Iridoid Glycosides from *Lamiophlomis rotata*

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The seven new iridoid diglycosides **1**–**7**, together with eleven known iridoid and phenylpropanoid glycosides, were isolated from the 50% EtOH extract of the roots of *Lamiophlomis rotata*. Their structures were elucidated by chemical and spectroscopic methods.

Introduction. – *Lamiophlomis rotata* (BENTH.) KUDO (Labiatae) is a Chinese folk medicine used to promote blood circulation, remove blood stasis, subdue swelling, and alleviate pain. Previously, phytochemical studies of this plant reported the presence of iridoids, iridoid monoglycosides, and phenylpropanoid glycosides [1–5]. Our chemical-constituents investigation on the 50% EtOH extract of the titled plant led to the isolation of seven new iridoid diglycosides, 6′-*O*-*β*-D-glucopyranosylphlorigidoside C (**1**), 6′-*O*-*α*-D-galactopyranosylphlorigidoside C (**2**), 6′-*O*-*β*-D-glucopyranosylsesamoside (**3**), 6′-*O*-*α*-D-galactopyranosylsesamoside (**4**), 6′-*O*-*β*-D-glucopyranosylbarlerin (**5**), 6′-*O*-*α*-D-galactopyranosylbarlerin (**6**), and 6′-*O*-*α*-D-galactopyranosylshanzhiside methyl ester (**7**), together with eleven known compounds, phlorigidoside C (**8**) [6], sesamoside (**9**), barlerin (**10**), shanzhiside methyl ester (**11**), shanzhisin methyl ester gentiobioside (**12**) [7], phloyoside I, phloyoside II [8], lamiophlomiside [3], and three phenylpropanoid glycosides, lamiophlomioside A [4], verbascoside [9], and forsythoside B [10][11]. The structures of the new compounds were determined by spectroscopic and chemical methods.

Results and Discussion. – Compounds **1** and **2** were isolated as amorphous powders, which possessed the same molecular formula, $C_{23}H_{34}O_{16}$, as deduced from the HR-ESI-MS. The structures of **1** and **2** were established to be 6′-*O*-*β*-D-glucopyranosylphlorigidoside C (**1**) and 6′-*O*-*α*-D-galactopyranosylphlorigidoside C (**2**), respectively, based on the analyses of 1D- and 2D-NMR (*Table*), as well as acidic hydrolysis and GC analysis (**1** gave D-glucose, and **2** afforded D-glucose and D-galactose).

The ^{1}H- and ^{13}C-NMR spectra of **1** and **2** were closely related to those of phlorigidoside C (**8**), except for the presence of signals of an additional *β*-D-glucopyranosyl group at *δ*(H) 4.34 (*d*, *J* = 7.7 Hz, H–C(1″)) and *δ*(C) 106.2 (C(1″)), 75.6 (C(2″)), 78.7 (C(3″)), 72.2 (C(4″)), 78.6 (C(5″)), and 63.3 (C(6″)) in **1**, and of an *α*-D-galactopyranosyl group at *δ*(H) 4.87 (*d*, *J* = 3.7 Hz, H–C(1″)) and *δ*(C) 100.8 (C(1″)), 70.7 (C(2″)), 72.1 (C(3″)), 71.4 (C(4″)), 73.0 (C(5″)), and 63.0 C(6″)) in **2**. The two glycosyl moieties were linked to C(6′) of the inner *β*-D-glucopyranosyl group, as suggested by the marked downfield

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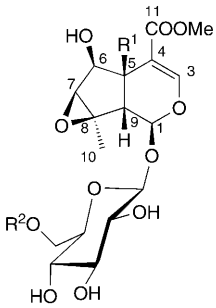

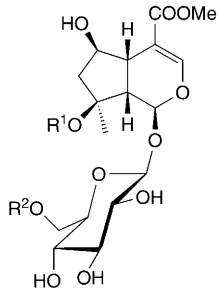

1 R^1 = H, R^2 = β-D-glucopyranosyl
2 R^1 = H, R^2 = α-D-galactopyranosyl
3 R^1 = OH, R^2 = β-D-glucopyranosyl
4 R^1 = OH, R^2 = α-D-galactopyranosyl
8 R^1 = R^2 = H
9 R^1 = OH, R^2 = H

5 R^1 = Ac, R^2 = β-D-glucopyranosyl
6 R^1 = Ac, R^2 = α-D-galactopyranosyl
7 R^1 = H, R^2 = α-D-galactopyranosyl
10 R^1 = Ac, R^2 = H
11 R^1 = R^2 = H
12 R^1 = H, R^2 = β-D-glucopyranosyl

Table. *^{13}C-NMR Data of* **1**–**7** (CD_3OD, 100 MHz)[1])

	1	**2**	**3**	**4**	**5**	**6**	**7**
C(1)	97.4 (*d*)	97.6 (*d*)	97.8 (*d*)	97.7 (*d*)	95.9 (*d*)	95.8 (*d*)	95.5 (*d*)
C(3)	154.7 (*d*)	154.7 (*d*)	155.7 (*d*)	155.7 (*d*)	154.1 (*d*)	154.1 (*d*)	153.1 (*d*)
C(4)	109.0 (*s*)	109.1 (*s*)	113.3 (*s*)	113.4 (*s*)	110.4 (*s*)	110.4 (*s*)	111.8 (*s*)
C(5)	38.9 (*d*)	39.0 (*d*)	75.1 (*s*)	75.3 (*s*)	43.0 (*d*)	43.0 (*d*)	41.9 (*d*)
C(6)	79.7 (*d*)	80.0 (*d*)	78.0 (*d*)	78.0 (*d*)	76.6 (*d*)	76.3 (*d*)	77.8 (*d*)
C(7)	65.5 (*d*)	65.1 (*d*)	66.3 (*d*)	66.1 (*d*)	48.1 (*t*)	48.3 (*t*)	49.5 (*t*)
C(8)	63.5 (*s*)	63.5 (*s*)	63.9 (*s*)	64.0 (*s*)	90.2 (*s*)	89.9 (*s*)	79.4 (*s*)
C(9)	45.6 (*d*)	45.6 (*d*)	54.7 (*d*)	54.6 (*d*)	50.1 (*d*)	50.1 (*d*)	52.1 (*d*)
C(10)	18.5 (*q*)	18.5 (*q*)	18.3 (*q*)	18.1 (*q*)	22.9 (*q*)	22.9 (*q*)	25.0 (*q*)
C(11)	171.4 (*s*)	171.3 (*s*)	169.5 (*s*)	169.4 (*s*)	169.6 (*s*)	169.4 (*s*)	170.0 (*s*)
MeO–C(11)	52.7 (*q*)	52.8 (*q*)	52.5 (*q*)	52.5 (*q*)	52.3 (*q*)	52.3 (*q*)	52.2 (*q*)
Me*C*O	–	–	–	–	173.4 (*s*)	173.1 (*s*)	–
*Me*CO	–	–	–	–	22.7 (*q*)	22.7 (*q*)	–
C(1′)	100.8 (*d*)	101.0 (*d*)	100.6 (*d*)	100.7 (*d*)	100.3 (*d*)	100.2 (*d*)	100.3 (*d*)
C(2′)	75.3 (*d*)	75.3 (*d*)	74.9 (*d*)	74.9 (*d*)	75.1 (*d*)	75.1 (*d*)	74.9 (*d*)
C(3′)	78.4 (*d*)	78.5 (*d*)	78.1 (*d*)	78.1 (*d*)	78.3 (*d*)	78.7 (*d*)	78.4 (*d*)
C(4′)	72.6 (*d*)	72.7 (*d*)	72.3 (*d*)	72.3 (*d*)	72.2 (*d*)	72.3 (*d*)	72.1 (*d*)
C(5′)	78.3 (*d*)	77.3 (*d*)	78.0 (*d*)	77.1 (*d*)	78.1 (*d*)	77.2 (*d*)	77.0 (*d*)
C(6′)	71.2 (*t*)	69.2 (*t*)	71.0 (*t*)	68.8 (*t*)	70.5 (*t*)	68.4 (*t*)	68.3 (*t*)
C(1″)	106.2 (*d*)	100.8 (*d*)	106.0 (*d*)	100.6 (*d*)	105.4 (*d*)	100.7 (*d*)	100.5 (*d*)
C(2″)	75.6 (*d*)	70.7 (*d*)	75.4 (*d*)	70.6 (*d*)	75.8 (*d*)	71.0 (*d*)	70.7 (*d*)
C(3″)	78.7 (*d*)	72.1 (*d*)	78.5 (*d*)	71.9 (*d*)	78.3 (*d*)	72.1 (*d*)	71.9 (*d*)
C(4″)	72.2 (*d*)	71.4 (*d*)	72.0 (*d*)	71.2 (*d*)	72.2 (*d*)	71.7 (*d*)	71.3 (*d*)
C(5″)	78.6 (*d*)	73.0 (*d*)	78.4 (*d*)	72.8 (*d*)	78.4 (*d*)	72.8 (*d*)	72.7 (*d*)
C(6″)	63.3 (*t*)	63.0 (*t*)	63.1 (*t*)	62.9 (*t*)	63.3 (*t*)	63.4 (*t*)	63.0 (*t*)

[1]) Trivial atom numbering of the iridoid moiety; for systematic names, see *Exper. Part*.

shift of the signal of C(6′) of the inner β-D-glucopyranosyl residue at δ 71.2 (Δδ = +7.6) in **1** and 69.2 (Δδ = +5.6) in **2**, as compared to the signal of C(6′) of **8**. This was confirmed by the HMBC cross-peaks of H–C(1″)/C(6′) of **1** and **2**.[1])

Compounds **3** and **4** had the same molecular formula $C_{23}H_{34}O_{17}$, as determined by the HR-ESI-MS. Glucoside **3** gave D-glucose and **4** furnished D-glucose and D-galactose as sugar moieties after acid hydrolysis. A combined analysis of ^{1}H- and ^{13}C-NMR (*Table*) and 2D NMR data elucidated **3** and **4** to be 6′-*O*-β-D-glucopyranosylsesamoside (**3**) and 6′-*O*-α-D-galactopyranosylsesamoside (**4**), respectively.

Similarly to the differences between **1/2** and **8**, the ^{1}H- and ^{13}C-NMR spectra of **3** and **4** showed that the differences between them and sesamoside (**9**) were an additional β-D-glucopyranosyl unit with signals at δ(H) 4.33 (*d*, *J* = 7.6 Hz) and δ(C) 106.0, 78.5, 78.4, 75.4, 72.0, and 63.1 in **3** and an additional α-D-galactopyranosyl moiety with signals at δ(H) 4.87 (*d*, *J* = 3.6 Hz) and δ(C) 100.6, 72.8, 71.9, 71.2, 70.6, and 62.9 in **4**, as well as a downfield shift of C(6′) (Δδ = +7.5 and +5.3 for **3** and **4**, resp.). These findings indicated that both the additional β-D-glucopyranosyl group in **3** and the α-D-galactopyranosyl group in **4** were attached to the OH group at C(6′). The conclusion was supported by the HMBC correlations between H–C(1″) and C(6′) in the two compounds.

The structures of **5** and **6** were deduced to be 6′-*O*-β-D-glucopyranosylbarlerin (**5**) and 6′-*O*-α-D-galactopyranosylbarlerin (**6**), which were in agreement with their HR-ESI-MS molecular-ion peaks and acid-hydrolysis experiments.

The ^{1}H- and ^{13}C-NMR spectra suggested that **5** and **6** were 6′-*O*-β-D-glucopyranosyl- and 6′-*O*-α-D-galactopyranosyl-substituted barlerin (**10**), respectively, based on the following evidences: *i*) the presence of extra signals of a β-D-glucopyranosyl group at δ(H) 4.46 (*d*, *J* = 7.5 Hz) and δ(C) 105.4, 78.4, 78.3, 75.8, 72.2, and 63.3 in **5**, and of an α-D-galactopyranosyl residue at δ(H) 4.91 (*d*, *J* = 3.5 Hz) and δ(C) 100.7, 72.8, 72.1, 71.7, 71.0, and 63.4 in **6**; *ii*) the downfield shift of C(6′) (Δδ = +7.1 and +5.0 for **5** and **6**, resp.). This was confirmed by the presence of cross-peaks between H–C(1″) and C(6′) in the HMBC spectra of **5** and **6**.

Compound **7** was an amorphous, optically active powder. Its molecular formula $C_{23}H_{36}O_{16}$ was deduced from the quasi-molecular-ion peak at *m/z* 591.1898 ($[M+Na]^+$) in the HR-ESI-MS. Upon acid hydrolysis, **7** yielded D-glucose and D-galactose. NMR Data analyses concluded the structure of **7** to be 6′-*O*-α-D-galactopyranosyl-shanzhiside methyl ester.

The ^{13}C- and ^{1}H-NMR spectra of **7** were similar to those of shanzhiside methyl ester (**11**). The differences were the presence of an extra α-D-galactopyranosyl group with signals at δ(H) 4.87 (*d*, *J* = 2.8 Hz) and δ(C) 100.5, 72.7, 71.9, 71.3, 70.7, and 63.0, as well as a downfield shift of C(6′) (Δδ = +4.9) and an upfield shift of C(5′) (Δδ = –1.9). According to glycosylation rules, this indicates that **7** is a 6′-*O*-α-D-galactopyranosyl derivative of **11**, which was confirmed by the HMBC cross peak H–C(1″)/C(6′).

Experimental Part

General. Column chromatography (CC): silica gel (200–300 or 400 mesh; *Qingdao Haiyang, Co.*, China), *ODS-A* gel (*Greenherbs Science & Technology Development Co., Ltd.,* Beijing, China), *D-1400* macroporous resin (*Yangzhou Pharmaceutical Factory,* China), and *Sephadex LH-20* (*Pharmacia Biotech AB,* Uppsala, Sweden). GC Analyses: *Perkin-Elmer Sigma-115* gas chromatograph; t_R in min. Prep. and semi-prep. HPLC: *Varian* HPLC system (*Prepstar-SD-1* pump, *UV-VIS 320* detector); prep.

column 12 μ *ODS-A* (*Merck*; 25 mm i.d. × 250 mm) and semi-prep column 5 μ *ODS-A* (*Kromasil*; 10 mm i.d. × 250 mm). Optical rotation: *Perkin-Elmer 341* polarimeter. UV Spectra: *Agilent 1100* spectrometer with a *DAD* detector; λ_{max} in nm. IR Spectra: *Nicolet-Magna 750-FTIR* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker DRX-400* instruments; at 400 (^{1}H) or 100 MHz (^{13}C) in CD_3OD; δ in ppm rel. to $SiMe_4$, J in Hz. ESI-MS and HR-ESI-MS: *LCQ-Deca* and *Q-Tof-Ultima* mass spectrometer, resp.

Plant Material. The fresh roots of *L. rotata* were collected in Tibet, China, in September 2003, and identified by Prof. *Da-Yuan Zhu*. A voucher (No. 03-09-12) specimen was deposited in the Herbarium of our institute.

Extraction and Isolation. The dried and powdered roots of *L. rotata* (1.5 kg) were successively extracted with 95% and 50% EtOH (each 3 × 3 l) under ultrasonication (each 1 h) at r.t. The concentrated 50% EtOH extract (*ca.* 200 g) was dissolved in H_2O (6 l) and subjected to CC (*D-1400* macroporous resin, ∅ 10 × 65 cm, H_2O, then 10, 30, 50, 70, and 95% (*v*/*v*) EtOH). The 10% EtOH fraction (5.2 g) was subjected to CC (SiO_2 (180 g), $CHCl_3$/MeOH 10 : 1 → 1 : 2, then MeOH): *Fr. A01–A15*. *Fr. A02* was purified by CC (*ODS-A*, MeOH/H_2O 1 : 9 → 4 : 6): **8** (30 mg), **9** (49 mg), **11** (25 mg), lamiophlomiside (26 mg), and phloyoside II (18 mg). Compounds **2** (6 mg) and **1** (12 mg) were obtained from *Fr. A05* and *Fr. A06*, resp., after purification by semi-prep. HPLC (MeOH/H_2O 6 : 94, 2.5 ml/min, 235 nm). *Fr. A04* yielded phloyoside I (23 mg) as solid powder. *Fr. A10* was separated by semi-prep. HPLC (MeOH/H_2O 15 : 85, 3 ml/min, 235 nm): **3** (25 mg) and **4** (9 mg). *Fr. A11* and *Fr. A12* were purified by semi-prep. HPLC (MeOH/H_2O 20 : 80, 3 ml/min, 235 nm): **7** (8 mg) and **12** (12 mg).

The 30% EtOH fraction (30 g) was subjected to CC (SiO_2 (350 g), $CHCl_3$/MeOH 20 : 1 → 1 : 2, then MeOH): *Fr. B01–B13*. *Fr. B08* was passed through a *Sephadex LH-20* column eluted with MeOH: *Fr. B08.1–B08.3*. *Fr. B08.1* was separated by prep. HPLC (solvent *A* = MeCN/H_2O 5 : 95, solvent *B* = MeOH; *A*/*B* 85 : 15, 15 ml/min, 235 nm): **5** (3 mg) and **6** (3 mg). Barlerin (**10**; 28 mg), lamiophlomioside A (48 mg), verbascoside (5 mg), and forsythoside B (28 mg) were isolated from *Fr. B02–B05*, resp., after repeated CC (1. SiO_2, $CHCl_3$/MeOH 15 : 1 → 2 : 1; 2. *ODS-A*, MeOH/H_2O 2 : 8 → 6 : 4).

*6′-*O*-β-*D*-Glucopyranosylphlorigidoside C* (*(1a*R*,1b*S*,2*S*,5aS,6*S*,6aS)-2-[(6-*O*-β-*D*-Glucopyranosyl-β-*D*-glucopyranosyl)oxy]-1a,1b,2,5a,6,6a-hexahydro-6-hydroxy-1a-methyloxireno[4,5]cyclopenta[1,2-*c*]-pyran-5-carboxylic Acid Methyl Ester*; **1**): Amorphous powder. $[\alpha]_D^{23} = -53.9$ ($c = 0.28$, H_2O). UV: 239, 205. IR: 3415, 2897, 1668, 1637, 1443, 1313, 1078, 960, 657. ^{1}H-NMR[2]): 7.53 (*s*, H–C(3)); 5.26 (*d*, $J = 9.7$, H–C(1)); 4.78 (*d*, $J = 8.0$, H–C(1′)); 4.34 (*d*, $J = 7.7$, H–C(1″)); 4.18 (*dd*, $J = 12.0$, 1.8, H_a–C(6′)); 4.09 (*dd*, $J = 7.8$, 1.2, H–C(6)); 3.86 (*dd*, $J = 11.8$, 2.3, H_a–C(6″)); 3.73 (*s*, MeO–C(11)); 3.68 (*dd*, $J = 12.0$, 4.2, H_b–C(6′)); 3.64 (*dd*, $J = 11.8$, 5.7, H_b–C(6″)); 3.51–3.55 (*m*, H–C(5′)); 3.39 (*d*, $J = 1.2$, H–C(7)); 3.39 (H–C(3′)); 3.23 (H–C(2′), H–C(3″), H–C(4″)); 3.20 (H–C(4′)); 3.18 (H–C(5″)); 2.66 (*t*-like, $J = 7.8$, H–C(5)); 2.39 (*dd*, $J = 9.7$, 7.5, H–C(9)); 1.54 (*s*, Me(10)). ESI-MS: 589.2 ($[M + Na]^+$). HR-ESI-MS: 589.1736 ($[M + Na]^+$, $C_{23}H_{34}O_{16}Na^+$; calc. 589.1745).

*6′-*O*-α-*D*-Galactopyranosylphlorigidoside C* (*(1a*R*,1b*S*,2*S*,5a*S*,6*S*,6a*S*)-2-[(6-*O*-α-*D*-Galactopyranosyl-β-*D*-glucopyranosyl)oxy]-1a,1b,2,5a,6,6a-hexahydro-6-hydroxy-1a-methyloxireno[4,5]cyclopenta[1,2-*c*]pyran-5-carboxylic Acid Methyl Ester*; **2**): Amorphous powder. $[\alpha]_D^{23} = -1.8$ ($c = 0.17$, H_2O). UV: 239, 205. IR: 3421, 2920, 1668, 1637, 1443, 1313, 1078, 960, 557. ^{1}H-NMR[2]): 7.54 (*s*, H–C(3)); 5.19 (*d*, $J = 9.7$, H–C(1)); 4.87 (*d*, $J = 3.7$, H–C(1″)); 4.77 (*d*, $J = 7.9$, H–C(1′)); 3.97 (*dd*, $J = 7.4$, 1.1, H–C(6)); 3.86 (H–C(4″)); 3.83 (H_a–C(6′)); 3.82 (H–C(5″)); 3.80 (H_b–C(6′)); 3.75 (H–C(2″)); 3.73 (*s*, MeO–C(11)); 3.70 (H–C(3″)); 3.67 (CH_2(6″)); 3.51–3.55 (*m*, H–C(5′)); 3.40 (H–C(3′)); 3.36 (*d*, $J = 1.1$, H–C(7)); 3.26 (H–C(2′), H–C(4′)); 2.66 (*t*-like, $J = 7.4$, H–C(5)); 2.39 (*dd*, $J = 9.7$, 7.4, H–C(9)); 1.55 (*s*, Me(10)). ESI-MS: 589.2 ($[M + Na]^+$). HR-ESI-MS: 589.1720 ($[M + Na]^+$, $C_{23}H_{34}O_{16}Na^+$; calc. 589.1745).

*6′-*O*-β-*D*-Glucopyranosylsesamoside* (= *(1a*R*,1b*S*,2*S*,5a*R*,6*R*,6a*S*)-2-[(6-*O*-β-*D*-Glucopyranosyl-β-*D*-glucopyranosyl)oxy]-1a,1b,2,5a,6,6a-hexahydro-6,6a-dihydroxy-1a-methyloxireno[4,5]cyclopenta[1,2-*c*]-pyran-5-carboxylic Acid Methyl Ester*; **3**): Amorphous powder. $[\alpha]_D^{20} = -62$ ($c = 0.18$, H_2O). UV: 234, 203. IR: 3415, 2918, 1720, 1635, 1387, 1313, 1082, 1034, 606. ^{1}H-NMR[2]): 7.55 (*s*, H–C(3)); 5.43 (*d*, $J = 9.3$, H–

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[2]) The ^{1}H-NMR signals of the glycosyl units overlapped; the δ values are those of the corresponding central position of the HMQC cross-peaks.

C(1)); 4.73 (*d*, *J* = 7.9, H–C(1′)); 4.39 (*d*, *J* = 1.3, H–C(6)); 4.33 (*d*, *J* = 7.6, H–C(1″)); 4.19 (*dd*, *J* = 12.1, 1.7, H_a–C(6′)); 3.86 (*dd*, *J* = 11.8, 1.9, H_a–C(6″)); 3.73 (*s*, MeO–C(11)); 3.69 (*dd*, *J* = 12.1, 5.2, H_b–C(6′)); 3.64 (*dd*, *J* = 11.8, 5.7, H_b–C(6″)); 3.50–3.55 (*m*, H–C(5′)); 3.51 (br. *s*, H–C(7)); 3.37 (*t*-like, *J* = 9.0, H–C(3′)); 3.34–3.20 (H–C(2′), H–C(4′), H–C(3″), H–C(4″), H–C(5″)); 3.16 (*dd*, *J* = 8.8, 7.6, H–C(2″)); 2.50 (*d*, *J* = 9.3, H–C(9)); 1.52 (*s*, Me(10)). ESI-MS: 605.2 ($[M+Na]^+$). HR-ESI-MS: 605.1695 ($[M+Na]^+$, $C_{23}H_{34}O_{17}Na^+$; calc. 605.1694).

*6′-*O*-α-*D*-Galactopyranosylsesamoside* (= *(1a*R*,1b*S*,2*S*,5a*R*,6*R*,6a*S*)-2-[(6-*O*-α-*D*-Galactopyranosyl-β-*D*-glucopyranosyl)oxy]-1a,1b,2,5a,6,6a-hexahydro-6,6a-dihydroxy-1a-methyloxireno[4,5]cyclopenta[1,2-*c*]pyran-5-carboxylic Acid Methyl Ester*; **4**): Amorphous powder. $[\alpha]_D^{20} = -9$ (*c* = 0.235, H_2O). UV: 233, 203. IR: 3415, 2926, 1686, 1635, 1406, 1313, 1209, 1151, 1082, 1030. ^{1}H-NMR[1)2]): 7.56 (*s*, H–C(3)); 5.39 (*d*, *J* = 8.8, H–C(1)); 4.87 (*d*, *J* = 3.6, H–C(1″)); 4.72 (*d*, *J* = 7.9, H–C(1′)); 4.31 (*d*, *J* = 1.5, H–C(6)); 3.87 (H–C(4″)); 3.83 (H–C(5″), CH_2(6′)); 3.76 (H–C(2″)); 3.73 (*s*, MeO–C(11)); 3.70 (H–C(3″)); 3.67 (CH_2(6″)); 3.50–3.55 (*m*, H–C(5′)); 3.48 (br. *s*, H–C(7)); 3.37 (*t*-like, *J* = 9.0, H–C(3′)); 3.29 (H–C(4′)); 3.25 (*dd*, *J* = 9.0, 7.9, H–C(2′)); 2.50 (*d*, *J* = 8.8, H–C(9)); 1.51 (*s*, Me(10)). ESI-MS: 605.2 ($[M+Na]^+$). HR-ESI-MS: 605.1704 ($[M+Na]^+$, $C_{23}H_{34}O_{17}Na^+$; calc. 605.1694).

*6′-*O*-β-*D*-Glucopyranosylbarlerin* (= *(1*S*,4a*S*,5*R*,7*S*,7a*S*)-7-(Acetyloxy)-1-[(6-*O*-β-*D*-glucopyranosyl-β-*D*-glucopyranosyl)oxy]-1,4a,5,6,7,7a-hexahydro-5-hydroxy-7-methylcyclopenta[*c*]pyran-4-carboxylic Acid Methyl Ester*; **5**): Amorphous powder. $[\alpha]_D^{23} = -74$ (*c* = 0.145, H_2O). UV: 236, 203. IR: 3412, 2924, 1707, 1639, 1441, 1383, 1292, 1188, 1082, 864, 611. ^{1}H-NMR[1)2]): 7.43 (*d*, *J* = 1.2, H–C(3)); 5.89 (*d*, *J* = 2.7, H–C(1)); 4.63 (*d*, *J* = 8.0, H–C(1′)); 4.46 (*d*, *J* = 7.5, H–C(1″)); 4.31 (*m*, H–C(6)); 4.18 (*dd*, *J* = 11.8, 1.5, H_a–C(6′)); 3.87 (*dd*, *J* = 11.9, 2.1, H_a–C(6″)); 3.77 (*dd*, *J* = 11.8, 6.6, H_b–C(6′)); 3.70 (*s*, MeO–C(11)); 3.66 (*dd*, *J* = 11.9, 5.5, H_b–C(6″)); 3.49–3.53 (*m*, H–C(5′)); 3.40 (*t*-like, *J* = 9.0, H–C(3′)); 3.33 (H–C(3″), H–C(5″)); 3.28 (H–C(4′), H–C(4″)); 3.16 (*dd*, *J* = 9.0, 8.0, H–C(2′)); 3.06 (br. *d*, *J* = 8.8, H–C(5)); 2.96 (*dd*, *J* = 8.8, 2.7, H–C(9)); 2.19 (br. *d*, *J* = 14.9, H_a–C(7)); 2.04 (*dd*, *J* = 14.9, 5.5, H_b–C(7)); 2.01 (*s*, AcO–C(8)); 1.52 (*s*, Me(10)). ESI-MS: 633.2 ($[M+Na]^+$). HR-ESI-MS: 633.2025 ($[M+Na]^+$, $C_{25}H_{38}O_{17}Na^+$; calc. 633.2007).

*6′-*O*-α-*D*-Galactopyranosylbarlerin* (= *(1*S*,4a*S*,5*R*,7*S*,7a*S*)-7-(Acetyloxy)-1-[(6-*O*-α-*D*-galactopyranosyl-β-*D*-glucopyranosyl)oxy]-1,4a,5,6,7,7a-hexahydro-5-hydroxy-7-methylcyclopenta[*c*]pyran-4-carboxylic Acid Methyl Ester*; **6**): Amorphous powder. $[\alpha]_D^{23} = -26$ (*c* = 0.115, H_2O). UV: 236, 203. IR: 3412, 2929, 1707, 1639, 1439, 1377, 1292, 1188, 1086, 1024, 866, 615. ^{1}H-NMR[1)2]): 7.43 (*d*, *J* = 1.1, H–C(3)); 5.95 (*d*, *J* = 2.0, H–C(1)); 4.91 (*d*, *J* = 3.5, H–C(1″)); 4.63 (*d*, *J* = 7.7, H–C(1′)); 4.34 (*m*, H–C(6)); 3.98 (H–C(5″)); 3.93 (H–C(4″)); 3.89 (H_a–C(6′)); 3.82 (H–C(3″)); 3.79 (H_b–C(6′)); 3.76 (H–C(2″)); 3.73 (CH_2(6″)); 3.71 (*s*, MeO–C(11)); 3.54–3.58 (*m*, H–C(5′)); 3.36 (*t*-like, *J* = 9.0, H–C(3′)); 3.28 (*t*-like, *J* = 9.0, H–C(4′)); 3.17 (*dd*, *J* = 9.0, 7.7, H–C(2′)); 3.07 (br. *d*, *J* = 8.8, H–C(5)); 2.99 (*dd*, *J* = 8.8, 2.0, H–C(9)); 2.17 (br. *d*, *J* = 15.0, H_a–C(7)); 2.01 (*s*, AcO–C(8)); 1.95 (*dd*, *J* = 15.0, 5.5, H_b–C(7)); 1.50 (*s*, Me(10)). ESI-MS: 633.2 ($[M+Na]^+$). HR-ESI-MS: 633.1963 ($[M+Na]^+$, $C_{25}H_{38}O_{17}Na^+$; calc. 633.2007).

*6′-*O*-α-*D*-Galactopyranosylshanzhiside Methyl Ester* (= *(1*S*,4a*S*,5*R*,7*S*,7a*S*)-1-[(6-*O*-α-*D*-Galactopyranosyl-β-*D*-glucopyranosyl)oxy]-1,4a,5,6,7,7a-hexahydro-5,7-dihydroxy-7-methylcyclopenta[*c*]pyran-4-carboxylic Acid Methyl Ester*; **7**): Amorphous powder. $[\alpha]_D^{20} = -29$ (*c* = 0.14, H_2O). UV: 237, 203. IR: 3408, 2929, 1691, 1641, 1439, 1383, 1309, 1084, 1057, 1020, 868, 579. ^{1}H-NMR[1)2]): 7.39 (*d*, *J* = 1.0, H–C(3)); 5.49 (*d*, *J* = 2.9, H–C(1)); 4.87 (*d*, *J* = 2.8, H–C(1″)); 4.64 (*d*, *J* = 8.0, H–C(1′)); 4.03 (*m*, H–C(6)); 3.91 (H–C(4″)); 3.89 (H–C(5″), H_a–C(6′)); 3.79 (H_b–C(6′)); 3.75 (H–C(2″), H–C(3″)); 3.72 (*s*, MeO–C(11)); 3.69 (CH_2(6″)); 3.50–3.55 (*m*, H–C(5′)); 3.37 (*t*-like, *J* = 8.8, H–C(3′)); 3.34 (H–C(4′)); 3.18 (*dd*, *J* = 8.8, 8.0, H–C(2′)); 3.00 (*dd*, *J* = 10.0, 3.0, H–C(5)); 2.60 (*dd*, *J* = 10.0, 2.9, H–C(9)); 1.98 (*dd*, *J* = 13.3, 6.4, H_a–C(7)); 1.81 (*dd*, *J* = 13.3, 5.8, H_b–C(7)); 1.25 (*s*, Me(10)). ESI-MS: 591.2 ($[M+Na]^+$). HR-ESI-MS: 591.1898 ($[M+Na]^+$, $C_{23}H_{36}O_{16}Na^+$; calc. 591.1901).

Acid Hydrolysis of **1**–**7**. An iridoid diglycoside **1**–**7** (*ca.* 2 mg) was refluxed with 2N HCl for 4 h. The mixture was neutralized with Ag_2CO_3 and filtered. The soln. was lyophilized to give the sugar fraction. The sugar fraction was dissolved in 1-(trimethylsilyl)-1*H*-imidazole pyridine 1:4 (*v*/*v*) (0.3 ml) and then stirred at 60° for 5 min. After centrifugation, the supernatant was analyzed by GC (*L-Chirasil-Val* column (0.32 mm × 25 m), injector and detector temp. 200°, temp. gradient starting at 100° for 1 min, then up to 180° at 5°/min). Sugars were identified by comparison with the retention times of authen-

tic samples of D-glucose (t_R 14.72) and D-galactose (t_R 13.98 and 14.96) after being treated with 1-(trimethylsilyl)-1*H*-imidazole in pyridine (**1**: t_R 14.71; **2**: t_R 13.97, 14.70, and 14.95; **3**: t_R 14.72; **4**: t_R 13.99, 14.72, and 14.97; **5**: t_R 14.71; **6**: t_R 13.96, 14.71, and 14.95; **7**: t_R 13.98, 14.72, and 14.97).

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