New Acylated Secoiridoid Glucosides from *Gentiana straminea* (Gentianaceae)

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Two new acylated secoiridoid glucosides, 4′-acetyl-6′-{[2-hydroxy-3-(1-β-D-glucopyranosyloxy)]benzoyloxy}sweroside and 3′,4′-diacetyl-6′-{[2-hydroxy-3-(1-β-D-glucopyranosyloxy)]benzoyloxy}swertiamarin, named gentistraminosides A (**1**) and B (**2**), were isolated from the MeOH extract of *Gentiana straminea* MAXIM (Gentianaceae), together with twelve known ones, including eight iridoid and secoiridoid glucosides, macrophylloside A (**3**), loganic acid (**4**), secologanic acid (**5**), swertiamarin (**6**), gentiopicroside (**7**), loganic acid methyl ester (**8**), 6′-*O*-β-D-glucopyranosyl gentiopicroside (**9**), and loganic acid 11-*O*-β-D-glucopyranosyl ester (**10**), one flavone *C*-glucoside, isovitexin (**11**), one chromenecarboxylic acid glycosyl ester, macrophylloside D (**12**), and two triterpenoids, 1α,2α,3β,24-tetrahydroxyolean-12-en-28-oic acid (**13**), and 3β,6α,24-trihydroxyolean-12-en-28-oic acid (**14**). Their structures were determined by means of detailed spectroscopic (NMR and MS) analysis.

Introduction. – ‘Qin-Jiao’ is a well-known traditional Chinese medicinal (TCM) herb commonly used for the treatment of jaundice, hepatitis, inflammation, pains, and rheumatism. In the *Chinese Pharmacopoeia*, the roots of four plants from the genus *Gentiana* (Gentianaceae), *G. macrophylla* PALL, *G. crassicaulis* DUTHIE ex BURK, *G. straminea* MAXIM, and *G. duhurica* FISCH, are used as the raw materials of ‘Qin-Jiao’ [1]. Iridoid and secoiridoid glucosides, *e.g.* loganic acid, gentiopicroside, and swertiamarin, were reported as the main compounds in *G. macrophylla* [2][3] and *G. straminea* [4–6], together with some phenolic and triterpenoid compounds. As a part of our ongoing phytochemical studies on gentianaceous medicinal plants [2][7–17], a detailed chemical investigation on the air-dried roots of *G. straminea*, one of the raw materials of ‘Qin-Jiao’ distributed on the Qinghai-Tibet Plateau, was carried out. This led to the isolation of two new acylated secoiridoid glucosides, **1** and **2**, together with twelve known compounds (*Fig. 1*). In this article, we present the isolation and structural elucidation of these new compounds by detailed one- and two-dimensional NMR spectroscopic analysis.

Results and Discussion. – The MeOH extract of the root of *G. straminea* was defatted with petroleum ether and then applied to repeated column chromatography on *Diaion HP-20*, SiO_2, *Chromatorex ODS*, and *RP-8* to afford two new compounds, **1** and **2**, in addition to twelve known ones. The known compounds were identified as eight iridoid and secoiridoid glucosides, *i.e.*, macrophylloside A (**3**) [3], loganic acid (**4**)

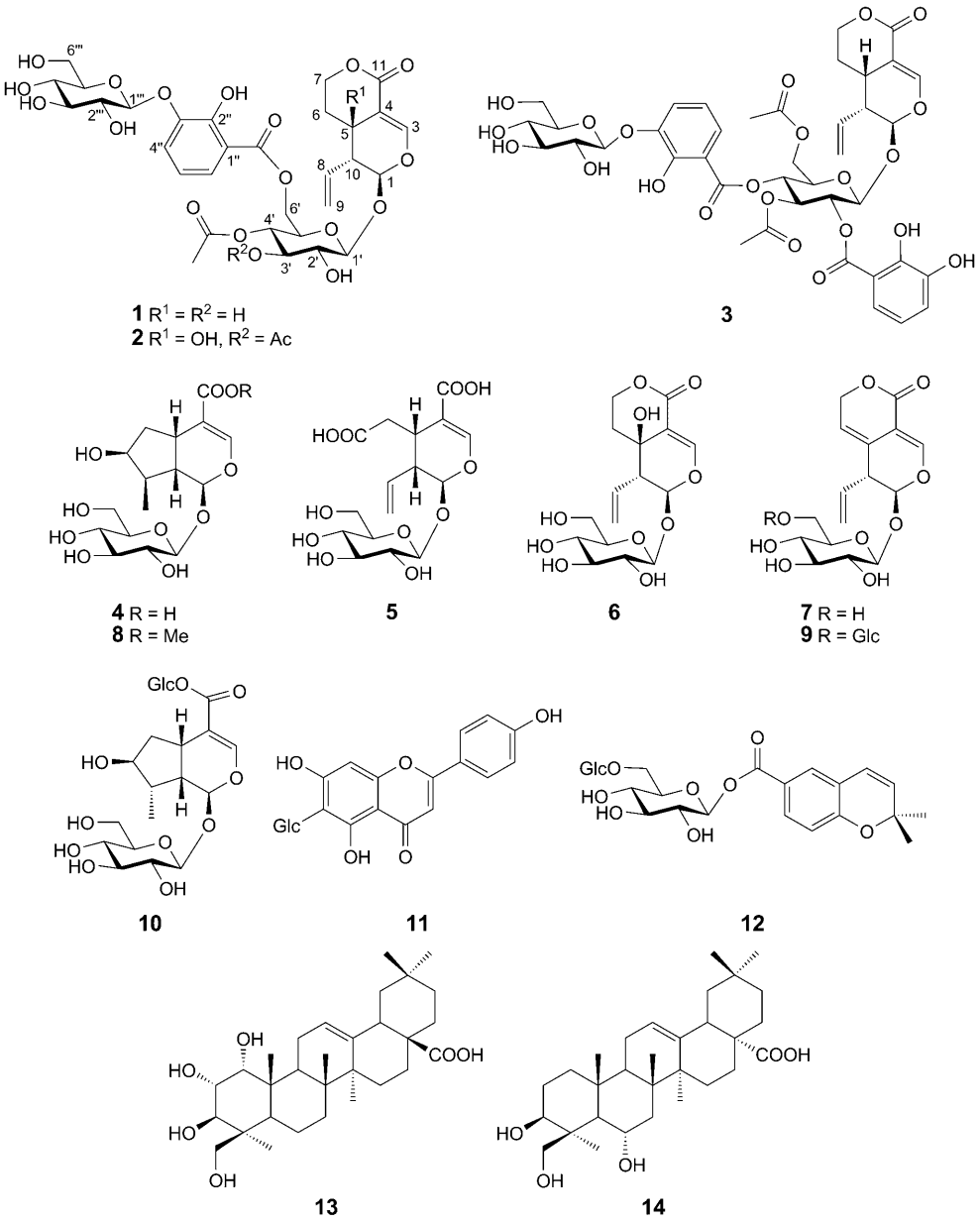

Fig. 1. *The structures of compounds* **1**–**14**

[2], secologanic acid (**5**) [18], swertiamarin (**6**) [19], gentiopicroside (**7**) [2], loganic acid methyl ester (**8**) [13], 6′-*O*-*β*-D-glucopyranosyl gentiopicroside (**9**) [20], and loganic acid 11-*O*-*β*-D-glucopyranosyl ester (**10**) [21], one flavone *C*-glucoside, *i.e.*, isovitexin (**11**) [22], one chromenecarboxylic acid glycosyl ester, *i.e.*, macrophylloside

D (**12**) [3], and two triterpenoids, *i.e.*, 1α,2α,3β,24-tetrahydroxyolean-12-en-28-oic acid (**13**) [10] and 3β,6α,24-trihydroxyolean-12-en-28-oic acid (**14**) [23], by direct comparison with authentic samples or comparison of the spectral data with literature values. Two new acylated secoiridoid glucosides, *i.e.*, 4′-acetyl-6′-{[2-hydroxy-3-(1-β-D-glucopyranosyloxy)]benzoyloxy}sweroside[1]) and 3′,4′-diacetyl-6′-{[2-hydroxy-3-(1-β-D-glucopyranosyloxy)]benzoyloxy}swertiamarin[1]), were named as gentistraminoside A (**1**) and B (**2**), respectively. Their structures were determined as follows.

Gentistraminoside A (**1**) was obtained as a yellow amorphous powder, and had a molecular formula $C_{31}H_{38}O_{18}$, derived from the negative-ion HR-FAB-MS (*m*/*z* 697.1965 $[M-H]^-$) and the ^{13}C-NMR spectrum. Comparison of the NMR data with those of macrophylloside A (**3**), and further 2D-NMR analysis allowed elucidation of the structure of gentistraminoside A as shown in formula **1**.

The IR spectrum of **1** indicated the presence of OH (3432 cm^{-1}) and CO groups (1761 cm^{-1}). The ^{1}H-NMR spectrum (*Table*) of **1** exhibited the characteristic signals of secoiridoid glucoside at δ(H) 7.58 (*s*, H−C(3)), 5.50 (*ddd*, *J* = 17.2, 9.8, 6.9, H−C(8)), 5.31 (*dd*, *J* = 6.9, 1.6, H−C(10a)), and 5.24 (*dd*, *J* = 17.2, 6.9, H−C(10b)). In addition, ^{1}H- and ^{13}C-NMR spectra (*Table*) of **1** indicated the presence of an AcO (δ(H) 1.99 (*s*), δ(C) 21.8, 171.1) and a 2,3-dihydroxybenozyl (δ(H) 7.45 (*dd*, *J* = 8.1, 1.6), 6.87 (*t*, *J* = 8.1), 7.62 (*dd*, *J* = 8.1, 1.6)) group, as well as an additional β-D-glucopyranosyl unit (δ(H) 4.89 (*d*, *J* = 8.0, H−C(1‴)), δ(C) 103.5 (C(1‴))). These NMR features were similar to those of **3**, except that **1** contained one Ac and one 2,3-dihydroxybenzoyl group less than **3**.

The locations of the substituents were determined by two-dimensional NMR-spectroscopic experiments, including HMQC, HMBC, and ROESY. The respective long-range correlations of CH_2(6′) (δ(H) 4.73 (*dd*, *J* = 6.3, 12.0) and 4.57 (*dd*, *J* = 2.2, 12.0)) and H−C(4′) (δ(H) 4.72–4.80) with the CO groups at δ(C) 170.9, and δ(C) 171.7 established that the 2,3-dihydroxybenzoyl and the AcO groups were located on C(6) and C(4) positions of the glucosyl unit, respectively (*Fig. 2*). The linkage position of the additional glucosyl unit on C(3) position of the 2,3-dihydroxybenzoyl group was demonstrated by the HMBC correlations of the anomeric H-atom (δ(H) 4.89 (*d*, *J* = 8.0)) of the additional glucose with C(3″) (δ(C) 147.3) of the 2,3-dihydroxybenzoyl group (*Fig. 2*). Other HMBC and ROESY correlations confirmed the structure of **1**. From the above data, the structure of gentistraminoside A was concluded to be as shown in formula **1**.

Gentistraminoside B (**2**), a yellow amorphous powder, possessed a molecular formula $C_{33}H_{40}O_{20}$, as deduced by the negative HR-FAB-MS (*m*/*z* 755.2043 $[M-H]^-$). On the basis of its NMR spectral data, together with the comparison with compounds **1** and **6**, the structure of **2** was determined to be as shown in *Fig. 1*.

The ^{1}H- and ^{13}C-NMR data (*Table*) of **2** were similar to those of **1**. However, in the ^{1}H-NMR of **2**, the *multiplet* at δ(H) 2.98 (*m*) assigned to H−C(5) in **1** was missing in **2**, and the signals of CH_2(7) of **2** were shifted downfield to δ(H) 4.71 (*ddd*, *J* = 13.0, 13.2, 2.3) and 4.31 (*ddd*, *J* = 13.0, 5.1, 1.5), compared to those of **1**. The downfield chemical shifts of CH_2(7) in **2** were similar to those of **6**. These observations revealed the presence of a 5β-OH group in **2**. Moreover, the ^{1}H- and ^{13}C-NMR spectra showed an

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[1]) For systematic names, see *Exper. Part.*

Table. *^{13}C- and ^{1}H-NMR Spectral Data of Compounds* **1** *and* **2**. Measured at 100 and 400 MHz in CD_3OD, respectively; δ in ppm, J in Hz.

Position	**1**		**2**	
	δ(C)	δ(H)	δ(C)	δ(H)
1	98.6	5.33 (*d*, *J* = 1.6)	99.8	5.54 (*d*, *J* = 1.6)
3	153.5	7.58 (*s*)	153.2	7.54 (*s*)
4	106.5		110.3	
5	28.7	2.94–2.98 (*m*)	64.2	
6	25.7	1.73 (*ddd*, *J* = 15.6, 14.7, 2.8), 1.66 (*ddd*, *J* = 15.6, 6.9, 2.6)	33.3	1.82 (*ddd*, *J* = 14.7, 2.3, 1.5), 1.73 (*ddd*, *J* = 14.7, 13.2, 5.1)
7	70.0	4.38 (*ddd*, *J* = 14.7, 12.1, 2.6), 4.29 (*ddd*, *J* = 12.1, 6.9, 2.8)	66.2	4.71 (*ddd*, *J* = 13.2, 13.0, 2.3), 4.31 (*ddd*, *J* = 13.0, 5.1, 1.5)
8	132.8	5.50 (*ddd*, *J* = 17.2, 9.8, 6.9)	133.1	5.34 (*ddd*, *J* = 17.2, 10.1, 6.9)
9	43.4	2.68 (*dd*, *J* = 9.8, 1.6)	52.1	2.88 (*dd*, *J* = 10.1, 1.6)
10	121.3	5.31 (*dd*, *J* = 6.9, 1.6), 5.24 (*dd*, *J* = 17.2, 6.9)	121.6	5.26 (*dd*, *J* = 17.2, 2.9), 5.20 (*dd*, *J* = 6.9, 2.9)
11	168.1		167.7	
1-*O*-Glc-1′	97.9	4.93 (*d*, *J* = 7.8)	98.7	4.93 (*d*, *J* = 7.8)
2′	74.7	3.34–3.39 (*m*)	74.7	3.98–4.10 (*m*)
3′	75.4	3.88–3.92 (*m*)	75.3	4.61 (*t*, *J* = 9.8)
4′	74.8	4.72–4.80 (*m*)	70.0	4.73–4.85 (*m*)
5′	75.3	3.90–4.08 (*m*)	75.4	4.26–4.31 (*m*)
6′	65.1	4.73 (*dd*, *J* = 12.0, 6.3), 4.57 (*dd*, *J* = 12.0, 2.2)	65.1	4.54 (*dd*, *J* = 12.2, 2.0), 4.48 (*dd*, *J* = 12.2, 4.6)
Acyl-1″	114.6		114.6	
2″	152.8		153.1	
3″	147.3		147.3	
4″	124.7	7.45 (*dd*, *J* = 8.1, 1.6)	124.8	7.42 (*dd*, *J* = 8.0, 1.3)
5″	120.1	6.87 (*t*, *J* = 8.1)	120.2	6.87 (*t*, *J* = 8.0)
6″	123.7	7.62 (*dd*, *J* = 8.1, 1.6)	124.6	7.61 (*dd*, *J* = 8.0, 1.3)
C=O	170.9		170.9	
3″-*O*-Glc-1‴	103.5	4.89 (*d*, *J* = 8.0)	103.0	4.89 (*d*, *J* = 8.0)
2‴	74.7	3.58–3.60 (*m*)	74.8	3.54–3.60 (*m*)
3‴	78.2	3.34–3.38 (*m*)	77.7	3.42–3.48 (*m*)
4‴	71.2	3.29–3.35 (*m*)	71.3	3.36–3.40 (*m*)
5‴	77.7	3.46–3.60 (*m*)	78.3	3.41–3.48 (*m*)
6‴	62.4	3.88 (*dd*, *J* = 11.3, 1.6), 3.70 (*dd*, *J* = 11.3, 4.9)	62.4	3.88 (*dd*, *J* = 11.9, 3.4), 3.76 (*dd*, *J* = 11.9, 5.0)
Me*C*OO	171.7		173.0	
Me*C*OO			172.5	
*Me*COO	21.8	1.99 (*s*)	20.9	1.99 (*s*)
*Me*COO			20.5	1.99 (*s*)

additional AcO group in **2**, whose location on C(3′) position was determined unambiguously by the long-range correlations of H–C(3′) (δ(H) 4.61 (*t*, *J* = 9.8)) with the CO group (δ(C) 172.5) of the AcO group in the HMBC spectrum. The structure of gentistraminoside B was further confirmed by the 2D-NMR experiments, including HMQC, HMBC and ROESY, and established as shown in **2**.

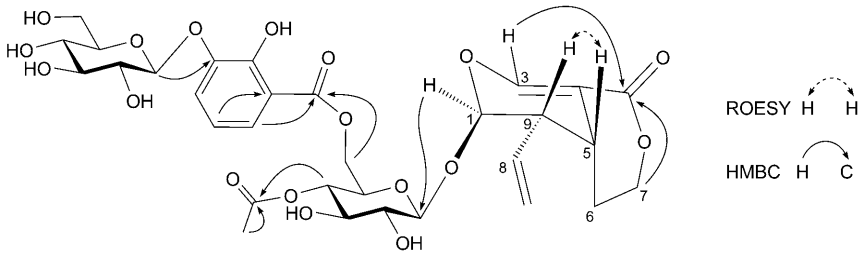

Fig. 2. *Important HMBC and ROESY data of* **1**

In this study, two new acylated secoiridoid glucosides, gentistraminosides A (**1**) and B (**2**), were isolated from the title plants, along with twelve known compounds. Of them, the five known iridoid and secoiridoid glucosides, **3**, **5**, and **8**–**10**, together with other three known compounds, **12**–**14**, were isolated for the first time from *G. straminea*. The parent compounds of **1** and **2** lacking the acetyl groups and the second glucosyl residue have been reported previously from *G. algida* Pall growing in northwestern of China [24]. This plant also contains further related derivatives [25]. Compounds **4**, **6**, **7**, and **9** are the major secoiridoid glucosides in *G. straminea*, which is similar to the situation found in *G. macrophylla*, another source of 'Qin-Jiao' [2][3]. In addition, both plants also contain the same acylated secoiridoid glucoside, macrophylloside A (**3**), and some phenolic compounds, such as isovitexin (**11**), and macrophylloside D (**12**). These results support the use of both *G. straminea* and *G. macrophylla* as source of 'Qin-Jiao'.

Expertimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Marine Chemical Factory*); *Diaion HP20SS* (*Mitsubishi Chemical Industry, Ltd*); *MCI gel CHP20P* (75–150 μm; *Mitsubishi Chemical Industry, Ltd.*); *Chromatorex ODS* (100–200 mesh; *Fuji Silysia Chemical Co. Ltd.*). TLC: silica gel *G* pre-coated plates (*Qingdao Haiyan Chemical Co.*) with $CHCl_3$/MeOH/H_2O (7:3:0.5). Spots were detected by spraying with 10% H_2SO_4 reagent followed by heating. GC analysis: *Agilent Technologies HP5890* gas chromatograph equipped with an H_2 flame ionization detector. The column was *30QC2/AC-5* quartz capillary column (30 m × 0.32 mm, *Agilent Technologies*) with the following conditions: column temperature: 180°/280°; programmed increase, 3°/min; carrier gas: N_2 (1 ml/min); injection and detector temperature: 250°; injection volume: 4 μl, split ratio: 1/50. Optical rotations: *SEPA-3000* automatic digital polarimeter. UV Spectra: *JASCO V-560* UV/VIS spectrophotometer. IR Spectra: *Bio-Rad FTS-135* spectrometer; in cm^{-1}. 1D- and 2D-NMR spectra: *Bruker DRX-500* instrument with TMS as internal standard. FAB-MS (negative ion mode) and HR-ESI-MS (negative ion mode) spectra: *VG AutoSpec 3000* and *API Qstar Pulsar LC/TOF* spectrometers, respectively; Matrix for FAB: glycerine.

Plant Material. The air-dried root of *G. straminea* MAXIM was collected from Tianshui, Ganshu, P. R. China, and identified by Prof. *Chong-Ren Yang*. A voucher specimen (KIB 0552256) was deposited in Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences (CAS).

Extraction and Isolation. The powdered root of *G. straminea* (320 g) was extracted with MeOH (3 × 3 l) at r.t. for 1 week each. The extract was evaporated and the residue was partitioned between H_2O (300 ml) and petroleum ether (PE; 300 ml × 3). The H_2O-soluble portion (40 g) was applied to CC on *Diaion HP20SS*, eluted with H_2O/MeOH (1:0 to 0:1) to give three fractions (*Fr. 1–3*). *Fr. 1* (9.228 g) was subjected to *Sephadex LH-20* (0 to 100% MeOH), CC on SiO_2 ($CHCl_3$/MeOH/H_2O, 9:1:0.1 to

7:3:0.5), *MCI*-gel *CHP20P* (30 to 100% MeOH) and *Chromatorex ODS* (40 to 100% MeOH) to afford **4** (363 mg), **5** (12 mg), **6** (219 mg), **7** (23 mg), **8** (216 mg), **9** (102 mg), and **10** (8 mg). *Fr. 2* (1.375 g) was chromatographed over *MCI*-gel *CHP20P* (10 to 100% MeOH) and SiO_2 column ($CHCl_3$/MeOH/H_2O, 9:1:0.1 to 7:3:0.5) to yield **1** (11 mg), **2** (16 mg), and **3** (60 mg). *Fr. 3* (2.498 g) was applied to *Chromatorex ODS* (60 to 100% MeOH) and SiO_2 CC ($CHCl_3$/MeOH/H_2O, 9:1:0.1 to 7:3:0.5) to give **11** (38 mg), **12** (23 mg), **13** (21 mg), and **14** (5 mg).

Enzymatic Hydrolysis of Compounds **1** *and* **2**. Solns. of **1** and **2** (2 mg and 1 mg, respectively) in H_2O (2 ml and 1 ml, resp.) were incubated with β-glucosidase (1 mg, from almonds, 20–40 units/mg solid, EC 3.2.1.21, *SIGMA*) at 37° for two weeks. The mixture was analyzed by TLC and glucose was identified by co-chromatography with an authentic sample (AcOEt/MeOH/H_2O/AcOH 6:2:1:1, R_f 0.51; i-PrOH/MeOH/H_2O 25:1:2, R_f 0.65). Spots were visualized by spraying with 10% H_2SO_4 followed by heating. TLC analysis indicated the presence of glucose in the H_2O layer of compounds **1** and **2**.

Determination of the Absolute Configuration of the Sugar Residues in Compounds **1** *and* **2**. The soln. of the sugar residue of compound **1** in 1.5 ml pyridine was added to L-cysteine methyl ester hydrochloride (1.5 mg) and kept at 60° for 1 h. Trimethylsilylimidazole (1.5 ml) was added to the mixture and kept at 60° for 30 min. The supernatant (4 µl) was analyzed by GC, and the retention time of D-glucose was 18.29 min. The absolute configuration of the glucose residues in **2** was assumed to be D on the basis of biogenetic considerations, which is also confirmed by the hydrolytic cleavage of **2** by the β-D-glucosidase.

Gemtistraminoside A (=*(4a*S,*5*R,*6*S*)-5-Ethenyl-4,4a,5,6-tetrahydro-1-oxo-1*H,*3*H*-pyrano[3,4-*c*]pyran-6-yl 4*-O-*Acetyl-6*-O-*{[3-(β-*D*-glucopyranosyloxy)-2-hydroxyphenyl]carbonyl}-β-*D*-glucopyranoside*; **1**). Yellow amorphous powder. $[\alpha]_D^{24} = -94.7$ ($c = 1.32$, MeOH). UV (MeOH): 237 (4.23), 312 (1.12). IR (KBr): 3426, 1761, 1687, 1617, 1467, 1320, 1249, 1071. ^{1}H- and ^{13}C-NMR: *Table*. FAB-MS (neg.): 697 ($[M-H]^-$), 535 ($[M-162\ (Glc)]^-$). HR-FAB-MS (neg.): 697.1965 ($[M-H]^-$, $C_{31}H_{37}O_{18}^-$; calc. 697.1979).

Gemtistraminoside B (=*(4a*R,*5*R,*6*S*)-5-Ethenyl-4,4a,5,6-tetrahydro-4a-hydroxy-1-oxo-1*H,*3*H*-pyrano[3,4-*c*]pyran-6-yl 3,4-Di-*O*-acetyl-6*-O-*{[3-(β-*D*-glucopyranosyloxy)-2-hydroxyphenyl]carbonyl}-β-*D*-glucopyranoside*; **2**): Yellow amorphous powder. $[\alpha]_D^{24} = -81.0$ ($c = 2.34$, MeOH). UV (MeOH): 244 (4.23), 312 (1.12). IR (KBr): 3427, 1719, 1640, 1288, 1076. ^{1}H- and ^{13}C-NMR: *Table*. FAB-MS: 755 ($[M-H]^-$), 593 ($[M-162\ (Glc)]^-$). HR-FAB-MS (neg.): 755.2043 ($[M-H]^-$, $C_{33}H_{39}O_{20}^-$; calc. 755.2034).

REFERENCES

[1] Editorial Board of Chinese Pharmacopoeia, 'Chinese Pharmacopoeia', Vol. 1, Chemistry and Industry Press, Beijing, 2005, pp. 64–65.
[2] Y.-H. Liu, X.-C. Li, Y.-Q. Liu, C.-R. Yang, *Acta Bot. Yunnan.* **1994**, *16*, 85.
[3] R. X. Tan, J.-L. Wolfender, L. X. Zhang, W. G. Ma, N. Fuzzati, A. Marston, K. Hostettmann, *Phytochemistry* **1996**, *42*, 1305.
[4] Y.-X. Wu, G. Chen, C.-Y. Yu, *J. Beijing Univ. Chem. Technol. (Nat. Sci. Ed.)* **2008**, *35(2)*, 64.
[5] J. Sun, Y.-L. Li, L.-J. Ji, Y.-H. Ma, W.-H. Xu, G.-C. Chen, *Acta Bot. Yunnan.* **2006**, *28*, 219.
[6] J. Sun, G. C. Chen, Y. L. Li, X. E. Zhao, H. L. Wang, *Chin. J. Anal. Lab*. **2006**, 28.
[7] W.-G. Ma, N. Fuzzati, J.-L. Wolfender, C.-R. Yang, K. Hostettmann, *Phytochemistry* **1996**, *43*, 805.
[8] W.-G. Ma, N. Fuzzati, J.-L. Wolfender, K. Hostettmann, C.-R. Yang, *Helv. Chim. Acta* **1994**, *77*, 1660.
[9] Y.-J. Zhang, C.-R. Yang, *Acta Bot. Yunnan.* **1994**, *16*, 401.
[10] Y.-J. Zhang, C.-R. Yang, *Phytochemistry* **1994**, *36*, 997.
[11] G.-P. Yu, X.-C. Li, Y.-Q. Liu, C.-R. Yang, *Acta Bot. Yunnan.* **1996**, *18*, 110.
[12] Y.-H. Liu, X.-C. Li, Y.-Q. Liu, C.-R. Yang, *Acta Bot. Yunnan.* **1994**, *16*, 417.
[13] I. Calis, M. F. Lahloub, O. Sticher, *Helv. Chim. Acta* **1984**, *67*, 160.
[14] M. Xu, D. Wang, Y.-J. Zhang, C.-R. Yang, *Acta Bot. Yunnan.* **2006**, *28*, 669.
[15] M. Xu, Y. J. Zhang, C. R. Yang, *J. Nat. Prod. Res. Dev.* **2007**, *19(Suppl)*, 9.
[16] M. Xu, D. Wang, Y.-J. Zhang, C.-R. Yang, *J. Nat. Prod.* **2007**, *70*, 880.
[17] M. Xu, Y. J. Zhang, C. R. Yang, *J. Asian Nat. Prod. Res* **2008**, *10*, 491.
[18] I. Calis, O. Sticher, *Phytochemistry* **1984**, *23*, 2539.

[19] E. M. Mpondo, J. Garcia, G. Cartier, G. Pellet, *Planta Med.* **1990**, *56*, 334.
[20] E. M. Mpondo, A. J. Chulia, *Planta Med*. **1988**, *54*, 185.
[21] E. Helfrich, H. Rimpler, *Phytochemistry* **2000**, *54*, 191.
[22] K. Hostettmann, G. Bellmann, R. Tabacchi, A. Jacot-Guillarmod, *Helv. Chim. Acta* **1973**, *56*, 3050.
[23] I. A. Khan, O. Sticher, T. Rali, *J. Nat. Prod.* **1993**, *56*, 2163.
[24] R. X. Tan, J. Hu, L. D. Dong, J..L. Wolfender, K. Hostettmann, *Planta Med.* **1997**, *63*, 567.
[25] R. X. Tan, J.-L. Wolfender, W. G. Ma, L. X. Zhang, K. Hostettmann, *Phytochemistry* **1996**, *41*, 111.

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