

FLAVONOL GLYCOSIDES FROM *RHODIOLA CRENULATA*

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**Key Word Index**—*Rhodiola crenulata*; Crassulaceae; flavonol glycosides; crenuloside.

**Abstract**—In addition to three known flavonol glycosides, kaempferol 7-O- $\alpha$ -L-rhamnopyranoside, rhodionin and rhodiosin, a new kaempferol glycoside was isolated from the roots of *Rhodiola crenulata*. The structure was identified as kaempferol 7-glucosyl(1  $\rightarrow$  3)rhamnoside by means of spectral analysis.

## INTRODUCTION

In China plants of the *Rhodiola* genus have similar effects as *Panax ginseng* and *Acanthopanax senticosus* [1]. As a Chinese medicinal plant, *Rhodiola crenulata* is mainly distributed in the high cold region of Yunnan, Sichuan province. *Rhodiola crenulata* growing in Tibet has been investigated previously [2]; two known flavonol glycosides, rhodionin and rhodiosin were isolated. We studied the chemical components of *R. crenulata* distributed in Yunnan for the first time. Four flavonol glycosides including a new compound were obtained from the roots of this plant. We now report the isolation and structural elucidation of the new kaempferol glycoside named crenuloside (1).

## RESULTS AND DISCUSSION

The *n*-butanol soluble portion of the ethanolic extract of the roots of *R. crenulata* was chromatographed on silica gel to afford 1. Crenuloside (1) was obtained as a yellow powder. The UV spectrum showed absorption bands at 266, 326 and 366 nm which gave bathochromic shifts by addition of shift reagents indicating the presence of free hydroxyl groups at C-3, C-5 and C-4'. The chemical shift assignment of the <sup>1</sup>H and <sup>13</sup>C NMR spectral data supported the identification of the aglycone moiety as kaempferol. Acid hydrolysis showed the presence of glucose and rhamnose. The result of the EI mass spectrum in which the acetates of 1 exhibited ion peaks at *m/z* 561 [glu(Ac)<sub>4</sub> - rham(Ac)<sub>2</sub> - OH]<sup>+</sup>, 331 [glu(Ac)<sub>4</sub> - OH]<sup>+</sup> and 229 [rham(Ac)<sub>2</sub> - H<sub>2</sub>O - H]<sup>+</sup> indicated that a sugar moiety was present as a biose, glucose was the terminal sugar and rhamnose was the inner one. Further information about the interlinkage and the sequence of the biose was obtained as follows. In the <sup>1</sup>H NMR spectrum, two anomeric protons of the inner

and terminal sugar were observed at  $\delta$  6.21 (*br s*) and 5.57 (*d*, *J* = 8 Hz). In the <sup>13</sup>C NMR spectrum, the chemical shifts of the rhamnose appeared further downfield at C-3, but upfield at C-2 and C-4. The results led to the conclusion that the biose is  $\beta$ -D-glucopyranosyl(1  $\rightarrow$  3)- $\alpha$ -L-rhamnopyranose. Glycosylation shifts of the aglycone were observed at C-7, C-6, C-8 and C-10. The chemical shift of the aglycone is upfield at C-7, but downfield at C-6, C-8 and C-10 compared to those of the kaempferol at the same carbon.

Therefore, 1 is kaempferol 7-O- $\beta$ -D-glucopyranosyl(1  $\rightarrow$  3)- $\alpha$ -L-rhamnopyranoside.

## EXPERIMENTAL

Plant material was collected from Lijian, Yunnan, 1991.

*Extraction and isolation of 1.* The dried and powdered root of *R. crenulata* was extracted with 70% aq. EtOH at room temp. The extracts were concd under red. press. The residue partitioned with petrol ether, CHCl<sub>3</sub>, EtOAc and *n*-BuOH. The *n*-butanol fr. was chromatographed on silica gel and eluted with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (7:3:0.5). The fr. containing 1 was rechromatographed on silica gel using CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (7:3:0.5). Pure 1 (40 mg) was obtained.

*Crenuloside (1).* A yellow powder. UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm: 266, 326, 366. + NaOMe: 246, 270, 422. + AlCl<sub>3</sub>: 268, 353, 425. + AlCl<sub>3</sub>-HCl: 267, 349, 423. + NaOAc: 256sh, 403, + NaOAc-H<sub>3</sub>BO<sub>3</sub>: 265sh, 324, 365. EIMS of acetates of 1 (70 eV) *m/z*: 561, 412, 370, 331, 328, 286, 271, 257, 229, 213, 187, 169, 153, 121, 111, 109. <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N):  $\delta$  1.59 (3H, *d*, *J* = 6 Hz, Rha-Me), 5.57 (1H, *d*, *J* = 8 Hz, Glu H-1), 6.21 (1H, *br s*, Rha H-1), 6.78 (1H, *d*, *J* = 2 Hz, H-6), 6.99 (1H, *d*, *J* = 2 Hz, H-8), 7.39 (2H, *d*, *J* = 9 Hz, H-3', H-5'), 8.55 (2H, *d*, *J* = 9 Hz, H-2', H-6'). <sup>13</sup>C NMR (C<sub>5</sub>D<sub>5</sub>N):  $\delta$  [aglycone moiety] 148.3 (C-2), 138.2 (C-3), 177.5 (C-4), 156.7 (C-5), 99.8 (C-6), 162.3 (C-7), 94.8 (C-8), 162.0 (C-9), 106.1 (C-10), 123.5 (C-1'), 130.7 (C-2'), 116.5 (C-3'), 161.0

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(C-4'), 116.5 (C-5'), 130.7 (C-6'); [sugar moiety] 99.9 (Rha C-1), 71.2 (Rha C-2), 82.6 (Rha C-3), 72.6 (Rha C-4), 71.1 (Rha C-5), 18.5 (Rha C-6), 106.7 (Glu C-1), 76.0 (Glu C-2), 78.6 (Glu C-3), 71.5 (Glu C-4), 78.5 (Glu C-5), 62.6 (Glu C-6).

#### REFERENCES

1. Min, H. Q., Xia, G. C. and Zhan, R. J. (1988) *Zhong-cao yao* **19**, 37.
2. Yu, W. Sh., Chen, X. M., Yan, N., Li, H. and Li, Y. F. (1992) *Tianran Chanwu Yanjiu yu Kaifa* **4**, 23.