Chinese Chemical Letters Vol. 15, No. 12, pp 1448-1450, 2004
http://www.imm.ac.cn/journal/ccl.html

A New Anthranquinone Glycoside from the Seeds of *Cassia obtusifolia*

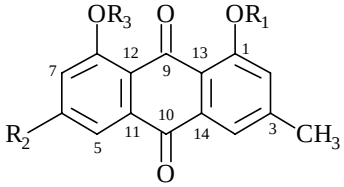
Chu Hua LI[1], Xiao Yi WEI[2], Xu E LI[1], Ping WU[2], Bao Jiang GUO[1]*

[1] College of Life Science, South China Normal University, Guangzhou 510631
[2] South China Institute of Botany, Chinese Academy of Sciences, Guangzhou 510650

Abstract: A new anthraquinone glycoside, emodin-1-*O*-β-gentiobioside **1**, together with three known compounds, chrysophanol-1-*O*-β-gentiobioside **2**, physcion-8-*O*-β-gentiobioside **3**, and chrysophanol-1-*O*-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside **4** was isolated from the seeds of *Cassia obtusifolia*. Its structure was elucidated on the basis of spectroscopic evidence.

Key words: *Cassia obtusifolia*, Leguminosae, anthraquinone glycosides, emodin-1-*O*-β-gentiobioside.

The seed of *Cassia obtusifolia* L., also called "Jue-ming-zi" in Chinese, is a reputed laxative and tonic Chinese medicine. The herb is traditionally used to improve visual acuity and to remove "heat" from the liver, and currently also used to treat hypercholesterolemia and hypertension[1]. Its antiseptic, diuretic, diarrheal, antioxidant and antimutagenic activities had been reported[1]. The predominant chemical constituents of the seeds had been found to be anthraquinones[1,2]. Our previous study displayed that the crude anthraquinone glycosides from the seeds could decrease the blood lipid level in hyperlipidemic rats[3]. In continuation of our study, we investigated the composition of the crude glycosides, and isolated a new anthraquinone glycoside, emodin-1-*O*-β-gentiobioside **1** together with three known compounds, chrysophanol-1-*O*-β-gentiobioside **2**, physcion-8-*O*-β-gentiobioside **3**, and chrysophanol-1-*O*-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside **4**. Here we describe the isolation and the characterization of the new compound.



1 R_1 = glc(1→6)glc, R_2 = OH, R_3 = H
2 R_1 = R_2 = H, R_3 = glc(1→6)glc
3 R_1 = H, R_2 = OCH_3, R_3 = glc(1→6)glc
4 R_1 = glc(1→3)glc(1→6)glc, R_2 = R_3 = H

* E-mail: guobj@scnu.edu.cn

The commercial unroasted seeds of *C. obtusifolia* were ground and extracted sequentially with petroleum ether, $CHCl_3$, ethyl acetate, and hot water. The aqueous extract was passed through a Diaion HP-20 column eluted successively with H_2O and 95% EtOH. The EtOH eluate, after concentration *in vacuo*, was subjected to repeated column chromatography over silica gel and polyamide to yield compounds **1**—**4**. The known compounds (**2**—**4**) were identified by comparison of their spectral data with those of previously reported[2,4-6].

Compound **1** was isolated as orange-brown amorphous solid. Its UV spectrum in MeOH gave maxima at λ_{max} (log ε) 423 (3.71), 284 (4.16), 253 (4.18), and 215 (4.35) nm. The positive APCIMS exhibited a peak due to $[M + H]^+$ at *m/z* 595. In combination with the ^{13}C NMR and DEPT data, it indicated a molecular formula of $C_{27}H_{30}O_{15}$ for **1**. The ^1H and ^{13}C NMR spectra of **1** readily indicated the presence of two monosaccharide units by signals for anomeric protons (δ 5.10 and 4.19) and carbons (δ 103.8 and 100.7). After excluding the signals due to the monosaccharide residues, the remaining 15 carbon signals in the ^{13}C NMR spectrum (see **Table 1**) and the proton signals including an aromatic methyl proton singlet at δ 2.46, a pair of doublets at δ 7.04 and 6.54, two broad singlets at δ 7.66 and 7.57, and a *peri*-hydroxyl proton broad singlet at δ 13.24 in the ^1H NMR spectrum (see **Table 1**) indicated the emodin moiety[7]. The proton and carbon signals of sugar moiety were identical with those of β-gentiobiose [β-D-glucopyranosyl-(1→6)-β-D-gluopyranoside] moiety[4,8]. The glycosylation site was determined at the hydroxyl group of C-1 by HMBC experiment (see **Figure 1**) in which a cross-peak was observed between H-1′ and C-1. Therefore, compound **1** was elucidated as emodin-1-*O*-β-gentiobioside.

It should note that the occurrence of **2** and **4** in this plant is reported for the first time.

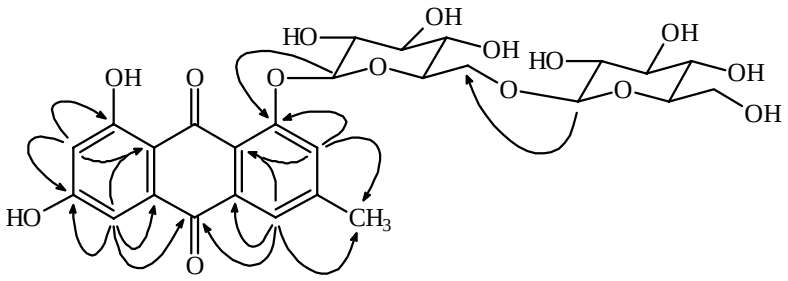
Table 1 ^1H and ^{13}C NMR chemical shifts and assignments for **1** (δ ppm)

Position	δ_H (*J* in Hz)	δ_C	Position	δ_H (*J* in Hz)	δ_C
1		158.2	Me	2.46 s	21.7
2	7.57 br s	123.4	8-OH	13.24 br s	
3		146.7	1′	5.10 d (8.0)	103.7
4	7.66 br s	121.6	2′	2.97 t (8.0)	73.5
5	7.04 d (2.0)	107.7	3′	3.10 t (8.0)	76.6
6		165.3	4′	3.04 t (8.0)	70.1
7	6.54 d (2.0)	108.2	5′	3.73 m	75.9
8		164.5	6′	4.00 br d (12.0), 3.64 m	69.0
9		185.9	1″	4.19 d (8.0)	100.7
10		182.3	2″	3.3—3.5[a]	73.3
11		134.3	3″	3.3—3.5	76.2
12		109.8	4″	3.18 t (8.0)	69.7
13		118.5	5″	3.04 t (8.0)	76.9
14		134.1	6″	3.64 m, 3.3—3.5	60.9

Note: ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in DMSO-d_6 and referenced to the residual DMSO at δ 2.49 and δ 39.5, respectively. The assignments were accomplished by the aid of ^1H-^1H COSY, ^{13}C-^1H COSY and HMBC spectra.

[a]Signal pattern unclear due to overlapping.

Figure 1 Selected HMBC correlations of **1**



Acknowledgments

The 1D and 2D NMR spectra were measured by Dr. Jingsun Fan, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou. This investigation was supported by programs from Guangdong Provincial Department of Science and Technology (No. C30113) and Guangzhou Municipal Department of Science and Technology (No. 2000Z3-E5041).

References

1. Y. J. Hao, Y. L. Sang, Y. Q. Zhao, *Chin. Trad. and Herb. Drugs*, **2001**, *32*, 858.
2. Y. J. Hao, Y. L. Sang, Y. Q. Zhao, *Chin. Trad. and Herb. Drugs*, **2003**, *34*, 18.
3. X. E. Li, S. Y. Yang, W. M. Zhao, B. J. Guo, *Chin. Trad. and Herb. Drugs*, **2002**, *33*, 429.
4. T. S. Lü, Y. H. Yi, S. L. Mao, *et al*., *Acta Pharmaceutica Sinica*, **2001**, *36*, 547.
5. L. Hozschuh, B. Kopp, W. Kubelka, *Planta Med.*, **1982**, *46*, 159.
6. S. M. Wong, M. M. Wong, O. Seligmann, H. Wagner, *Phytochemistry*, **1989**, *28*, 211.
7. L. O. Demirezer, A. Kuüruzüm-Uz, I. Bergere, H. J. Schiewe, A. Zeeck, *Phytochemistry*, **2001**, *58*, 1213.
8. S. M. Wong, M. M. Wong, O. Seligmann, H. Wagner, *Planta Med.*, **1989**, *55*, 276.

Received 27 October, 2003