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A NAPHTHALENE GLYCOSIDE FROM *CASSIA TORA*

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Key Word Index—*Cassia tora*; Leguminosae; naphthalene glycoside; cassitoroside.

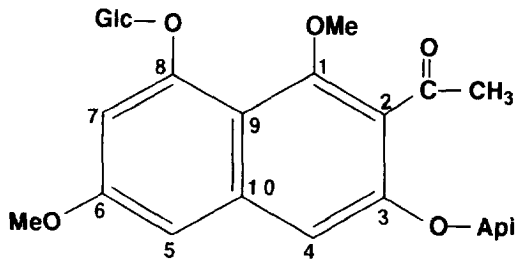
Abstract—From the seeds of *Cassia tora*, a new naphthalene glycoside was isolated and characterized as 2-acetyl-3-*O*-β-D-apiofuranosyloxy-8-*O*-β-D-glucopyranosyloxy-1,6-dimethoxynaphthalene (cassitoroside).

INTRODUCTION

The seed of *Cassia tora* L. (Leguminosae) are used in Chinese herbal medicine to improve vision and it is also reputed for its medicinal value as an asperient, antiasthenic and diuretic [1]. Previously we reported that the methanolic extract of the seeds of *C. tora* exerts an radical scavenging activity on 1,1-diphenyl-2-picrylhydrazyl (DPPH) [2]. From this methanolic extract, 2-hydroxyemodin (alaternin), cassiaside and rubrofusarin gentiobioside were isolated as active principles, together with the inactive components, chrysophanol, physcion, sitosterol, chryso-obtusin, emodin, aurantio-obtusin and chrysophanol triglucoside [3]. In a course of continuous work on this plant, a new naphthalene glycoside named cassitoroside was isolated and characterized.

RESULTS AND DISCUSSION

Column chromatography of the butanol-soluble part of the methanol extract of the seeds yielded pale yellow crystals (**1**), mp 234 ~ 236°, which gave characteristic naphthalene glycoside colour reactions, brownish-red with 5% fast blue diazo salt B solution, and a positive Molisch test. The IR spectrum of **1** showed a broad hydroxyl and α,β-unsaturated carbonyl absorptions at 3350 and 1625 cm^{-1}, respectively. The UV spectrum of **1** exhibited typical absorption maxima for naphthalene at 231, 276, 314 and 396 nm [4]. The quasi-molecular ion peaks at *m/z* 557 [MH^+] and 579 [MNa^+] in the positive-ion FAB-MS were consistent with the molecular formula $C_{25}H_{32}O_{14}$. The ^1H NMR spectrum of **1** in methanol-d_4 (Table 1) exhibited the presence of an acetyl (δ2.61), two methoxyl (δ3.96, 3.91) groups and three aromatic protons ascribable to an isolated (δ6.64) and a pair of *meta*-coupled ones (δ6.87, 6.56, J = 2.0 Hz). It also showed the proton signals due to the sugar moieties between δ3.38 ~ 5.48 including two anomeric proton



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signals (δ5.10, 5.48). The sugars appear to be β-D-apiofuranose and β-D-glucopyranose according to ^{13}C NMR data (Table 1). In fact, acid hydrolysis of **1** afforded 1 mol each of D-apiose and D-glucose. Detailed analysis of the ^1H and ^{13}C NMR spectra (Table 1), aided by HMQC [5] and HMBC [6] experiments, allowed establishment of the structure of **1**. Carbon-13 signals of the protonated carbons in **1** were readily assigned by careful analysis of the HMQC spectrum and by comparisons with the ^{13}C NMR data for related naphthalene glycosides [7–10]. The oxygenated quaternary carbon signals of C-1, 3, 6 and 8 were assigned based on the C–H long-range coupling pattern in the proton-coupled ^{13}C NMR spectrum. The signal at δ163.1 was a singlet, suggesting that it should be assigned to C-1. The signals at δ161.4, 160.3 and 158.2 appeared as triplet, doublet and multiplet, respectively. Accordingly, the signals at δ161.4, 160.3 and 158.2 were assigned to C-8, C-3 and C-6, respectively. The configuration of glucopyranose and apiofuranose moieties were determined to be β not only by the J value of the anomeric proton signals, but also by comparison of the ^{13}C NMR data with those for corresponding methyl α-D- and β-D-glycosides [11, 12] (Table 2).

Table 1. 500 MHz ^{1}H and 125 MHz ^{13}C NMR data for **1** in CD_3OD (coupling constants in Hz in parentheses)

	1*	
Position	δ_H	δ_C
1	—	163.1
2		110.9
3	—	160.3
4	6.64 *s*	98.2
5	6.87 *d* (2.0)	104.1
6		158.2
7	6.56 *d* (2.0)	98.0
8		161.4
9		108.4
10		141.9
1′	5.10 *d* (7.6)	100.6
2′	3.68 *dd* (9.0, 7.6)	78.7†
3′	3.62 *t* (9.0)	78.6†
4′	3.38 *dd* (9.0, 8.8)	71.5
5′	3.52 *ddd* (8.8, 6.4, 2.4)	78.3
6′	3.94 *dd* (12.3, 2.4)	62.6
	3.69 *dd* (12.3, 6.4)	
1″	5.48 *d* (1.6)	110.8
2″	3.93 *d* (1.6)	78.1
3″		80.7
4″	3.82 *d* (10.0)	75.5
	4.11 *d* (10.0)	
5″	3.55 *s*	66.1
1-OCH_3	3.96 *s*	56.7
6-OCH_3	3.91 *s*	56.0
2-$\underline{CO}CH_3$	—	202.7
2-$CO\underline{CH_3}$	2.61 *s*	33.1

*Assignments are based on the results of proton-coupled ^{13}C NMR, HMQC and HMBC data.
†Assignments may be reversed.

The glycosidic linkage site of β-D-glucopyranose was determined to be C-8, based on the long-range C–H coupling between H-1′ and C-8 in the HMBC experiment. Two methoxyl groups were found to be attached to C-1 and C-6 according to long-range C–H coupling between OCH_3 (δ3.96) and C-1, OCH_3 (δ3.91) and C-6, respectively, in the HMBC experiment. Considering the biogenetic pathway and the coupling pattern of the naphthalene ring protons, only C-3 is available for another glycosidic linkage. Thus, **1** must be 2-acetyl-3-*O*-β-D-apiofuranosyloxy-8-*O*-β-D-glucopyranosyloxy-1,6-dimethoxynaphthalene, and is named cassitoroside. This is the first report of naphthalene-containing D-apiose in spite of frequent occurrence of naphthalene glycosides [7–10] in nature, especially in *Cassia* species [8, 10].

EXPERIMENTAL

FAB-mass spectra were obtained using a direct inlet system, and glycerol was used as a matrix. The NMR chemical shifts were referenced to residual solvent peaks (3.3 ppm in ^{1}H NMR, 49 ppm in ^{13}C NMR) and were recorded in δ values. Multiplicities of ^{1}H and ^{13}C NMR signals are indicated as *s* (singlet), *d* (doublet), and *t* (triplet). CC was done with silica gel (Merck; 70–230 mesh). TLC was carried out on pre-coated Merck Kieselgel 60 F_{254} plates (0.25 mm), and spots were detected under UV light using 50% H_2SO_4 reagent.

Plant material. The seeds of *C. tora* were purchased from a commercial supplier, in 1993, and authenticated by Prof. H. J. Chi. A voucher specimen has been deposited in the Herbarium of the Natural Products Research Institute, Seoul National University.

Isolation of **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 in a previous paper [3] to give a butanol-soluble fraction (90 g). This was subjected to CC on silica gel and eluted with EtOAc–MeOH of increasing polarity. The eluates were collected in 250 ml portions, monitored by TLC, and finally combined into 17 frs. Fr. 13 (1 g) was rechromatographed on a silica gel column, with EtOAc–MeOH–H_2O (300:35:10) to give **1** (80 mg). Pale yellow needles; mp 234 ~ 6°; UV λ_{max}^{MeOH} nm (log ε): 231 (5.12), 276 (5.03), 314 (4.44), 396 (4.32). Positive ion FAB–MS [matrix, glycerol] *m/z*: see text; MS (EI) *m/z* (rel. int.): 262 [M − Glc − Api]$^+$, 247 [262 − Me]$^+$, 232 [247 − Me]$^+$; ^{1}H and ^{13}C NMR (Table 1).

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Table 2. ^{1}H and ^{13}C NMR data for corresponding methyl α-D and β-D-glycosides in pyridine-d_5

		Carbons						
Glycosides	Anomeric H	C-1	C-2	C-3	C-4	C-5	C-6	C-OMe
Methyl α-D-apiofuranoside [11]	4.98 (4.6)	104.5	75.2	77.7	73.4	65.5		55.0
Methyl β-D-apiofuranoside [11]	4.96 (3.5)	111.5	77.7	80.3	74.9	65.5		55.3
Methyl α-D-glucopyranoside [12]	5.14 (3.5)	101.3	73.7	75.3	72.0	74.0	62.8	55.0
Methyl β-D-glucopyranoside [12]	4.71 (7.3)	105.5	75.0	78.4	71.3	78.3	62.6	56.7

Coupling constants in Hz in parentheses.

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