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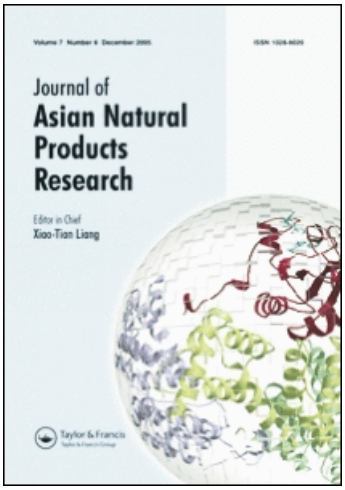

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Iridoidal glucosides from *Gentiana rhodantha*

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Six new iridoidal glucosides, 2′-*O*-(3″-hydroxybenzoyl)-8-epikingiside (**1**), 2′-*O*-(3″-hydroxybenzoyl)-kingiside (**2**), 6′-*O*-*p*-coumaroyl-8-epikingiside (**3**), loganic acid 11-*O*-β-glucopyranosyl ester (**4**), 6′-*O*-β-glucopyranosyl secologanoside (**5**), and 6′-*O*-β-glucopyranosyl secologanol (**6**), together with seven known iridoidal glucosides, loganic acid (**7**), 6′-*O*-β-D-glucopyranosyl loganic acid (**8**), 8-epikingiside (**9**), kingiside (**10**), secologanoside (**11**), secoxyloganin (**12**), and alpigenoside (**13**), were isolated from the whole plant of *Gentiana rhodantha* (Gentianaceae). Their structures were elucidated by detailed spectroscopic analysis and chemical methods.

Keywords: Gentianaceae; *Gentiana rhodantha*; iridoidal glucosides; kingiside; loganic acid

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1. Introduction

Gentiana rhodantha Franch ex Hemsl. (Gentianaceae) is an annual herb native to the southwest of China. The whole plant is used as a folk medicine for the treatment of inflammation, cholecystitis and tuberculosis. In previous phytochemical studies, three new acylated secoiridoid glucosides, rhodenthosides A–C, have been reported from this plant.[1,2] As a part of our research on gentianaceous medicinal plants,[3–6] the recent investigation led to the isolation of 13 iridoidal glycosides including six new ones (**1**–**6**) (Figure 1) from the whole plant of this species. This paper presents a full account of the isolation and structural elucidation of these new compounds by detailed one- and two-dimensional NMR spectroscopic analysis and chemical methods.

2. Results and discussion

The whole plants of *G. rhodantha* were extracted with MeOH, and the extract was partitioned between petroleum ether and H_2O. The aqueous phases were fractioned by a column chromatography (CC) over macropore absorption resin (Diaion HP-20SS), and then subjected to repeated CC on Sephadex LH-20, silica gel, MCI-gel CHP20P, and Chromatorex ODS to afford iridoidal glucosides **1**–**13**. On the basis of the spectroscopic evidences and by comparison with the reported values, the known compounds were identified as loganic acid (**7**),[7] 6′-*O*-β-D-glucopyranosyl loganic acid (**8**),[8] 8-epikingiside (**9**),[9] kingiside (**10**),[10] secologanoside (**11**),[11] secoxyloganin (**12**),[12] and alpigenoside (**13**),[12,13] respectively. Therein, compounds **7** and **8** and **11**–**13** were isolated for the first time from the title plant.

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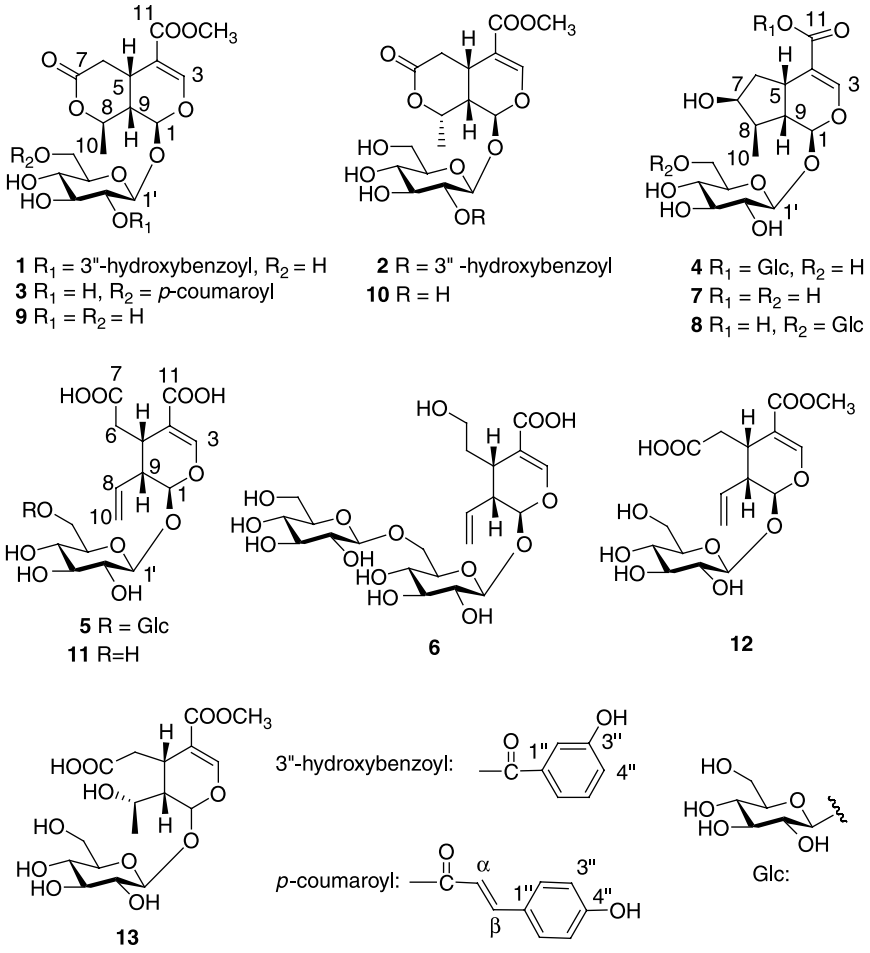

Figure 1. Structures of compounds **1**–**13**.

All of the new compounds were individually hydrolyzed with 2 M HCl to give glucose as the sugar residues, which were identified by direct co-TLC comparison and polarimetric analysis.

Compound **1** was obtained as a white amorphous powder. Its molecular formula was assigned as $C_{24}H_{28}O_{13}$ based on the ^{13}C NMR spectral data and negative HRFABMS spectrum, in which it displayed a quasi-molecular ion peak at *m/z* 523.1464 $[M - H]^-$. The ^1H and ^{13}C NMR chemical shifts (Table 1) due to a secondary methyl, a methoxy, a carbonyl, a carboxyl, four methines (including two oxygen-bearing and one olefinic oxygen-bearing ones), one olefinic quaternary carbon, and a β-glucopyranosyl unit indicated that compound **1** was a secoiridoidal glucoside. These NMR spectral features were very similar to those of 8-epikingiside (**9**),[10] except for the appearance of a set of additional signals [δ_H 7.39 (t, $J = 2.4$ Hz), 7.03 (ddd, $J = 7.9$, 2.4, 0.9 Hz), 7.27 (t, $J = 7.9$ Hz), 7.48 (ddd, $J = 7.9$, 2.4, 0.9 Hz); and δ_C 134.4, 117.4, 158.6, 121.3, 130.5, 121.9 and 167.1] assignable to a 3-hydroxybenozyl group. The obvious substituted effects of carbon signals due to downfield shift in glucosyl C-2′ (δ_C 75.1) and upfield shift in glucosyl C-3′ (δ_C 75.8) suggested that the additional 3-hydroxybenzoyl group was linked to the C-2′

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Table 1. ^{13}C (100 MHz) and ^{1}H (400 MHz) NMR spectral data of compounds **1–3** (in CD_3OD; δ in ppm, J in Hz).

	1		**2**		**3**	
Positions	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	95.4	5.54 (d, $J = 5.0$)	93.8	5.70 (d, $J = 2.9$)	96.4	5.29 (d, $J = 7.9$)
3	153.2	7.25 (d, $J = 1.2$)	153.7	7.22 (s)	154.4	7.51 (s)
4	110.6		111.6		109.3	
5	26.5	2.97 (brq, $J = 6.9$)	26.4	3.15 (dt, $J = 8.5, 4.9$)	28.4	2.98 (m)
6	33.8	2.57 (dd, $J = 16.9, 8.4$)	33.7	2.73 (dd, $J = 16.0, 4.5$)	34.7	2.29 (dd, $J = 16.4, 8.5$)
		2.83 (dd, $J = 16.9, 6.3$)		2.89 (dd, $J = 16.0, 5.6$)		2.78 (dd, $J = 16.4, 5.4$)
7	174.2		175.0		174.6	
8	75.8	4.36 (dq, $J = 8.2, 6.4$)	75.6	4.70 (dq, $J = 6.4, 6.4$)	75.8	4.34 (brq, $J = 6.3$)
9	42.4	2.09 (td, $J = 7.9, 5.0$)	39.8	2.55 (ddd, $J = 2.9, 6.4, 8.5$)	41.7	2.07 (brq, $J = 7.4$)
10	20.8	1.46 (d, $J = 6.4$)	17.2	1.46 (d, $J = 6.7$)	21.7	1.41 (d, $J = 6.3$)
11	167.7		167.2		168.9	
COOCH_3	51.8	3.45 (s)	51.7	3.34 (s)	52.0	3.67 (s)
1-*O*-Glc-1′	98.3	4.98 (d, $J = 8.1$)	97.4	5.00 (d, $J = 8.0$)	98.7	4.73 (d, $J = 8.0$)
2′	75.1	4.95 (dd, $J = 8.1, 9.2$)	75.0	4.96 (dd, $J = 8.0, 8.9$)	74.6	3.25 (dd, $J = 8.0, 8.7$)
3′	75.8	3.70 (dd, $J = 9.2, 8.7$)	75.2	3.74 (t, $J = 8.9$)	77.6	3.42 (dd, $J = 8.7, 6.6$)
4′	71.8	3.41 (dd, $J = 8.7, 9.0$)	71.6	3.47 (dd, $J = 8.0, 8.7$)	71.5	3.31 (m)
5′	78.7	3.47 (m)	78.3	3.48 (m)	75.6	3.56 (m)
6′	62.7	3.97 (dd, $J = 12.0, 1.9$)	62.6	3.99 (dd, $J = 12.6, 1.0$)	63.6	4.35 (dd, $J = 12.0, 5.7$)
		3.72 (dd, $J = 12.0, 4.5$)		3.75 (dd, $J = 12.6, 5.4$)		4.58 (dd, $J = 12.0, 2.1$)
Acyl-1″	134.4		132.2		126.9	
2″	117.4	7.39 (t, $J = 2.4$)	117.2	7.42 (d, $J = 2.0$)	131.3	7.45 (d, $J = 8.5$)
3″	158.6		158.5		116.8	6.80 (d, J = 8.5)
4″	121.3	7.03 (ddd, $J = 7.9, 2.4$)	121.3	7.07 (dd, $J = 8.0, 2.0$)	161.3	
5″	130.5	7.27 (t, $J = 7.9$)	130.5	7.31 (t, $J = 8.0$)	116.8	6.80 (d, $J = 8.5$)
6″	121.9	7.48 (ddd, $J = 7.9, 2.4$)	121.8	7.49 (dd, $J = 8.0, 2.0$)	131.3	7.45 (d, $J = 8.5$)
α					114.8	6.32 (d, $J = 16.0$)
β					147.0	7.59 (d, $J = 16.0$)
7″(C═O)	167.1		166.8		168.2	

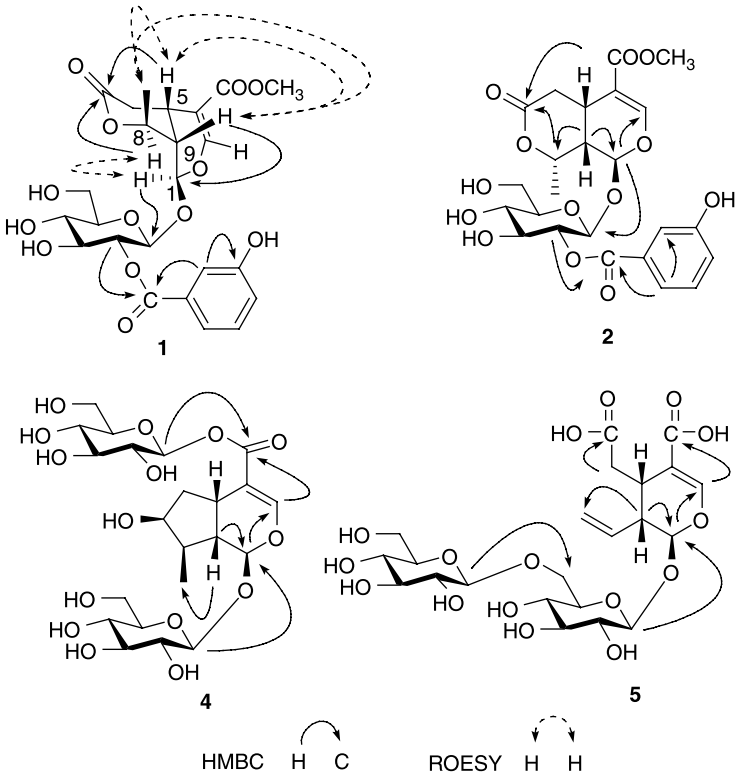

Figure 2. Key HMBC and ROESY correlations of **1**, **2**, **4** and **5**.

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position of the β-glucopyranosyl moiety of **1**. It was further confirmed by the long-range correlations of the glucosyl H-2′ [δ_H 4.95 (dd, $J = 8.1$, 9.2 Hz)] with the carboxyl carbon (δ_C 167.1) of the 3-hydroxybenzoyl group observed in the HMBC experiment (Figure 2). Moreover, the correlations between H-8 [δ_H 4.36 (dq, $J = 8.2$, 6.4 Hz)] and H-1 [δ_H 5.54 (d, $J = 5.0$ Hz)] in the ROESY spectrum revealed the β-orientation of the C-8 methyl group (Figure 2). Therefore, the structure of **1** was determined to be 2′-*O*-(3″-hydroxybenzoyl)-8-epikingiside.

Compound **2** was determined to have a molecular formula $C_{24}H_{28}O_{13}$ on the basis of the negative HRFABMS (*m/z* 523.1441 $[M - H]^-$), which is the same as that of **1**. The ^1H and ^{13}C NMR spectral data (Table 1) of **2** were identical with those of **1**, except for the obvious difference of C-10 and C-9 (δ_C 17.2 and 39.8 for **2**; δ_C 20.8 and 42.4 for **1**), which is the same as that in kingiside (δ_C 17.6 and 39.0 for C-10 and C-9, respectively).[9] The above evidence indicated that **2** was a C-8 epimer of **1**. Interpretation of the ROESY spectrum, in which the correlation of H-8 [δ_H 4.70 (dq, $J = 6.4$, 6.4 Hz)] with H-5 [δ_H 3.15 (dt, $J = 8.5$, 4.9)] was observed, revealed the α-orientation of the C-8 methyl group.[9] Therefore, the structure of **2** was established as 2′-*O*-(3″-hydroxybenzoyl)-kingiside.

The molecular formula of compound **3** was determined to be $C_{26}H_{30}O_{13}$ by the negative HRFABMS (*m/z* 549.1621 $[M - H]^-$). The ^1H and ^{13}C NMR spectral data (Table 1) of **3** were very similar to those of **1**, except that the 3-hydroxybenzoyl group in **1** was substituted by a *p*-coumaroyl group in **3**. The location of the *p*-coumaroyl group at the glucosyl C-6′ position was readily determined by the obvious downfield chemical shift of glucosyl H-6′ [δ_H 4.35 (dd,

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Table 2. ^{13}C (100 MHz) and ^{1}H (400 MHz) NMR spectral data of compounds **4**–**6** (in CD_3OD; δ in ppm, J in Hz).

	4		**5**		**6**	
Positions	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	97.8	5.36 (d, $J = 4.0$)	97.5	5.40 (d, $J = 3.2$)	97.6	5.39 (d, $J = 4$)
3	154.0	7.60 (s)	152.3	7.20 (s)	150.3	7.27 (s)
4	113.3		114.8		111.8	
5	31.4	3.09 (m)	30.9	3.24 (m)	29.7	3.23 (m)
6	42.1	1.88 (ddd, $J = 14.0, 4.8, 2.4$)	38.3	2.14 (m)	33.5	1.85 (dt, $J = 14.2, 6.5$)
		2.21 (ddd, $J = 14.0, 8.0, 6.0$)		2.85 (m)		1.69 (ddd, $J = 14.2, 8.7, 6.5$)
7	75.1	4.16 (m)	181.3	–	62.2	4.17 (brd, $J = 10.1$)
8	44.8	1.75 (ddq, $J = 13.6,9.6,6.8$)	135.1	5.73 (dt, $J = 17.0, 9.6$)	134.4	5.67 (ddd, $J = 17.0, 10.0, 9.5$)
9	46.3	2.14 (ddd, $J = 9.6, 4.0,3.6$)	45.3	2.84 (m)	45.0	2.24 (ddd, $J = 9.5, 6.8, 4.5$)
10	13.2	1.10 (d, $J = 6.8$)	120.3	5.26 (dd, $J = 15.0, 3.6$)	120.8	5.29 (dd, $J = 9.5, 4.0$)
				5.31 (dd, $J = 9.6, 3.6$)		5.22 (dd, $J = 14.0, 4.0$)
11	168.0		175.3		169.5	
1-*O*-Glc-1′	99.8	4.89 (d, $J = 7.9$)	99.8	4.84 (d, $J = 8.0$)	99.6	4.79 (d, $J = 7.6$)
2′	75.1	3.24 (m)	74.8	3.26 (m)	74.6	3.25 (m)
3′	78.4	3.49 (m)	77.7	3.61 (m)	77.7	3.57 (m)
4′	71.2	3.36–3.42 (m)	71.3	3.43–3.51 (m)	71.0	3.32–3.48 (m)
5′	78.0	3.36–3.42 (m)	77.3	3.43–3.51 (m)	77.3	3.32–3.48 (m)
6′	62.3	3.93 (dd, $J = 14.4, 6.0$)	69.8	4.41 (dd, $J = 13.2, 4.8$)	69.7	3.87 (dd, $J = 12.0, 5.0$)
		3.73 (dd, $J = 14.4, 4.4$)		3.84 (dd, $J = 13.2, 2.0$)		3.83 (dd, $J = 12.0, 1.0$)
Glc-1”	95.2	5.51 (d, $J = 8.0$)	104.7	4.48 (d, $J = 7.2$)	104.4	4.50 (d, $J = 7.8$)
2”	74.3	3.36–3.42 (m)	74.3	3.26 (m)	74.0	3.25 (m)
3”	78.4	3.49 (m)	77.6	3.61 (m)	77.5	3.57 (m)
4”	70.7	3.36–3.42 (m)	71.2	3.43–3.51 (m)	70.9	3.32–3.48 (m)
5”	77.2	3.36–3.42 (m)	77.0	3.43–3.51 (m)	77.1	3.32–3.48 (m)
6”	62.0	3.83 (dd, $J = 12.0, 6.0$)	62.4	3.88 (dd, $J = 12.5, 5.5$)	62.2	3.89 (dd, $J = 12.5, 5.5$)
		3.90 (dd, $J = 12.0, 2.0$)		3.70 (dd, $J = 12.5, 1.0$)		3.70 (dd, $J = 12.5, 1.0$)

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$J = 12.0$, 5.7 Hz) and 4.58 (dd, $J = 12.0$, 2.1 Hz)] and the upfield chemical shift of C-5′ (δ_C 75.6). The HMBC spectrum showed the correlation of glucosyl H-6′ with the carboxyl carbon (δ_C 168.2) of the *p*-coumaroyl group. Moreover, the ROESY correlations of H-8 [δ_H 4.34 (brq, $J = 6.3$ Hz)] with H-1 [δ_H 5.29 (d, $J = 7.9$ Hz)] confirmed the β-orientation for the C-8 methyl group. Thus, the structure of **3** was elucidated as 6′-*O*-*p*-coumaroyl-8-epikingiside.

The molecular formula $C_{22}H_{34}O_{15}$ of compound **4** was established by the negative HRFABMS (*m/z* 537.1808 $[M - H]^-$). Its NMR spectral data (Table 2) were closely related to those of loganic acid (**7**), except for a set of additional signals for the β-glucopyranosyl unit. The upfield chemical shift (δ_C 95.2) of the additional anomeric carbon suggested that the additional β-glucopyranosyl unit was esterified and linked to the C-11 position of the carboxyl group. In the HMBC spectrum, the anomeric proton (δ_H 5.51) of the second glucose was correlated with the carboxyl carbon (δ_C 168.0), which further confirmed this deduction. Accordingly, the structure of **4** was assigned to be loganic acid 11-*O*-β-D-glucopyranosyl ester.

Compound **5** was isolated as a yellow amorphous powder with a molecular formula $C_{22}H_{32}O_{16}$, as deduced from the negative HRFABMS (*m/z* 551.1609 $[M - H]^-$). Except for a set of signals due to one more β-glucopyranosyl unit, the ^1H and ^{13}C NMR spectra (Table 2) of **5** were very similar to those of secologanoside (**11**).[11] The downfield shift of glucosyl C-6′ signal (δ_C 69.8) suggested that the second glucopyranosyl unit was at the C-6′ position of the inner glucose, which was confirmed by the HMBC correlations between the anomeric proton of the terminal glucose at δ_H 4.48 (H-1″) and the C-6′ of the inner glucose. Thus, compound **5** was determined to be 6′-*O*-β-glucopyranosyl secologanoside.

Compound **6** was obtained as a white amorphous powder. It has a molecular formula, $C_{22}H_{34}O_{15}$, based on HRFABMS (*m/z* 537.1820 $[M - H]^-$). The ^1H and ^{13}C NMR spectra (Table 2) indicated the presence of one more β-glucopyranosyl unit than a secologanol unit.[14] The position of the additional glucosyl group was indicated by the downfield shift of the inner glucosyl C-6′ (+6.9 ppm) and confirmed by the HMBC correlations between the anomeric proton of the terminal glucose at δ_H 4.50 (H-1″) and the methylene carbon at δ_C 69.7 (C-6′) of the inner glucosyl unit. Therefore, the structure of compound **6** was elucidated to be 6′-*O*-β-glucopyranosyl secologanol.

Thirteen iridoidal glycosides were isolated from the whole plant of *G. rhodantha.* It is noted that loganic acid (**7**) may be an important biosynthesis precursor of the molecular diversity of iridoidal glucosides in this plant. All of the isolated compounds were possibly derived from **7** through the enzymatic reaction of glycosylation and oxidation.

3. Experimental

3.1 General experimental procedures

NMR spectra were measured in CD_3OD on a Bruker AM-400 and DRX-500 instrument with TMS as an internal standard. Optical rotations were measured on a SEPA-3000 automatic digital polarimeter. FABMS (negative ion mode) and HRFABMS (negative ion mode) spectra were recorded on VG Auto-Spec 3000 and API Qstar Pulsar LC/TOF spectrometers, respectively. IR spectra were measured on a Bio-Rad FTS-135 spectrometer (in cm^{-1}). CC were performed over Diaion HP20SS (Mitsubishi Chemical Industry Ltd, Tokyo, Japan), MCI-gel CHP20P (75–150 μm; Mitsubishi Chemical Industry), Chromatorex ODS (100–200 mesh; Fuji Silysia Chemical Co. Ltd, Kasugai, Japan), Sephadex LH-20 (25–100 μm; Pharmacia Fine Chemical Co. Ltd Uppsala, Sweden), and silica gel (200–300 mesh; Qingdao Marine Chemical Factory, Qingdao, China). TLC was carried out on silica gel G pre-coated plates (Qingdao Marine Chemical Factory) by developing with $CHCl_3$–MeOH–H_2O (7:3:0.5). Spots were visualized by spraying with 10% sulfuric acid followed by heating.

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3.2 Plant material

The air-dried whole plant of *G. rhodantha* Franch ex Hemsl. was collected from Wensan, Yunnan province, China, on July 2004, and was identified by Professor Chong-Ren Yang. A voucher specimen (KUN 0552165) has been deposited in the herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

3.3 Extraction and isolation

The powdered air-dried whole plant of *G. rhodantha* (2 kg) was extracted with MeOH (2000 ml) at room temperature three times. After the removal of the solvent, the resulting residue (100 g) was suspended in H_2O (500 ml) and defatted with petroleum ether. The aqueous layer was subjected to a column of Diaion HP20SS, eluting with H_2O–MeOH (1:0–0:1) to give four fractions (A_1–A_4). Fraction A_2 (26 g) was subjected to repeated CC on Sephadex LH-20 (H_2O–MeOH, 1:0–0:1), silica gel ($CHCl_3$–MeOH–H_2O, 7:3:0.5), MCI-gel CHP20P (H_2O–MeOH, 9:1–6:4) and Chromatorex ODS (H_2O–MeOH, 7:3) to afford **4** (13 mg), **5** (12 mg), **6** (5 mg), **7** (172 mg), **8** (14 mg), **10** (71 mg), and **11** (370 mg). Fraction A_3 (14.6 g) was chromatographed over MCI-gel CHP20P (H_2O–MeOH, 7:3–4:6), Chromatorex ODS (H_2O–MeOH, 6:4), and silica gel ($CHCl_3$–MeOH–H_2O, 8:2:0.2) columns to yield **9** (374 mg), **12** (56 mg), and **13** (42 mg). Fraction A_4 (24.73 g) was applied to Sephadex LH-20 (H_2O–MeOH, 6:4–2:8), Chromatorex ODS (H_2O–MeOH, 5:5), and silica gel CC (eluting with $CHCl_3$–MeOH–H_2O, 8:2:0.2) to give **1** (354 mg), **2** (87 mg) and **3** (39 mg).

3.3.1 2′-O-(3″-Hydroxybenzoyl)-8-epikingiside (1)

A white amorphous powder; mp 125–127°C, $[\alpha]_D^{26}$ −67.4 (*c* 0.7, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3429 (OH), 1716 (lactone C=O), 1636, 1453, 1287, 1104, 981, 754; for ^1H and ^{13}C NMR (CD_3OD) spectral data, see Table 1; FABMS (negative) *m/z*: 523 $[M-H]^-$, 241 $[M-121(C_7H_5O_2)\text{-}162(glc)]^-$; HRFABMS (negative) *m/z*: 523.1464 $[M-H]^-$ (calcd for $C_{24}H_{27}O_{13}$, 523.1451).

3.3.2 2′-O-(3″-Hydroxybenzoyl)-kingiside (2)

A white amorphous powder; mp 118–120°C, $[\alpha]_D^{26}$ −86.6 (*c* 0.7, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3427 (OH), 1719 (lactone C=O), 1640, 1288, 1076; for ^1H and ^{13}C NMR (CD_3OD) spectral data, see Table 1; FABMS (negative) *m/z*: 523 $[M-H]^-$, 241 $[M-121(C_7H_5O_2)\text{-}162(glc)]^-$; HRFABMS (negative) *m/z*: 523.1441 $[M-H]^-$ (calcd for $C_{24}H_{27}O_{13}$, 523.1451).

3.3.3 6′-O-p-Coumaroyl-8-epikingiside (3)

A yellow amorphous powder; mp 128–130°C, $[\alpha]_D^{26}$ −34.3 (*c* 1.8, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3421, 1707, 1604, 1514, 1441, 1279, 1167, 1077; for ^1H and ^{13}C NMR (CD_3OD) spectral data, see Table 1; FABMS (negative) *m/z*: 550 $[M]^-$, 325, 198; HRFABMS (negative) *m/z*: 549.1621 $[M-H]^-$ (calcd for $C_{26}H_{29}O_{13}$, 549.1608).

3.3.4 Loganic acid 11-O-β-glucopyranosyl ester (4)

A white amorphous powder; mp >350°C, $[\alpha]_D^{28}$ −50.0 (*c* 0.1, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3427 (OH), 1719 (lactone C=O), 1640, 1288, 1076; for ^1H and ^{13}C NMR (CD_3OD) spectral data, see Table 2; FABMS (negative) *m/z*: 537 $[M-H]^-$, 375 $[M-H\text{-}162(glc)]^-$; HRFABMS (negative) *m/z*: 537.1808 $[M-H]^-$ (calcd for $C_{22}H_{33}O_{15}$, 537.1819).

3.3.5 6′-O-β-Glucopyranosyl secologanoside (5)

A yellow amorphous powder; mp >350°C, $[\alpha]_D^{26}$ −86.7 (*c* 1.8, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3425, 1639, 1074; for ^1H and ^{13}C NMR (CD_3OD) spectral data, see Table 2; FABMS (negative) *m/z*: 551 $[M-H]^-$, 389 $[M-H\text{-}162\ (glc)]^-$; HRFABMS (negative) *m/z*:

551.1609 $[M - H]^-$ (calcd for $C_{22}H_{31}O_{16}$, 551.1612).

*3.3.6 6′-O-β-Glucopyranosyl secologanol (**6**)*

A white amorphous powder; mp $>350°C$, $[\alpha]_D^{26} -59.0$ (*c* 0.5, MeOH); IR ν_{max}^{KBr} (cm^{-1}): 3425, 1639, 1074; for ^1H and ^{13}C NMR (CD_3OD) spectral data, see Table 2; FABMS (negative) *m/z*: 537 $[M - H]^-$, 375 $[M - H\text{-}162\ (glc)]^-$; HRFABMS (negative) *m/z*: 537.1820 $[M - H]^-$ (calcd for $C_{22}H_{33}O_{15}$, 537.1819).

3.4 Acidic hydrolysis of compounds 1–6

A solution of **1** (5 mg) in MeOH (2 ml) with 2 M HCl was refluxed for 6 h. The reaction mixture was evaporated *in vacuo* to dryness, dissolved in H_2O (2 ml), and extracted with $CHCl_3$ for four times (2 ml). The aqueous layer was passed through an Amberlite IRA-401 (OH^- form), and the eluate was concentrated to dryness to give a residue, which was subjected to a preparative TLC on silica gel, using EtOAc–MeOH–H_2O–HOAc (6:2:1:1), to yield D-glucose (1.52 mg), identified by direct co-TLC comparison with the authentic sample [EtOAc–MeOH–H_2O–HOAc (6:2:1:1), R_f 0.5; isopropanol–MeOH–H_2O (25:1:2), R_f 0.6] and polarimetric analysis $\{[\alpha]_D^{16} + 52.6$ (*c* 0.76, H_2O)}. Spots were visualized by spraying with 10% sulfuric acid followed by heating.

Compounds **2–6** (each 2 mg) were hydrolyzed individually with 2 M HCl as described for **1**. Each reaction mixture was evaporated *in vacuo* to dryness, dissolved in H_2O (2 ml), neutralized with 2% NaOH (3 ml), and subjected to TLC analysis as described for **1**. D-Glucose was detected from each neutralized product of compounds **2–6** by direct co-TLC comparison with authentic sugar.

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