

Three New Monoterpene Glucosides from *Lamium amplexicaule*

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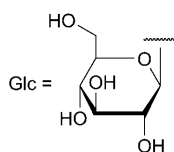
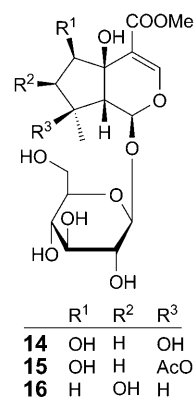
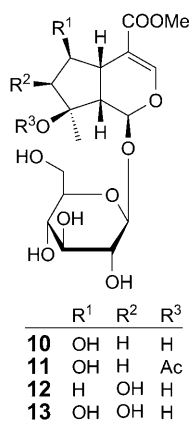
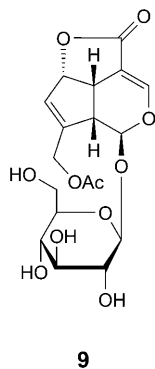
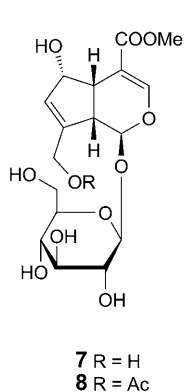
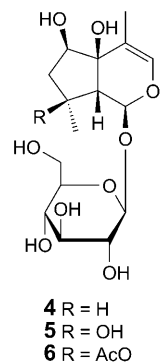
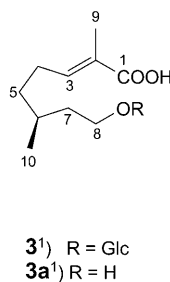
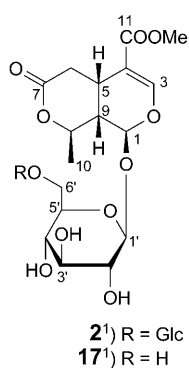
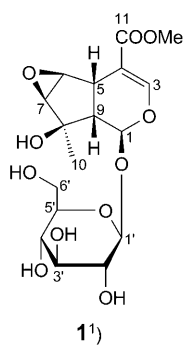
Three new monoterpene glucosides, lamiuamplexosides A–C (**1–3**), along with thirteen known glucosides, were isolated from the whole plant of *Lamium amplexicaule* L. The structures of **1–3** were elucidated on the basis of spectroscopic, chemical, and physicochemical evidence.

Introduction. – The genus *Lamium* L. (Labiatae) comprises about 40 species of annuals and perennials occurring from North Africa to Eurasia [1]. In a previous paper, we reported the isolation and structural elucidation of iridoid glucosides and phenylethanoid glucosides from the whole plant of *L. purpureum* L. [2]. As a part of our continuing studies on the glucosides of the genus *Lamium* plants, we examined the constituents of glucosides of *L. amplexicaule* L. There are reports of the isolation of iridoid glucosides [3–8] and flavonoid glucosides [9] from this plant. Careful reinvestigation of a MeOH extract of the whole plant of *L. amplexicaule* led to the isolation of three new glucosides, lamiuamplexosides A–C¹⁾ (**1–3**, resp.), together with the thirteen known glucosides **4–16**. This article deals with the isolation and structural elucidation of the new compounds.

Results and Discussion. – The whole plant of *L. amplexicaule* was extracted with MeOH. The MeOH extract was partitioned between H₂O and CHCl₃, H₂O and AcOEt, and H₂O and BuOH. The BuOH-soluble fraction was subjected to column chromatography (silica gel and *Sephadex LH-20*) and prep. HPLC to afford a new compound, named lamiuamplexoside A (**1**), and nine known compounds, **4**, **6–8**, **10–13**, and **15**. The H₂O-soluble fraction was subjected to column chromatography (*Diaion HP-20* and silica gel) and prep. HPLC to afford two new compounds, named lamiuamplexoside B (**2**) and lamiuamplexoside C (**3**), and four known compounds, **5**, **9**, **14**, and **16**.

Lamiuamplexoside A (**1**) was obtained as an amorphous powder. The molecular formula of **1** was determined as C₁₇H₂₄O₁₁ based on the positive-mode HR-FAB-MS (*m/z* 405.1384 ([*M* + H]⁺)). Acid hydrolysis of **1** gave D-glucose, which was identified by its retention time and optical rotation by means of chiral detection by HPLC. The ¹H-NMR spectrum of **1** in CD₃OD (*Table 1*) exhibited signals due to one Me (δ (H) 1.23 (*s*)), two CH, one MeO (δ (H) 3.73 (*s*)), and three CH–O groups (δ (H) 3.19 (*d*,

¹⁾ Arbitrary atom numbering; for systematic names, see *Exper. Part*.



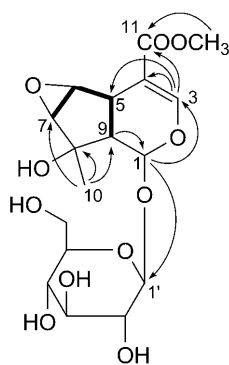
$J = 3.2$ Hz), 3.81 (*dd*, $J = 3.2, 1.2$ Hz), and 5.69 (*s*)) and one C=C–H moiety. Furthermore, one anomeric signal ($\delta(\text{H})$ 4.60 (*d*, $J = 8.1$ Hz)) was recognized. The coupling constant of an anomeric signal indicated that the glucosyl linkage is in β -configuration. The ^{13}C -NMR spectrum of **1** in CD_3OD (Table I) showed signals due one O-bearing, quaternary, sp^3 -type C-atom ($\delta(\text{C})$ 77.8) and one C=O group ($\delta(\text{C})$ 168.6). The $^1\text{H}, ^1\text{H}$ -COSY data of **1** (Fig. I) implied connectivities of H–C(5) to H–C(6), of H–C(5) to H–C(9), and of H–C(6) to H–C(7). The HMBC spectrum (Fig. I) showed the correlations H–C(1)/C(3) and C(1'), H–C(3)/C(4), C(5), and C(11), H–C(9)/C(1), Me(10)/C(7), C(8), and C(9), and MeO/C(11). According to the molecular formula of **1**, there were six degrees of unsaturation. One C=O group, one C=C–H moiety, an iridoid skeleton, and one β -Glc unit accounted for five of those. The remaining degree of unsaturation was assumed to be due to an epoxide ring formed between C(6) and C(7), as inferred from the ^{13}C -NMR data ($\delta(\text{C})$ 57.8 (C(6))

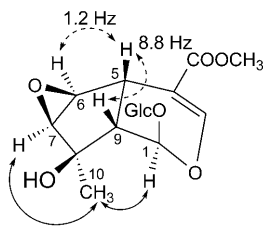
Table 1. ^1H - and ^{13}C -NMR (400 and 100 MHz, resp.) Data of Compound **1**¹ in CD_3OD . δ in ppm, J in Hz.

	$\delta(\text{H})$	$\delta(\text{C})$
H–C(1)	5.69 (s)	94.3
H–C(3)	7.47 (s)	154.1
C(4)		107.4
H–C(5)	3.24 (dd, $J=8.8, 1.2$)	33.0
H–C(6)	3.81 (dd, $J=3.2, 1.2$)	57.8
H–C(7)	3.19 (d, $J=3.2$)	63.4
C(8)		77.8
H–C(9)	2.27 (d, $J=8.8$)	46.5
Me(10)	1.23 (s)	21.4
C(11)		168.6
H–C(1')	4.60 (d, $J=8.1$)	99.8
H–C(2')	3.14 (dd, $J=9.0, 8.1$)	74.6
H–C(3')	^{a)}	78.0
H–C(4')	^{a)}	71.6
H–C(5')	^{a)}	78.4
$\text{CH}_2(6')$	3.65 (dd, $J=12.0, 5.6$), 3.87 (dd, $J=12.0, 2.0$)	62.8
MeO–C(11)	3.73 (s)	51.8

^{a)} Overlapped by the solvent signal.

and 63.4 (C(7))) [10]. Therefore, the constitution of **1** was deduced. The relative configuration of **1** was determined as follows. In the ^1H -NMR spectrum, the coupling constant ($J=8.8$ Hz) between $\text{H}_\beta\text{--C}(5)$ and $\text{H}_\beta\text{--C}(9)$ indicates the *cis* relationship of these H-atoms, and that ($J=1.2$ Hz) between $\text{H}_\beta\text{--C}(5)$ and $\text{H}_\alpha\text{--C}(6)$ indicates the *trans* relationship of these H-atoms, *i.e.*, β -orientation of the epoxide ring (Fig. 2) [11]. In an NOE experiment, irradiation of Me(10) enhanced the signals of $\text{H}_\alpha\text{--C}(1)$ (4.31%) and $\text{H}_\alpha\text{--C}(7)$ (4.46%). These observations revealed that the β -D-glucopyranosyloxy group at C(1) and the OH group at C(8) are on the same face (β) of the ring system (Fig. 2). From these data, the structure of **1** was elucidated as *rel*-(1a*R*,1b*R*,5-*R*,5a*R*,6*S*,6a*R*)-5-(β -D-glucopyranosyloxy)-1a,1b,5,5a,6,6a-hexahydro-6-hydroxy-6-methyloxireno[3,4]cyclopenta[1,2-*c*]pyran-2-carboxylic acid methyl ester, the absolute configuration of which remains to be established.

Fig. 1. ^1H , ^1H -COSY (—) and HMBC ($\text{H} \rightarrow \text{C}$) of **1**¹

Fig. 2. Selected coupling constant ($\longleftrightarrow$) and NOEs ($\leftrightarrow$) of **1**¹

Lamiauxplexoside B (**2**) was obtained as an amorphous powder. The molecular formula of **2** was determined as $C_{23}H_{34}O_{16}$ based on the positive-mode HR-FAB-MS (m/z 589.1744 ($[M + Na]^+$)). The ^{13}C -NMR spectrum of **2** in CD_3OD (Table 2) was similar to that of 8-epikingiside (= (1*R*,4*aS*,8*S*,8*aS*)-8-(β -D-glucopyranosyloxy)-4,4*a*,8,8*a*-tetrahydro-1-methyl-3-oxo-1*H*,3*H*-pyrano[3,4-*c*]pyran-5-carboxylic acid methyl ester; **17**) (see Table 2) [12][13], except for the presence of an additional hexosyl moiety and a difference in the chemical shift of $CH_2(6')$ ($\delta(C)$ 70.8 ($\Delta\delta = +8.0$)) due to glucosylation [14]. Acid hydrolysis of **2** gave only D-glucose, as described above for **1**. In the 1H -NMR spectrum of **2** in CD_3OD (Table 2), two

Table 2. 1H - and ^{13}C -NMR (600 and 150 MHz, resp.) Data of Compounds **2**¹, and ^{13}C -NMR (150 MHz) Data of Compound **17**¹) in CD_3OD . δ in ppm, J in Hz.

	2		17
	$\delta(H)$	$\delta(C)$	$\delta(C)$
H–C(1)	5.48 (<i>d</i> , $J = 8.1$)	96.9	96.2
H–C(3)	7.58 (<i>d</i> , $J = 1.1$)	154.5	154.4
C(4)		109.4	109.5
H–C(5)	3.06 (<i>ddd</i> , $J = 11.7, 7.0, 3.7$)	28.3	28.1
$CH_2(6)$	2.54 (<i>dd</i> , $J = 16.5, 11.7, H_a$), 2.86 (<i>dd</i> , $J = 16.5, 3.7, H_\beta$)	34.9	34.6
C(7)		175.0	174.7
H–C(8)	4.53 (<i>dq</i> , $J = 7.7, 6.6$)	75.9	75.7
H–C(9)	2.13 (<i>ddd</i> , $J = 8.1, 7.7, 7.0$)	41.9	41.8
Me(10)	1.51 (<i>d</i> , $J = 6.6$)	21.9	21.7
C(11)		168.4	168.3
H–C(1')	4.70 (<i>d</i> , $J = 8.1$)	101.2	100.6
H–C(2')	3.16 (<i>dd</i> , $J = 9.2, 8.1$)	74.7	74.6
H–C(3')	^{a)}	78.0	78.4
H–C(4')	^{a)}	71.9	71.6
H–C(5')	^{a)}	77.4	77.8
$CH_2(6')$	3.72 (<i>dd</i> , $J = 11.7, 5.9$), 4.20 (<i>dd</i> , $J = 11.7, 2.2$)	70.8	62.8
H–C(1'')	4.30 (<i>d</i> , $J = 8.1$)	105.6	
H–C(2'')	3.18 (<i>dd</i> , $J = 9.2, 8.1$)	75.2	
H–C(3'')	^{a)}	77.9	
H–C(4'')	^{a)}	71.6	
H–C(5'')	^{a)}	78.0	
$CH_2(6'')$	3.65 (<i>dd</i> , $J = 11.7, 5.9$), 3.86 (<i>dd</i> , $J = 11.5, 1.5$)	62.8	
MeO–C(11)	3.72 (<i>s</i>)	52.0	52.0

^{a)} Overlapped by the solvent signal.

anomeric signals ($\delta(\text{H})$ 4.30 ($d, J = 8.1$ Hz) and 4.70 ($d, J = 8.1$ Hz)) were recognized. The coupling constants of the latter indicated that the glucosyl linkages are in β -configuration. Consequently, the structure of **2** was elucidated as *rel*-(1*R*,4*aS*,8*S*,8*aS*)-8-[(6-*O*- β -D-glucopyranosyl- β -D-glucopyranosyl)oxy]-4,4*a*,8,8*a*-tetrahydro-1-methyl-3-oxo-1*H*,3*H*-pyrano[3,4-*c*]pyran-5-carboxylic acid methyl ester. The absolute configuration of **2** could not be determined yet.

Lamiuamplexoside C (**3**) was obtained as an amorphous powder. The negative-mode FAB-MS of **3** showed a quasimolecular ion at m/z 347 ($[M - \text{H}]^-$). The ^1H -NMR spectrum of **3** in CD_3OD (Table 3) exhibited signals due to two Me ($\delta(\text{H})$ 0.93 ($d, J = 6.4$ Hz) and 1.84 ($d, J = 1.2$ Hz)), one CH, three CH_2 , and one $\text{CH}_2\text{-O}$ group ($\delta(\text{H})$ 3.59–3.63 (m) and 3.91–3.95 (m)) and one $\text{C}=\text{C}\text{-H}$ moiety. Furthermore, one anomeric signal ($\delta(\text{H})$ 4.24 ($d, J = 7.8$ Hz)) was recognized. The coupling constant of the latter indicated that the glucosyl linkage is in β -configuration. The ^{13}C -NMR spectrum of **3** in CD_3OD (Table 3) showed signals due one β -Glc unit and one $\text{C}=\text{O}$ group ($\delta(\text{C})$ 169.8). The $^1\text{H}, ^1\text{H}$ -COSY data of **3** (Fig. 3) implied connectivities of $\text{H}-\text{C}(3)$ to $\text{CH}_2(4)$, of $\text{CH}_2(4)$ to $\text{CH}_2(5)$, of $\text{CH}_2(5)$ to $\text{H}-\text{C}(6)$, of $\text{H}-\text{C}(6)$ to $\text{CH}_2(7)$, of $\text{H}-\text{C}(6)$ to Me(10), and of $\text{CH}_2(7)$ to $\text{CH}_2(8)$. The HMBC spectrum (Fig. 3) showed the correlations Me(9)/C(1), C(2), and C(3) and $\text{H}-\text{C}(1')/\text{C}(8)$. The $\text{C}=\text{C}$ bond between C(2) and C(3) was (*E*)-configured, based on a NOESY cross-peak between $\text{CH}_2(4)$ and Me(9) (Fig. 3). On enzymatic hydrolysis with cellulose and β -glucosidase (*ca.* 3:1), **3** yielded (2*E*,6*S*)-8-hydroxy-2,6-dimethyloct-2-enoic acid (**3a**) [15] and D-glucose, which was identified as described above for **1**. The absolute configuration at C(6) of **3a** was determined as (*S*) by comparison of the optical-rotation values with those reported in the literature [15]. Thus, the structure of **3** was elucidated as (2*E*,6*S*)-8-(β -D-glucopyranosyloxy)-2,6-dimethyloct-2-enoic acid. The

Table 3. ^1H - and ^{13}C -NMR (400 and 100 MHz, resp.) Data of Compound **3** in CD_3OD . δ in ppm, J in Hz.

	$\delta(\text{H})$	$\delta(\text{C})$
C(1)		169.8
C(2)		129.0
H-C(3)	6.81 (<i>ddq</i> , $J = 7.6, 7.6, 1.2$)	143.6
$\text{CH}_2(4)$	2.18–2.25 (<i>m</i>)	27.1
$\text{CH}_2(5)$	1.24–1.31 (<i>m</i>), 1.47–1.53 (<i>m</i>)	36.9
H-C(6)	1.67–1.72 (<i>m</i>)	30.5
$\text{CH}_2(7)$	1.43–1.46 (<i>m</i>), 1.63–1.66 (<i>m</i>)	37.6
$\text{CH}_2(8)$	3.59–3.63 (<i>m</i>), 3.91–3.95 (<i>m</i>)	68.8
Me(9)	1.84 (<i>d</i> , $J = 1.2$)	12.6
Me(10)	0.93 (<i>d</i> , $J = 6.4$)	19.9
H-C(1')	4.24 (<i>d</i> , $J = 7.8$)	104.3
H-C(2')	3.16 (<i>dd</i> , $J = 9.0, 7.8$)	75.2
H-C(3')	^{a)}	77.9
H-C(4')	^{a)}	71.7
H-C(5')	^{a)}	78.2
$\text{CH}_2(6')$	3.66 (<i>dd</i> , $J = 12.0, 5.4$), 3.86 (<i>dd</i> , $J = 12.0, 2.0$)	62.9

^{a)} Overlapped by the solvent signal.

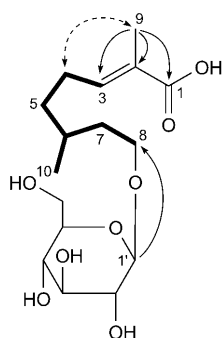


Fig. 3. $^1\text{H},^1\text{H}$ -COSY (—), HMBC ($\text{H} \rightarrow \text{C}$), and NOESY (· · · · ·) Correlations of **3**)

corresponding compound with (6*R*) configuration has been already reported from the dried stems of *Cistanche tubulosa* (SCHRENK) R. WIGHT (Orobanchaceae) [16].

In addition to the three new glucosides, the other thirteen known glucosides, 8-deoxylamiol (**4**) [17], lamiol (**5**) [3], lamioside (**6**) [7], 6*α*-hydroxygeniposide (**7**) [18], daphylloside (**8**) [19], asperuloside (**9**) [20], shanzhiside methyl ester (**10**) [7], barlerin (**11**) [7], caryoptoside (**12**) [21], lamalbid (**13**) [7], 6*β*-hydroxyipolamide (**14**) [22], phlorigidoside B (**15**) [23], and 5-hydroxy-8-epiloganin (**16**) [24], were identified on the basis of their optical-rotation values and NMR and MS data. This is the first report of compounds **4**, **7**, **8**, **12**, **14**, **15**, and **16** from *L. amplexicaule*.

Iridoid monoglucosides with COOMe or Me groups at C(4) are considered as chemotaxonomic markers for *Lamium* species [1][25][26]. The co-occurrence of lamiuamplexoside A (**1**) with shanzhiside methyl ester (**10**) and caryoptoside (**12**) in this plant suggests that the former compound plays a role as a precursor for the formation of the latter compounds [27]. Lamiuamplexoside B (**2**), with a gentiobiosyl moiety, is the first secoiridoid diglucoside isolated from this genus. Also, lamiuamplexoside C (**3**) is the first acyclic monoterpenoid glucoside isolated from this genus.

We are grateful to Mr. S. Satoh and Mr. T. Matsuki for NMR and MS measurements.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2 ; 70–230 mesh; Merck), Diaion HP-20 (250–300 μm ; Mitsubishi Chemical Corporation), and Sephadex LH-20 (18–111 μm ; GE Healthcare Bio-Sciences AB). HPLC: CCPM pump (Tosoh), UV-8020 UV/VIS detector (Tosoh), and Jasco-OR-2090 plus chiral detector; t_R in min. Optical rotations: Jasco-DIP-360 digital polarimeter. UV Spectra: Beckman-DU-64 spectrophotometer; λ_{max} ($\log \epsilon$) in nm. NMR Spectra: Jeol-JNM-LA 600 (^1H at 600 and ^{13}C at 150 MHz) and Jeol-JNM-LA 400 (^1H at 400 and ^{13}C at 100 MHz) spectrometers; chemical shifts δ in ppm rel. to Me_4Si , J in Hz. FAB-MS: Jeol-JMS-DX-303 mass spectrometer; glycerol as matrix; in m/z .

Plant Material. The whole plants of *Lamium amplexicaule* were collected in Sendai City, Miyagi Prefecture, Japan, in April 2007. A voucher specimen (LA-2007-01) was deposited with the Laboratory of Molecular Structural Analysis, Tohoku Pharmaceutical University.

Extraction and Isolation. The fresh whole plants (including roots, stems, leaves, and flowers) of *Lamium amplexicaule* (900 g) were extracted three times (14 d each time) with MeOH (3 l) at r.t. The MeOH extract was filtered and concentrated, and the residue (21.0 g) was suspended in H_2O (1 l). This suspension was extracted with CHCl_3 (3×1 l), AcOEt (3×1 l), and BuOH (3×1 l).

The BuOH-soluble fraction was concentrated to afford a residue (8.0 g), which was subjected to CC (SiO₂, CHCl₃/MeOH/H₂O 30:10:1): *Fractions 1–16* (by TLC). *Fr. 3*, on prep. HPLC (TSKgel-ODS-120T column (300 × 7.8 mm, 10 μm; Tosoh), MeOH/H₂O 1:2, 1.5 ml/min) gave **8** (10.0 mg, *t_R* 22.8), **15** (0.4 mg, *t_R* 30.4), and **11** (23.3 mg, *t_R* 40.0). *Fr. 4* was purified by CC (Sephadex LH-20, MeOH/H₂O 1:1): **6** (28.9 mg). *Fr. 6*, on prep. HPLC (TSKgel-Amide-80 column (300 × 7.8 mm, 10 μm; Tosoh), MeCN/H₂O 9:1, 1.5 ml/min) gave **1** (2.6 mg, *t_R* 26.0), **4** (3.1 mg, *t_R* 35.6), **10** (8.1 mg, *t_R* 37.4), and **7/12** (*t_R* 39.6). The mixture **7/12**, on prep. HPLC (TSKgel-ODS-120T column (300 × 7.8 mm, 10 μm; Tosoh), MeOH/H₂O 1:2, 1.5 ml/min) gave **7** (0.3 mg, *t_R* 9.0) and **12** (0.7 mg, *t_R* 12.8). *Fr. 9* was purified by CC (Sephadex LH-20, MeOH/H₂O 1:1) to afford **13** (52.6 mg).

The H₂O-soluble fraction was passed through a Diaion HP-20 column, and the adsorbed material was eluted with H₂O and MeOH. The MeOH eluate was concentrated to afford a residue (2.1 g), which was subjected to CC (SiO₂, CHCl₃/MeOH/H₂O 30:10:1): *Fractions 1–14* (by TLC). *Fr. 2*, on prep. HPLC (TSKgel-ODS-120T column (300 × 7.8 mm, 10 μm; Tosoh), MeOH/H₂O 1:4, 1.5 ml/min) gave **9** (2.4 mg, *t_R* 28.7). *Fr. 4*, on prep. HPLC (TSKgel-ODS-120T column (300 × 7.8 mm, 10 μm; Tosoh), MeOH/H₂O 1:3, 1.5 ml/min) gave **5** (1.0 mg, *t_R* 14.0), **14** (4.8 mg, *t_R* 16.4), **2** (1.0 mg, *t_R* 15.4), and **16** (1.1 mg, *t_R* 21.8). *Fr. 10*, on prep. HPLC (TSKgel-ODS-120T column (300 × 7.8 mm, 10 μm; Tosoh), MeOH/H₂O 1:3, 1.0 ml/min) gave **3** (2.3 mg, *t_R* 12.2).

Lamiumplexoside A (= rel-(1aR,1bR,5R,5aR,6S,6aR)-5-(β-D-Glucopyranosyloxy)-1a,1b,5,5a,6,6a-hexahydro-6-hydroxy-6-methyloxireno[3,4]cyclopenta[1,2-c]pyran-2-carboxylic Acid Methyl Ester; **1**): Amorphous powder. $[\alpha]_D^{25} = -75.3$ (*c* = 0.26, MeOH). UV (MeOH): 231 (3.9). ¹H- and ¹³C-NMR: Table 1. FAB-MS (pos.): 405 ($[M + H]^+$). HR-FAB-MS (pos.): 405.1384 ($[M + H]^+$, C₁₇H₂₅O₁₁⁺; calc. 405.1397).

Lamiumplexoside B (= rel-(1R,4aS,8S,8aS)-8-[(6-O-β-D-Glucopyranosyl-β-D-glucopyranosyl)-oxy]-4,4a,8,8a-tetrahydro-1-methyl-3-oxo-1H,3H-pyrano[3,4-c]pyran-5-carboxylic Acid Methyl Ester; **2**): Amorphous powder. $[\alpha]_D^{19} = -58.2$ (*c* = 0.10, MeOH). UV (MeOH): 231 (3.9). ¹H- and ¹³C-NMR: Table 2. FAB-MS (pos.): 589 ($[M + Na]^+$). HR-FAB-MS (pos.): 589.1744 ($[M + Na]^+$, C₂₃H₃₄NaO₁₆⁺; calc. 589.1744).

Lamiumplexoside C (= (2E,6S)-8-(β-D-Glucopyranosyloxy)-2,6-dimethyloct-2-enoic Acid; **3**): Amorphous powder. $[\alpha]_D^{22} = -19.5$ (*c* = 0.23, MeOH). ¹H- and ¹³C-NMR: Table 3. FAB-MS (neg.): 347 ($[M - H]^-$).

Acid Hydrolysis of 1 and 2. Each of the compounds **1** and **2** (ca. 0.3 mg) was refluxed with 5% HCl soln. for 5 h. The mixture was neutralized with Ag₂CO₃ and filtered. The soln. was concentrated and dried to give a sugar fraction. The sugar fraction was analyzed by HPLC (Shodex-SUGAR-KS-801 column (300 × 8.0 mm; Showa Denko), H₂O, 1.0 ml/min, chiral detection): *t_R* 7.5 (D-glucose, pos. optical rotation).

Enzymatic Hydrolysis of 3. Compound **3** (2.3 mg) was treated with cellulase (from *Aspergillus niger*, 0.39 units/mg; Sigma Chemical Corporation; 3.0 mg) and β-glucosidase (from almond, 5.5 units/mg; Sigma Chemical Corporation; 1.0 mg) in an AcOH/AcONa buffer soln. (0.02M, pH 4.6; 5.0 ml). The mixture was stirred at 37° for 3 d, then extracted with an equal amount of AcOEt (3 ×), and the AcOEt layer was concentrated. The residue was dried to give the aglycone **3a**, which was identified as (2E,6S)-8-hydroxy-2,6-dimethyloct-2-enoic acid by the optical-rotation value ($[\alpha]_D^{20} = -10.0$ (*c* = 0.10, MeOH)) and ¹H-NMR data [15]. The sugar fraction, obtained by concentration of the aq. layer, was analyzed by HPLC (Shodex-SUGAR-KS-801 column (300 × 8.0 mm; Showa Denko), H₂O, 1.0 ml/min, chiral detection): *t_R* 7.5 (D-glucose, pos. optical rotation).

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