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(*S*)-5,7′-BIPHYSCION 8-GLUCOSIDE FROM *CASSIA TOROSA**

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Key Word Index—*Cassia torosa*; Leguminosae; bianthraquinone glycoside; torososide A; (*S*)-5,7′-biphysicon 8-glucoside.

Abstract—A novel bianthraquinone glucoside, torososide A, was isolated from the leaves of *Cassia torosa*. The structure of torososide A was established as (*S*)-5,7′-biphyscion 8-β-D-glucoside on the basis of spectral and chemical evidence.

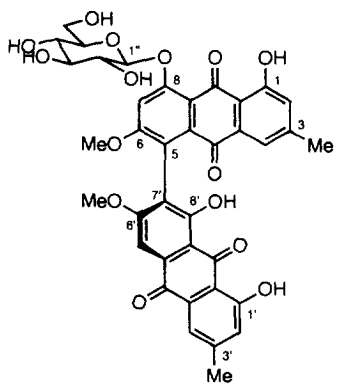
INTRODUCTION

We have reported previously the isolation of anthraquinone, anthrones, hydroanthracenes, naphthalenic lactones, and flavonoids from ripe and unripe seeds, seedlings, roots, and leaves of *Cassia torosa* Cav. In the present paper, we report the isolation and the structural elucidation of a new dimeric anthraquinone glycoside, torososide A from the same plant. This is the first report of a bianthraquinone glycoside from a natural source.

RESULTS AND DISCUSSION

Torosaside A (**1**) gave a red coloration in methanolic sodium hydroxide and in the magnesium acetate test [2]. The UV spectrum showed maxima at 221, 280, 434, 463sh, and the IR spectrum exhibited absorption bands due to hydroxyls (3414 cm^{-1}), non-chelated quinone (1703 cm^{-1}), chelated quinone (1649 cm^{-1}) and aromatic rings (1621, 1511, 1486 cm^{-1}). Torosaside A (**1**) was suggested to be an anthraquinone glycoside from the characteristic color reaction, spectral properties and its hydrolysis with β-glucosidase. Fragmentation of the FD-MS of **1** observed at *m/z* 729 $[M + 1]^+$ and 567 $[M + 1 -$ hexose$]^+$ suggested a dimeric anthraquinone glycoside. The ^1H NMR spectrum of **1** showed the presence of two aromatic methyl groups (δ2.39, 2.52), two methoxyl groups (δ3.89, 3.93), six aromatic protons (δ7.11, 7.19, 7.28, 7.54, 7.60, 7.67), three chelated hydroxyls (δ12.03, 12.21, 12.81), and sugar protons (δ3.2–5.22) (Table 1).

Treatment of **1** with β-glucosidase gave 5,7′-biphyscion (**1a**), ^1H NMR data of which were identical with those of floribundone-1 [3]. However, CD cotton curves of **1a** showed opposite curves from those of floribundone-1.



1

Table 1. ^1H NMR spectral data of compounds **1** and **1a** (400 MHz, Me_2CO-d_6, TMS as int. standard)

H	1	1a
2	7.11 *br s*	7.08 *br s*
Me-3	2.39 *br s*	2.39 br *s*
4	7.28 *br s*	7.41 *br s*
OMe-6	3.89 *s*	3.89 *s*
7	7.54 *s*	6.88 s
OH-1	12.81 *s*	12.12 *s*
OH-8	—	13.08 *s*
2′	7.19 *br s*	7.13 *br s*
Me-3′	2.52 *br s*	2.52 *br s*
4′	7.67 *br s*	7.68 *br s*
5′	7.60 *s*	7.57 *s*
OMe-6′	3.93 *s*	3.92 *s*
OH-1′	12.21 *s*	12.21 *s*
OH-8′	12.03 *s*	12.08 *s*
Sugar moiety		
1″	5.22 *d* (*J* = 6.8 Hz)	

*Part 32 in the series 'Studies on the Constituents of Purgative Crude Drugs.' For part 31 see ref. [1].

That is, the CD-coupling at the longest wavelength was found with negative first (465 nm) and positive second (410 nm) Cotton effects due to the long axis of the two anthraquinone moieties showed that the two long axes of the anthraquinone nuclei in **1a** are twisted in an anti-clockwise manner [3], that is *S*. Accordingly, **1a** is an atropisomer of floribundone-1.

CD cotton curves of **1** were the same as those of **1a**, that is negative first (454 nm) and positive second (398 nm). The location of the sugar moiety in **1** was confirmed to be at the 8 hydroxyl by comparison of the ^{1}H NMR spectral data of **1** and **1a**. That is to say, that H-7 (δ 7.54) signal in **1** had shifted downfield by 0.66 ppm owing to the glycosylation shift, compared with that of **1a**. On the basis of the evidence presented, the structure of torosaside A (**1**) is (*S*)-5,7′-biphyscion 8-β-D-glucoside.

EXPERIMENTAL

Plant material was obtained from Drug Plant Garden of the College of Pharmacy, Nihon University.

Extraction and isolation. The dried aerial parts (5.5 kg) of *C. torosa* were extracted with MeOH (77 l × 3) under reflux. The MeOH extract was concd *in vacuo* to give a dark mass, which was suspended in H_2O and extracted with Et_2O. The Et_2O extract (11.5 g) was sepd on a silica gel column with first $CHCl_3$ to give frs 1–3 and then with $CHCl_3$–MeOH mixtures to give frs 4–12. Frs 9 and 10 (3% MeOH–$CHCl_3$) were chromatographed on a Sephedex LH-20 column with MeOH–H_2O as eluent to give torosaflavone A (67 mg), luteolin (23 mg), and **1** (10 mg), respectively.

Torososide A (**1**). Recrystallization (EtOAc) gave orange needles, mp 222–223°. UV λ_{max}^{MeOH} nm (log ε): 221 (4.48), 280 (4.38), 434 (3.98), 463sh (3.78). IR ν_{max}^{KBr} cm^{-1}: 3414, 2932, 1703, 1649, 1621, 1511, 1486, 1440, 1361, 1255, 1203, 1181, 1136, 1105, 1087, 1039, 910, 838, 767, 610, 560, 426. CD (MeOH; c 2.45 × 10^{-5}) $\Delta\varepsilon^{23}$: 454 (− 12.8), 398 (+ 5.7), 294 (+ 38.1), 273 (− 64.1). FD-MS *m/z*: 729 [M + 1]$^+$, 567 [M + 1 − hexose]$^+$.

Enzymatic hydrolysis of compound **1**. A solution of **1** (3 mg) and β-glucosidase (5 mg) in H_2O (3 ml) was kept for 48 hr at 37°. The resultant ppt. was recrystallized from MeOH to afford **1a** (1.5 mg), which was identified as (*S*)-5,7′-biphyscion by comparison with an authentic sample (TLC, ^{1}H NMR, and CD), mp > 300°, CD (MeOH; c 1.06 × 10^{-3}) $\Delta\varepsilon^{23}$ 465 (− 27.5), 410 (+ 12.6), 297 (+ 61.0), 276 (− 86.5).

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