, d, J=8.2 Hz, H-5′), 7.09 (1H, dd, J=8.2, 2.0 Hz, H-6′), 7.19 (1H, d, J=2.0 Hz, H-2′), 7.66 (1H, d, J=16.0 Hz, H-7′). ^{13}C-NMR (100 MHz, CD_3OD) δ: 131.6 (C-1), 117.2 (C-2), 144.7 (C-3), 146.2 (C-4), 116.6 (C-5), 121.3 (C-6), 72.3 (C-α), 36.6 (C-β), 127.7 (C-1′), 111.9 (C-2′), 149.5 (C-3′), 149.8 (C-4′), 117.2 (C-5′), 124.4 (C-6′), 147.9 (C-7′), 115.1 (C-8′), 168.2 (C-9′), 56.5 (CH_3O-3′), 104.2 (C-1″), 76.2 (C-2″), 83.0 (C-3″), 70.4 (C-4″), 76.1 (C-5″), 62.4 (C-6″), 102.4 (C-1‴), 83.1 (C-2‴), 71.9 (C-3‴), 74.2 (C-4‴), 70.5 (C-5‴), 18.5 (C-6‴), 107.6 (C-1⁗), 72.9 (C-2⁗), 74.9 (C-3⁗), 70.5 (C-4⁗), 77.0 (C-5⁗), 62.9 (C-6⁗).

Lamiuside C (**3**): Amorphous powder. $[\alpha]_D^{22}$ −27.2° (c=0.17, MeOH). UV λ_{max} (MeOH) nm (log ε): 215 (4.3), 289 (4.1), 328 (4.2). HR-FAB-MS m/z: 809.2501 ($[M+Na]^+$, Calcd for $C_{35}H_{46}O_{20}Na$: 809.2480). ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.23 (3H, d, J=6.1 Hz, H-6‴), 2.77 (2H, br t, J=7.6 Hz, H-β), 3.70 (1H, dd, J=9.5, 4.6 Hz, Ha-α), 3.97 (1H, dd, J=9.5, 6.1 Hz, Hb-α), 4.33 (1H, d, J=8.1 Hz, H-1″), 4.36 (1H, m, Ha-6′), 4.38 (1H, d, J=7.6 Hz, H-1⁗), 4.49 (1H, dd, J=12.0, 2.0 Hz, Hb-6′), 5.57 (1H, br s, H-1‴), 6.28 (1H, d, J=16.0 Hz, H-8′), 6.53 (1H, dd, J=8.1, 2.0 Hz, H-6), 6.63 (1H, d, J=8.1 Hz, H-5), 6.68 (1H, d, J=2.0 Hz, H-2), 6.76 (1H, d, J=8.3 Hz, H-5′), 6.89 (1H, dd, J=8.3, 2.0 Hz, H-6′), 7.03 (1H, d, J=2.0 Hz, H-2′), 7.55 (1H, d, J=16.0 Hz, H-7′). ^{13}C-NMR (100 MHz, CD_3OD) δ: 131.5 (C-1), 117.2 (C-2), 144.7 (C-3), 146.2 (C-4), 116.4 (C-5), 121.3 (C-6), 72.4 (C-α), 36.7 (C-β), 127.7 (C-1′), 115.1 (C-2′), 149.7 (C-3′), 146.9 (C-4′), 116.6 (C-5′), 123.2 (C-6′), 147.3 (C-7′), 114.9 (C-8′), 169.2 (C-9′), 104.4 (C-1″), 75.8 (C-2″), 84.3 (C-3″), 70.4 (C-4″), 75.5 (C-5″), 64.7 (C-6″), 101.8 (C-1‴), 82.8 (C-2‴), 72.2 (C-3‴), 74.4 (C-4‴), 70.0 (C-5‴), 18.0 (C-6‴), 107.6 (C-1⁗), 73.0 (C-2⁗), 75.0 (C-3⁗), 70.5 (C-4⁗), 77.0 (C-5⁗), 62.8 (C-6⁗).

Lamiuside D (**4**): Amorphous powder. $[\alpha]_D^{24}$ −21.9° (c=0.13, MeOH). UV λ_{max} (MeOH) nm (log ε): 217 (4.3), 289 (4.1), 329 (4.2). HR-FAB-MS m/z: 839.2569 ($[M+Na]^+$, Calcd for $C_{36}H_{48}O_{21}Na$: 839.2587). ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.06 (3H, d, J=6.3 Hz, H-6‴), 3.34 (3H, s, CH_3O-β), 4.35, 4.36 (total 1H, each d, J=7.6 Hz, H-1″), 4.41 (1H, d, J=7.8 Hz, H-1⁗), 4.87 (1H, dd, J=9.7, 9.3 Hz, H-4″), 5.57 (1H, br s, H-1‴), 6.26 (1H, d, J=16.1 Hz, H-8′), 6.65 (1H, dd, J=8.1, 2.0 Hz, H-6), 6.75 (1H, d, J=8.1 Hz, H-5), 6.76 (1H, d, J=2.0 Hz, H-2), 6.76 (1H, d, J=8.3 Hz, H-5′), 6.95 (1H, dd, J=8.3, 2.2 Hz, H-6′), 7.04 (1H, d, J=2.2 Hz, H-2′), 7.58 (1H, d, J=16.1 Hz, H-7′). ^{13}C-NMR (100 MHz, CD_3OD) δ: 131.0 (C-1), 115.1/115.2 (C-2), 146.6 (C-3), 146.6 (C-4), 116.3 (C-5), 119.9 (C-6), 75.0/75.1 (C-α), 83.7/84.5 (C-β), 56.8 (CH_3O-β), 127.7 (C-1′), 115.3 (C-2′), 149.9 (C-3′), 146.9 (C-4′), 116.6 (C-5′), 123.3 (C-6′), 148.1 (C-7′), 114.7 (C-8′), 168.2 (C-9′), 104.1/104.6 (C-1″), 76.1/76.2 (C-2″), 83.1 (C-3″), 70.4 (C-4″), 76.0 (C-5″), 62.4/62.6 (C-6″), 102.2 (C-1‴), 83.1 (C-2‴), 71.9 (C-3‴), 74.2 (C-4‴), 70.4 (C-5‴), 18.5 (C-6‴), 107.7 (C-1⁗), 72.9 (C-2⁗), 75.0 (C-3⁗), 70.4 (C-4⁗), 77.0 (C-5⁗), 62.8 (C-6⁗).

Lamiuside E (**5**): Amorphous powder. $[\alpha]_D^{27}$ −30.3° (c=0.05, MeOH). UV λ_{max} (MeOH) nm (log ε): 216 (4.2), 287 (4.0), 327 (4.2). HR-FAB-MS m/z: 837.2782 ($[M+Na]^+$, Calcd for $C_{37}H_{50}O_{20}Na$: 837.2794). ^{1}H-NMR (400 MHz, CD_3OD): δ: 1.14 (3H, d, J=6.4 Hz, H-6‴), 2.81 (2H, br t, J=6.8 Hz, H-β), 3.81, 3.90 (each 3H, s, CH_3O-4, CH_3O-3′), 4.28 (1H, d, J=7.8 Hz, H-1⁗), 4.37 (1H, d, J=7.3 Hz, H-1″), 5.15 (1H, br s, H-1‴), 5.80 (1H, d, J=12.7 Hz, H-8′), 6.69 (1H, br d, J=7.8 Hz, H-6), 6.74 (1H, br s, H-2), 6.77 (1H, d, J=7.7 Hz, H-5′), 6.82 (1H, d, J=7.8 Hz, H-5), 6.94 (1H, d, J=12.7 Hz, H-7′), 7.17 (1H, br d, J=7.8 Hz, H-6′), 7.88 (1H, br s, H-2′).

Acid Hydrolysis of 1—5 Each of the compounds, **1**—**5** (*ca.* 0.3 mg), was refluxed with 5% HCl for 2 h. The reaction mixture was neutralized with Ag_2CO_3 and filtered. The solution was concentrated *in vacuo* and dried to give a sugar fraction. The sugar fraction was analyzed by HPLC under the following conditions: column, TSKgel Amide-80 (7.8 mm i.d.×30 cm, Tosoh; column temperature, 40 °C; mobile phase, CH_3CN–H_2O (5 : 1); flow rate, 1.0 ml/min; chiral detection. Identification of L-rhamnose, D-glucose and D-galactose present in the sugar fraction was carried out by the comparison of these retention times and optical rotations with those of authentic samples; t_R (min) 24.6 (L-rhamnose, negative optical rotation), 50.1 (D-glucose, positive optical rotation), 51.0 (D-galactose, positive optical rotation).

Measurement of DPPH Radical-Scavenging Activity[17] EtOH solution of compounds **1**—**4** (4.0×10^{-5} M, 1.0 ml) were each added to 0.5 mM DPPH/EtOH solution (1.0 ml), and the absorbance of each mixture was determined at 517 nm after 30 min. The radical-scavenging activity was determined by comparing the absorbance with that of blank (100%) containing only DPPH and solvent. *dl*-α-Tocopherol was used as a standard, and measurement was done in triplicate. % reduction=$100\times[(Abs_{blank}-Abs_{sample})/Abs_{blank}]$.

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