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ALATERNIN GLUCOSIDE ISOMER FROM *CASSIA TORA*

HEE JUNG LEE, JAE SUE CHOI,* JEE HYUNG JUNG† and SAM SIK KANG‡

Dept. of Food and Life Science, Pukyong National University, 608-737 Pusan, Korea; †College of Pharmacy, Pusan National University, 609-735 Pusan, Korea; ‡Natural Products Research Institute, Seoul National University, 110-460 Seoul, Korea

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Key Word Index—*Cassia tora*; Leguminosae; anthraquinone; alaternin 2-O-β-D-glucopyranoside.

Abstract—From the seeds of *Cassia tora*, an anthraquinone glucoside was isolated and characterized as alaternin 2-O-β-D-glucopyranoside. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

As a part of our study on the antioxidant constituents of *Cassia tora L*, we have reported on the isolation of alaternin, cassiaside and rubrofusarin gentiobioside along with the inactive components physcion, β-sitosterol, chrysophanol, emodin, cassitoroside and chrysophanol triglucoside from this plant [1, 2]. In this paper we report on the isolation and structure elucidation of a compound **1** which differs from alaternin 1-O-β-D-glucoside only in the glycosidic linkage site.

RESULTS AND DISCUSSION

Column chromatography of the butanol-soluble part of the methanol extract of the seeds yielded a compound (**1**), which gave a characteristic anthraquinone glycoside colour reactions, brownish-red with 5% sodium hydroxide solution and a positive Molisch test. Its ^{1}HNMR spectrum in DMSO-d_6 (Table 1) established the presence of a methyl (δ2.37) and three aromatic protons ascribable to an isolated (δ7.48) and a pair of *meta*-coupled aromatic protons (δ6.53, 7.02, J = 1.2 Hz). It also confirmed the presence of a sugar moiety (δ3.0 ~ 5.10) and an anomeric proton (δ5.10).

The ^{13}CNMR data indicated that the sugar was β-D-glucopyranose (Table 1). Acid hydrolysis of **1** afforded one mol of D-glucose along with alaternin as the aglycone. The latter was identified by direct comparison with an authentic sample [3]. Thus, compound **1** was shown to be an alaternin monoglucoside. A comparison of the ^{13}CNMR spectrum of **1** with that of alaternin revealed that the signals due to C–1 and C–3 of the alaternin were shifted by −4.3 and −5.2 ppm, respectively, while the other resonances appeared almost unchanged (Table 1). Such changes in the chemical shifts can only be explained if the hydroxyl group at C–2 of the alaternin is glucosylated. Compound **1** was therefore determined as alaternin 2-O-β-D-glucopyranoside. Further detailed analysis of the ^{1}H– and ^{13}C–NMR spectra (Table 1), aided by HMQC and HMBC experiments, confirmed the structure of **1**.

The ^{13}CNMR-signals of **1** were readily assigned by comparison with those of related anthraquinones [3], and by analyses of the HMQC and HMBC correlations. The configuration of the glucopyranose moiety was determined to be β not only by the J value of the anomeric proton signal but also by comparison of the ^{13}CNMR data with those of corresponding methyl α-D- and β-D-glucosides [4]. The glycosidic linkage site of β-D-glucose was determined to be C–2 based on the long range ^{13}C–^{1}H coupling between H-1′(δ5.10) of the β-D-glucose unit part and C–2 (δ148.1) of the aglycone unit observed in the HMBC spectrum. This is the first report of the presence of this compound in *C. tora*, although, alaternin-1-O-β-D-glucoside has been isolated from *Cassia obtusifolia* [5].

EXPERIMENTAL

^{1}H– and ^{13}C–NMR: Varian UNITY-300 spectrometer, chemical shifts referenced to residual solvent peaks (2.5 ppm, ^{1}H–NMR; 39.5 ppm, ^{13}C–NMR); CC: silica gel (Merck, 70–230 mesh); TLC: precoated Merck Kieselgel 60 F_{254} plates (0.25 mm).

Plant materials

Seeds of *Cassia tora* were purchased from a commercial supplier in 1993, and authenticated by Prof.

* Author to whom correspondence should be addressed.

Table 1. ^{1}H and ^{13}C–NMR data for **1** and alaternin in DMSO-d_6 (coupling constants in Hz in parentheses)

	δH		δC	
Position	1*	Alaternin	1	Alaternin
1			153.5	149.2
2			148.1	150.1
3			140.8	135.6
4	7.48 *s*	7.47	121.6	122.9
5	7.05 **t** (1.2)	7.08	108.7	108.5
6			165.6	165.6
7	6.53 **t** (1.2)	6.52	107.7	107.2
8			164.4	164.4
9			189.7	190.1
10			180.5	179.9
11			135.0	131.3
12			109.0	109.0
13			114.9	113.9
14			127.7	122.9
1′	5.10*d* (7.2)		102.8	
2′	3.30*dd* (9.0, 7.2)		74.3	
3′	3.25*t* (9.0)		76.4	
4′	3.16*dd* (3.5, 4.4)		69.8	
5′	3.12*ddd* (1.3, 1.6, 1.3)		77.3	
6′	3.61*dd* (5.1, 5.2) 3.43*dd* (5.1, 5.2)		60.8	
3–CH_3	2.37*s*		17.6	16.20

*Assignments are based on an analysis of the HMQC and HMBC data

H. J. Chi. A voucher specimen (no. 930824) has been deposited at the Herbarium of the Natural Products Research Institute, Seoul National University.

Isolation of compound **1**.

The powdered seeds (3.0 kg) of *C. tora* were extracted with MeOH and concd to give a dark residue, which was partitioned according to the procedure described in a previous paper [1] to give a BuOH-soluble fraction (90 g). This was subjected to CC on silica gel and eluted with mixtures of ETOAc and MeOH of increasing polarity. The eluates were collected in 250 ml portions and finally combined into 17 fractions. Fraction 11 (0.7 g) was rechromatographed on a silica gel column, with CH_2Cl_2–MeOH (5:1) to give **1** (25 mg) as an amorphous powder.

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