植 物 学 报
Acta Botanica Sinica 2002, **44** (2): 224– 226

A New Glucoside from *Rhodiola fastigiata* (Crassulaceae)

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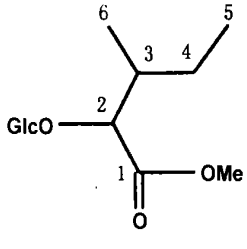
Abstract: A new glucoside, fastigitin A (**1**), namely 2_O_β_*D*_glucopyransyl_3_methyl_methyl pinalate, together with twelve known constituents (**2**– **13**), was isolated from the root of *Rhodiola fastigiata* (Hook. f. et Thoms.) S. H. Fu collected from Nujiang Lisu autonomous region, Yunnan, China. Their structures were identified by spectral (including 2D_NMR techniques) and chemical methods. Compounds **2** and **5**– **9** were obtained from this plant for the first time.

Key words: *Rhodiola fastigiata*; Crassulaceae; glucoside; fastigitin A

The root of *Rhodiola fastigiata*, which mainly distributed in the higher sea level region of Yunnan and Tibet, China, is traditionally used for promoting blood circulation and relieving cough, as well as a tonic[1, 2]. Previous research on this plant has achieved in the separation of tyrosol, salidroside and some other kind of compounds[3]. In this paper we report the isolation and structural elucidation of a new glucoside (**1**) together with twelve known constituents Δ^1_octenyl_3_O_β_*D*_glucopyranoside (**2**)[4], tyrosol (**3**), salidroside (**4**)[3, 5, 6], dihydroconiferyl alcohol γ_O_β_*D*_glucopyranoside (**5**)[7], (+)_isolariciresinol (**6**), (+)_isolariciresinol_9_O_β_*D*_glucopyranoside (**7**)[8], cedrusin (**8**)[9], luteolin_7_ethylether (**9**)[10], 4′_methoxyl_herbacetin (**10**)[3], gallic acid (**11**)[5, 6], β_sitosterol (**12**) and daucosterol (**13**)[11] from this plant.

1 Results and Discussion

Fastigitin A (**1**) was obtained as white wax, $[\alpha]_D^{20.1}$ – 22.10° (*c* = 3.30, C_5H_5N). Its molecular formula was determined to be $C_{13}H_{24}O_8$ by the negative HRFABMS spectrum (found m / z $[M-1]^-$ 307.137 3, calcd. 307.139 3). The IR spectrum indicated the presence of hydroxyl and carbonyl groups (3 540 br., 1 734 cm^{-1}). The ^{1}H_NMR and ^{13}C_NMR spectra (Table 1) also showed that compound **1** had a carbonyl group (δ_C 173.52) and no double bonds. Thus, compound **1** possessed only one ring based on a calculation of unsaturated degrees (*n* = 2). Moreover, the ^{1}H-NMR and ^{13}C_NMR spectral data of compound **1** suggested that it could be a monoglycoside with an aglycone moiety containing seven carbons, which was identified by its ^{1}H_NMR, ^{13}C_NMR spectra and 2D-NMR experiments.



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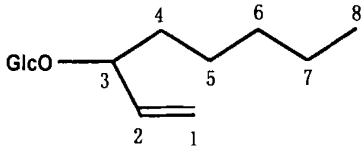

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Table 1 ^{13}C_NMR spectral data of compounds **1** and **2** (125.8 MHz, in C_5D_5N)

C	1	2
Aglycone moiety		
1	173.52 (s)	117.49 (t)
2	83.24 (d)	139.42 (d)
3	38.56 (d)	78.42 (d)
4	25.50 (t)	36.07 (t)
5	11.65 (q)	25.18 (t)
6	15.00 (q)	32.10 (t)
7		22.84 (t)
8		14.21 (q)
OCH_3	51.58 (q)	
Glucosyl group		
1′	105.78 (d)	101.28 (d)
2′	75.11 (d)	75.31 (d)
3′	78.48 (d)	78.76 (d)
4′	71.77 (d)	72.00 (d)
5′	78.38 (d)	78.42 (d)
6′	62.89 (t)	63.04 (t)

From ^{1}H_NMR, ^{13}C_NMR and DEPT spectra, in addition to a sugar moiety, the presence of three methyl groups, one methylene, two methines and a quaternary carbon was clearly observed. According to the ^{1}H_^{1}H COSY and HMBC spectra of compound **1** (Table 2), two partial structures A and B (Fig. 1) were revealed, and the latter spectrum also showed that the two partial structures were connected as C (Fig. 1).

* Received: 2000-11-20 Accepted: 2001-03-19
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Table 2 The correlation of ^1H-^1H COSY and HMBC of compound **1**

^1H-^1H COSY		HMBC	
Proton	**1** (^1H)	C	**1** (^1H)
Aglycone_1		Aglycone_1	(2), 3, OCH_3
2	3	2	(3), 4, 6, Glc_1
3	2, 4, 6	3	(2), (4), 5, (6)
4	3, 5	4	2, (3), (5), 6
5	4	5	3, (4)
6	3	6	2, (3), 4
		Glc_1	2

Two_bond correlation was shown in brackets.

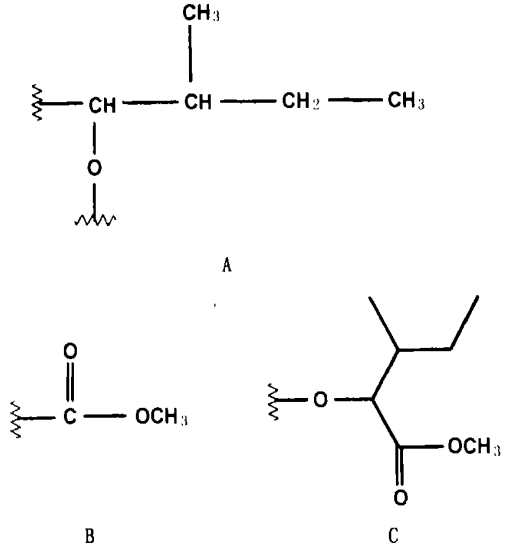

Fig. 1. The partial structures of compound **1**.

The exhaustive acidic hydrolysis of compound **1** gave glucose (identified by TLC comparing with the authentic sample), indicating that the sugar moiety in compound **1** was glucosyl group. The anomeric proton H_1′ (δ 4.90, d, J= 7.8 Hz) of compound **1** revealed the β_glycoside linkage. From the HMBC spectrum, two pairs of the significant ^1H-^{13}C long_range correlations between H_1′ and C_2, H_2 and C_1′ were observed clearly, it was determined that the glucosyl unit of compound **1** was attached to C_2 position of aglycone moiety. Therefore, fastigitin A was identified as 2_O_β_*D*_glucopyransyl_3_methyl_methyl pinalate.

The structures of the twelve known constituents were identified by comparing their spectral data and physical constants with those in the literature or by direct comparison with authentic samples.

2 Experimental

2.1 General experimental procedures

All melting points were measured on an XRC_1 micromelting point apparatus and uncorrected. Optical rotations were measured with an SEPA_300 polarimeter. IR spectra were measured on a Bio_Rad FTS_135 spectrometer with KBr pellets. MS spectra were recorded on a VG Auto Spec_3000 spectrometer. 1D_ and 2D_NMR spectra were run on a Bruker AM_400 and DRX_500 instrument with TMS as internal standard, respectively.

2.2 Plant material

The research samples were collected in Nujiang Lisu Autonomous Region, Yunnan Province and identified as *Rhodiola fastigiata* (Hook. f. et Thoms.) S. H. Fu by Prof. LI Xi_Wen. A voucher specimen is deposited in the Herbarium of Kunming Institute of Botany, the Chinese Academy of Sciences.

2.3 Extraction and isolation

Dried and powdered roots (0.4 kg) of *R. fastigiata* were extracted with 70% EtOH (4 × 1.5 L) under reflux to give a crude extract (97.5 g). The extract was dissolved in 50% EtOH and then defatted with petroleum_ether (60– 90 ℃). After the removal of EtOH, the residue was extracted with EtOAc (7 × 0.5 L) and *n*_BuOH (5 × 0.8 L), respectively, to afford 7.8 g EtOAc residue and 38 g *n*_BuOH residue.

The EtOAc residue (7.8 g) was chromatographed on a polyamide column eluting with $CHCl_3$/MeOH gradient system (1∶0– 0∶1) to separate it into five fractions (Ⅰ– Ⅴ). Fraction Ⅱ was subjected to CC on silica gel (300– 400 mesh) eluting with $CHCl_3$/MeOH (60∶1) and ether to afford **2** (14 mg), **3** (11 mg), **6** (31 mg), **12** (22 mg) and **13** (31 mg). Fraction Ⅲ was chromatographed on medium pressure column developing with $CHCl_3$/i_PrOH (15∶1) to yield **8** (6 mg), **9** (15 mg), **10** (10 mg), respectively. After repeated silica gel CC eluting with $CHCl_3$/MeOH/H_2O (8∶2∶0.1) and $CHCl_3$/i_PrOH (9∶1), **4** (18 mg), **5** (12 mg), **7** (24 mg) were obtained from fraction Ⅳ, respectively. The compound **11** (30 mg) was obtained by CC on MCI gel CHP_20P eluting with MeOH/H_2O (1∶9) from fraction Ⅴ.

The *n*_BuOH extract (38 g) was subjected to Al_2O_3 column eluting with $CHCl_3$ by increasing amount of EtOH to afford six fractions (Ⅰ– Ⅵ). Compound **1** (210 mg) was isolated from the fraction Ⅳ by CC on RP_18 developing with MeOH/H_2O (4∶6).

2.4 Identification

Acid hydrolysis of compound 1 Compound **1** was hydrolyzed at 100 ℃ for 1 h on TLC plate in a chamber filled with concentrated HCl and the products were separated with solvent system (*n*_BuOH/EtOH/H_2O (4∶1∶5)). Glucose was identified by comparison with authentic sample.

Fastigitin A (1) $C_{13}H_{24}O_8$, white wax, $[\alpha]_D^{20.1}$ – 22.10° (*c* 3.28, C_5H_5N), IR ν_{max}^{KBr} cm^{-1}: 3 540 (br.), 3 336, 2 965, 2 927, 2 880, 1 734, 1 462, 1 443, 1 381, 1 279, 1 164, 1 125, 901; ^1H_NMR (500 MHz, C_5D_5N): δ 4.33 (1H, d, J= 6.3 Hz, H_2), 2.02 (1H, m, H_3), 1.65 (1H, m, H_4a), 1.28 (1H, m, H_4b), 0.85 (3H, t, J = 7.3 Hz, H_5), 1.11 (3H, d, J = 6.8 Hz, H_6), 3.72 (3H, s, OCH_3), 4.90 (1H, d, J= 7.8 Hz, H_1′), 4.05 (1H, t, J= 7.8 Hz, H_2′), 4.18 (2H, m, H_3′ and H_4′), 3.91 (1H, m, H_5′), 4.44 (1H, d, J= 11.5 Hz, H_6′a), 4.28 (1H, dd, J= 11.5, 5.4 Hz, H_6′b); negative FABMS m/z: 307 $[M-1]^-$ (44), 179 (43), 162

(12), 131 (45); ^{13}C-NMR spectral data, see Table 1.

Acknowledgements: The authors are grateful to Mr. LI Qiao-Sheng and Mr. ZHOU Yuan-Chuan of Gaoligong Mountain Biological Resource Development Ltd. Co. of Lushui County, Yunnan Province, China for supplying the plant materials.

References:

[1] Ming H-Q(明海泉), Xia G-C(夏光成), Zhang R-J(张瑞钧). Research progress on *Rhodiola* L. *Zhongcaoyao* (中草药), 1988, **19**: 37. (in Chinese)

[2] Ni Z-C(倪志诚). The Economic Flora of Tibetica. Beijing: Science Press, 1990. 252. (in Chinese)

[3] Peng J-N(彭江南), Ge Y-C(葛永潮), Li X-H(李晓辉). Study on the chemical constituents of *Rhodiola fastigiata*. *Acta Pharm Sin*(药学学报), 1996, **31**: 798-800. (in Chinese with English abstract)

[4] Pfab I, Heinrich G, Francke W. Glykosidisch gebundene Komponenten des atherischen Ols von *Monarda fistulosa*. *Biochem Physiol Pflanzen*, 1980, **175**: 194-207. (in German)

[5] Qiu L-G(邱林刚), Wang Y-F(王叶富), Ni Z-C(倪志诚), Jiang S-P(蒋思萍), Ma Z-W(马忠武), He G-F(何关福). Study on the constituents of *Rhodiola sacra*. *Nat Prod Res & Devep*(天然产物研究与开发), 1991, **3**: 6-9. (in Chinese)

[6] Wang S(王曙), Wang F-P(王锋鹏). Studies on the chemical components of *Rhodiola crenulata*. *Acta Pharm Sin*(药学学报), 1992, **27**: 117-120. (in Chinese with English abstract)

[7] Higuchi R, Aritome M, Donnelly D M X. Monolignol and dilignol glycosides from *Pinus contorta* leaves. *Phytochemistry*, 1977, **16**: 1007-1011.

[8] Takani M, Ohya K, Takahashi K. Studies on constituents of medicinal plants XXII. Constituents of *Schizandra nigra* Max. *Chem Pharm Bull*, 1979, **27**: 1422-1425.

[9] Agrawal P K, Pastogi R P, Osterdahi B G. ^{13}C-NMR spectral analysis of dihydrobenzofruan lignans. *Org Magn Reson*, 1983, **21**: 119-121.

[10] Wang M-T(汪茂田), Zhao T-Z(赵天增), Ji C-R(冀春茹), Feng W-S(冯卫生), Liu Y-Z(刘延泽). Flavonoid glycosides from *Daphne genkwa*. *Zhongcaoyao*(中草药), 1985, **16**: 2-4. (in Chinese)

[11] Yang H(杨辉), Xie J-L(谢金伦), Sun H-D(孙汉董). Study on chemical constituents of *Saussurea lappa* Ⅱ. *Acta Bot Yunnanica*(云南植物研究), 1997, **19**(1): 92-96. (in Chinese with English abstract)

长鞭红景天中一个新的葡萄糖甙

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摘要: 从云南怒江产的长鞭红景天(*Rhodiola fastigiata* (Hook. f. et Thoms.) S. H. Fu)根茎中分离得到13个化合物,它们的结构通过波谱和化学方法得到鉴定。其中,化合物**1**被鉴定为新的葡萄糖甙(2-O-β-*D*-吡喃葡糖基-3-甲基-戊酸甲酯),命名为长鞭红景天素甲,化合物**2**和**5~9**首次从该植物中分离得到。

关键词: 长鞭红景天; 景天科; 葡萄糖甙; 长鞭红景天素甲

中图分类号: R914 文献标识码: A 文章编号: 0577-7496(2002)02-0224-03

收稿日期: 2000-11-20 接收日期: 2001-03-19

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(责任编辑: 王 葳)