# Three New Monoterpene Glucosides from *Lamium amplexicaule*

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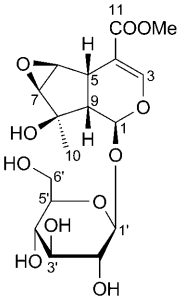
Three new monoterpene glucosides, lamiuamplexosides A–C (**1**–**3**), along with thirteen known glucosides, were isolated from the whole plant of *Lamium amplexicaule* L. The structures of **1**–**3** were elucidated on the basis of spectroscopic, chemical, and physicochemical evidence.

**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–C[1]) (**1**–**3**, resp.), together with the thirteen known glucosides **4**–**16**. This article deals with the isolation and structural elucidation of the new compounds.

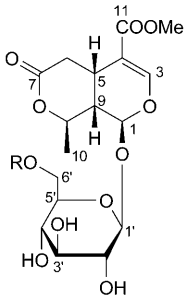
**Results and Discussion.** – The whole plant of *L. amplexicaule* was extracted with MeOH. The MeOH extract was partitioned between $H_2O$ and $CHCl_3$, $H_2O$ and AcOEt, and $H_2O$ and BuOH. The BuOH-soluble fraction was subjected to column chromatography (silica gel and *Sephadex LH-20*) and prep. HPLC to afford a new compound, named lamiuamplexoside A (**1**), and nine known compounds, **4**, **6**–**8**, **10**–**13**, and **15**. The $H_2O$-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 $C_{17}H_{24}O_{11}$ 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 $^1$H-NMR spectrum of **1** in $CD_3OD$ (*Table 1*) exhibited signals due to one Me ($\delta$(H) 1.23 (*s*)), two CH, one MeO ($\delta$(H) 3.73 (*s*)), and three CH–O groups ($\delta$(H) 3.19 (*d*,

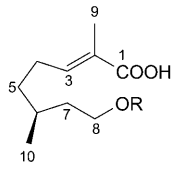
[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part.*



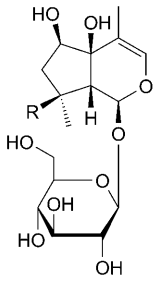
**1**[1])



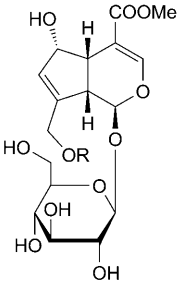
**2**[1]) R = Glc
**17**[1]) R = H



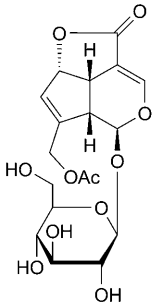
**3**[1]) R = Glc
**3a**[1]) R = H



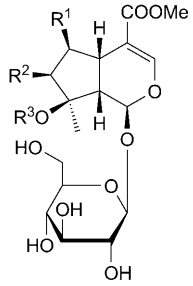
**4** R = H
**5** R = OH
**6** R = AcO



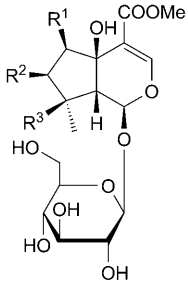
**7** R = H
**8** R = Ac



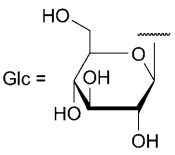
**9**



| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **10** | OH | H | H |
| **11** | OH | H | Ac |
| **12** | H | OH | H |
| **13** | OH | OH | H |



| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **14** | OH | H | OH |
| **15** | OH | H | AcO |
| **16** | H | OH | H |



Glc =

$J = 3.2$ Hz), 3.81 (*dd*, $J = 3.2$, 1.2 Hz), and 5.69 (*s*)) and one C=C–H moiety. Furthermore, one anomeric signal ($\delta$(H) 4.60 (*d*, $J = 8.1$ Hz)) was recognized. The coupling constant of an anomeric signal indicated that the glucosyl linkage is in $\beta$-configuration. The $^{13}$C-NMR spectrum of **1** in $CD_3OD$ (*Table 1*) showed signals due one O-bearing, quaternary, $sp^3$-type C-atom ($\delta$(C) 77.8) and one C=O group ($\delta$(C) 168.6). The $^1$H,$^1$H-COSY data of **1** (*Fig. 1*) 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. 1*) 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 $\beta$-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 ($\delta$(C) 57.8 (C(6))

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

| | $\delta$(H) | $\delta$(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 |
| $CH_2$(6′) | 3.65 (*dd*, $J$ = 12.0, 5.6), 3.87 (*dd*, $J$ = 12.0, 2.0) | 62.8 |
| *Me*O–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 $^1$H-NMR spectrum, the coupling constant ($J$ = 8.8 Hz) between $H_\beta$–C(5) and $H_\beta$–C(9) indicates the *cis* relationship of these H-atoms, and that ($J$ = 1.2 Hz) between $H_\beta$–C(5) and $H_\alpha$–C(6) indicates the *trans* relationship of these H-atoms, *i.e.*, $\beta$-orientation of the epoxide ring (*Fig. 2*) [11]. In an NOE experiment, irradiation of Me(10) enhanced the signals of $H_\alpha$–C(1) (4.31%) and $H_\alpha$–C(7) (4.46%). These observations revealed that the $\beta$-D-glucopyranosyloxy group at C(1) and the OH group at C(8) are on the same face ($\beta$) 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-($\beta$-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.

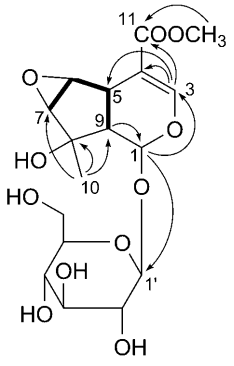



Fig. 1. *$^1$H,$^1$H-COSY* (—) *and HMBC* (H → C) *of* **1**[1])

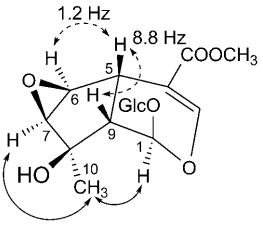



Fig. 2. *Selected coupling constant* (←- - -→) *and NOEs* (↔) *of* **1**[1])

Lamiuamplexoside 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*,4a*S*,8*S*,8a*S*)-8-(β-D-glucopyranosyloxy)-4,4a,8,8a-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 $CH_2(6')$ (δ(C) 70.8 (Δδ = +8.0)) due to glucosylation [14]. Acid hydrolysis of **2** gave only D-glucose, as described above for **1**. In the $^1$H-NMR spectrum of **2** in $CD_3OD$ (*Table 2*), two

Table 2. *$^1$H- 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** |
|---|---|---|---|
| | δ(H) | δ(C) | δ(C) |
| H−C(1) | 5.48 (*d*, *J* = 8.1) | 96.9 | 96.2 |
| H−C(3) | 7.58 (*d*, *J* = 1.1) | 154.5 | 154.4 |
| C(4) | | 109.4 | 109.5 |
| H−C(5) | 3.06 (*ddd*, *J*= 11.7, 7.0, 3.7) | 28.3 | 28.1 |
| $CH_2$(6) | 2.54 (*dd*, *J* = 16.5, 11.7, $H_\alpha$), 2.86 (*dd*, *J* = 16.5, 3.7, $H_\beta$) | 34.9 | 34.6 |
| C(7) | | 175.0 | 174.7 |
| H−C(8) | 4.53 (*dq*, *J* = 7.7, 6.6) | 75.9 | 75.7 |
| H−C(9) | 2.13 (*ddd*, *J* = 8.1, 7.7, 7.0) | 41.9 | 41.8 |
| Me(10) | 1.51 (*d*, *J* = 6.6) | 21.9 | 21.7 |
| C(11) | | 168.4 | 168.3 |
| H−C(1′) | 4.70 (*d*, *J* = 8.1) | 101.2 | 100.6 |
| H−C(2′) | 3.16 (*dd*, *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 (*dd*, *J* = 11.7, 5.9), 4.20 (*dd*, *J* = 11.7, 2.2) | 70.8 | 62.8 |
| H−C(1″) | 4.30 (*d*, *J* = 8.1) | 105.6 | |
| H−C(2″) | 3.18 (*dd*, *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 (*dd*, *J* = 11.7, 5.9), 3.86 (*dd*, *J* = 11.5, 1.5) | 62.8 | |
| MeO−C(11) | 3.72 (*s*) | 52.0 | 52.0 |

[a]) Overlapped by the solvent signal.

anomeric signals ($\delta$(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 $\beta$-configuration. Consequently, the structure of **2** was elucidated as *rel*-(1*R*,4a*S*,8*S*,8a*S*)-8-[(6-*O*-$\beta$-D-glucopyranosyl-$\beta$-D-glucopyranosyl)oxy]-4,4a,8,8a-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 ($[M-H]^-$). The $^1$H-NMR spectrum of **3** in $CD_3OD$ (*Table 3*) exhibited signals due to two Me ($\delta$(H) 0.93 (*d*, *J* = 6.4 Hz) and 1.84 (*d*, *J* = 1.2 Hz)), one CH, three $CH_2$, and one $CH_2$–O group ($\delta$(H) 3.59–3.63 (*m*) and 3.91–3.95 (*m*)) and one C=C–H moiety. Furthermore, one anomeric signal ($\delta$(H) 4.24 (*d*, *J* = 7.8 Hz)) was recognized. The coupling constant of the latter indicated that the glucosyl linkage is in $\beta$-configuration. The $^{13}$C-NMR spectrum of **3** in $CD_3OD$ (*Table 3*) showed signals due one $\beta$-Glc unit and one C=O group ($\delta$(C) 169.8). The $^1$H,$^1$H-COSY data of **3** (*Fig. 3*) implied connectivities of H–C(3) to $CH_2$(4), of $CH_2$(4) to $CH_2$(5), of $CH_2$(5) to H–C(6), of H–C(6) to $CH_2$(7), of H–C(6) to Me(10), and of $CH_2$(7) to $CH_2$(8). The HMBC spectrum (*Fig. 3*) showed the correlations Me(9)/C(1), C(2), and C(3) and H–C(1′)/C(8). The C=C bond between C(2) and C(3) was (*E*)-configured, based on a NOESY cross-peak between $CH_2$(4) and Me(9) (*Fig. 3*). On enzymatic hydrolysis with cellulose and $\beta$-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-($\beta$-D-glucopyranosyloxy)-2,6-dimethyloct-2-enoic acid. The

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

| | $\delta$(H) | $\delta$(C) |
|---|---|---|
| C(1) | | 169.8 |
| C(2) | | 129.0 |
| H–C(3) | 6.81 (*ddq*, *J* = 7.6, 7.6, 1.2) | 143.6 |
| $CH_2$(4) | 2.18–2.25 (*m*) | 27.1 |
| $CH_2$(5) | 1.24–1.31 (*m*), 1.47–1.53 (*m*) | 36.9 |
| H–C(6) | 1.67–1.72 (*m*) | 30.5 |
| $CH_2$(7) | 1.43–1.46 (*m*), 1.63–1.66 (*m*) | 37.6 |
| $CH_2$(8) | 3.59–3.63 (*m*), 3.91–3.95 (*m*) | 68.8 |
| Me(9) | 1.84 (*d*, *J* = 1.2) | 12.6 |
| Me(10) | 0.93 (*d*, *J* = 6.4) | 19.9 |
| H–C(1′) | 4.24 (*d*, *J* = 7.8) | 104.3 |
| H–C(2′) | 3.16 (*dd*, *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 |
| $CH_2$(6′) | 3.66 (*dd*, *J* = 12.0, 5.4), 3.86 (*dd*, *J* = 12.0, 2.0) | 62.9 |

[a]) Overlapped by the solvent signal.

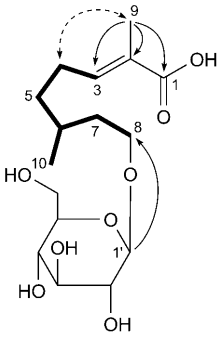



Fig. 3. *$^1H,^1H$-COSY* (—), *HMBC* (H → C), and *NOESY* (←---→) *Correlations of* **3**[1])

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$\alpha$-hydroxygeniposide (**7**) [18], daphylloside (**8**) [19], asperuloside (**9**) [20], shanzhiside methyl ester (**10**) [7], barlerin (**11**) [7], caryoptoside (**12**) [21], lamalbid (**13**) [7], 6$\beta$-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; $\lambda_{max}$ (log $\varepsilon$) 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 $\delta$ 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 ($SiO_2$, $CHCl_3$/MeOH/$H_2O$ 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/$H_2O$ 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/$H_2O$ 1:1): **6** (28.9 mg). *Fr. 6*, on prep. HPLC (*TSKgel-Amide-80* column (300 × 7.8 mm, 10 μm; *Tosoh*), MeCN/$H_2O$ 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/$H_2O$ 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/$H_2O$ 1:1) to afford **13** (52.6 mg).

The $H_2O$-soluble fraction was passed through a *Diaion HP-20* column, and the adsorbed material was eluted with $H_2O$ and MeOH. The MeOH eluate was concentrated to afford a residue (2.1 g), which was subjected to CC ($SiO_2$, $CHCl_3$/MeOH/$H_2O$ 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/$H_2O$ 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/$H_2O$ 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/$H_2O$ 1:3, 1.0 ml/min) gave **3** (2.3 mg, $t_R$ 12.2).

*Lamiuamplexoside A* (= 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*; **1**): Amorphous powder. $[\alpha]_D^{25} = -75.3$ ($c = 0.26$, MeOH). UV (MeOH): 231 (3.9). $^1$H- and $^{13}$C-NMR: *Table 1*. FAB-MS (pos.): 405 ($[M+H]^+$). HR-FAB-MS (pos.): 405.1384 ($[M+H]^+$, $C_{17}H_{25}O_{11}^+$; calc. 405.1397).

*Lamiuamplexoside B* (= rel-*(1*R*,4a*S*,8*S*,8a*S*)-8-[(6-*O*-β-D-Glucopyranosyl-β-D-glucopyranosyl)-oxy]-4,4a,8,8a-tetrahydro-1-methyl-3-oxo-1*H*,3*H*-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). $^1$H- and $^{13}$C-NMR: *Table 2*. FAB-MS (pos.): 589 ($[M+Na]^+$). HR-FAB-MS (pos.): 589.1744 ($[M+Na]^+$, $C_{23}H_{34}NaO_{16}^+$; calc. 589.1744).

*Lamiuamplexoside C* (=*(2*E*,6*S*)-8-(β-D-Glucopyranosyloxy)-2,6-dimethyloct-2-enoic Acid*; **3**): Amorphous powder. $[\alpha]_D^{22} = -19.5$ ($c = 0.23$, MeOH). $^1$H- and $^{13}$C-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 $Ag_2CO_3$ 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*), $H_2O$, 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 (2*E*,6*S*)-8-hydroxy-2,6-dimethyloct-2-enoic acid by the optical-rotation value ($[\alpha]_D^{20} = -10.0$ (c = 0.10, MeOH)) and $^1$H-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*), $H_2O$, 1.0 ml/min, chiral detection): $t_R$ 7.5 (D-glucose, pos. optical rotation).

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