

## (+)-FLORIBUNDONE 3 FROM THE PODS OF *SENNA SEPTEMTRIONALIS*

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**ABSTRACT.** A new bianthraquinone, 5,7'-physcion-fallacinol (1,1',8,8',-tetrahydroxy-6,6'-dimethoxy-3-methyl-3'-hydroxymethylene-5,7'-bianthracene-9,9',10,10'-tetraone) is reported from the pods of *Senna septemtrionalis*. In addition, the known compounds chrysophanol, physcion, torosachryson, emodin, floribundone-1 and torosanin-9',10'-quinone are identified on the basis of their colour reactions, comparison with authentic samples and spectroscopic data.

### INTRODUCTION

*Senna septemtrionalis* Viv. (Syn. *C. floribunda* Sensus auctt., *Cassia septemtrionalis* Viv., *Cassia laevigata* Willd), family Leguminosae, is a woody herb, shrub or small tree. Its height is in the range of 1-5 m and grows mainly between 1700 and 2400 m altitudes. It is one of the 18 *Senna* species that grow in Ethiopia and is widely distributed in Arsi, Harrarge, Illubabor, Keffa, and Shewa regions [1].

The pods, roots, seeds and flowers of this plant of Indian origin have yielded chrysophanol, emodin, 8-mono-, and digalactosides of physcion, flavonoids including ombuin and quercetin [2-7]. Recent reports on the leaves of the plant from Ethiopia have revealed the isolation of bianthracene derivatives based on torosachryson, physcion anthrone and physcion [8, 9]. We have now studied the constituents of the pods of *S. septemtrionalis* and we hereby report the isolation and structure elucidation of a new bianthraquinone, based on physcion and fallacinol, in addition to six known anthracene derivatives.

### RESULTS AND DISCUSSION

The chloroform extract of the pods of *S. septemtrionalis*, after repeated silica gel, Sephadex LH-20 column chromatography and preparative TLC gave chrysophanol, emodin, physcion, torosachryson (4), torosanin-9',10'-quinone (3), floribundone-1 (2), in addition to a new bianthraquinone 5,7'-physcion-fallacinol (1), which we called (+)-floribundone 3.

The known metabolites, chrysophanol, physcion, emodin, floribundone-1 (2), torosanin-9',10'-quinone (3) and torosachryson (4) were identified from their <sup>1</sup>H NMR spectra and by TLC comparison with authentic samples previously obtained from the leaves of *S. multiglandulosa* [10] and leaves of *S. didymobotrya* [11].

Compound 1 is homogenous on TLC ( $R_f$  0.51, silica gel, CHCl<sub>3</sub>-EtOAc, 4:1 and  $R_f$  0.39, silica

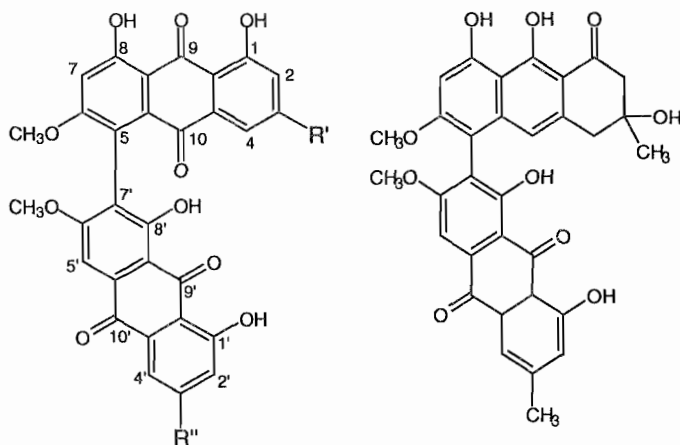
Table 1. <sup>1</sup>H NMR spectral data for compound **1** (300 MHz, CDCl<sub>3</sub>) and compound **2** (400 MHz, CDCl<sub>3</sub>) [8] J in Hz.

H	1	2
1-OH	12.09 <sup>a</sup> s	12.10 <sup>a</sup> s
2-H	7.05 <i>br d</i> , J=2.0	7.04 <i>br d</i> J=2.0
3-Me	2.36 s	2.35 s
4-H	7.42 <i>br d</i> , J=2.0	7.42 <i>br d</i> , J=2.0
5-H	-	-
6-OMe	3.84 <sup>b</sup> s	3.82 <sup>b</sup> s
7-H	6.82 s	6.82 s
8-OH	12.05 <sup>a</sup> s	12.05 <sup>a</sup> s
1'-OH	12.20 <sup>a</sup> s	12.20 <sup>a</sup> s
2'-H	7.34 <i>br d</i> , J=2.0	7.06 <i>br d</i> , J=2.0
3'-Me	-	2.45 s
3'-CH <sub>2</sub> OH	4.85 s	-
4'-H	7.82 <i>br d</i> , J=2.0	7.67 <i>br d</i> , J=2.0
5'-H	7.57 s	7.57 s
6'-OMe	3.89 <sup>b</sup> s	3.85 <sup>b</sup> s
8'-OH	13.06 s	13.10 s

<sup>a,b</sup>Values with the same superscripts in a column may be interchanged.

gel, CHCl<sub>3</sub>-MeOH, 100:1). It is a yellow pigment that turned from light yellow into pink on TLC when sprayed with 5% methanolic KOH. The colour change is characteristic of hydroxy anthraquinones [12]. The UV-Vis spectrum of **1** displayed absorption maxima at 244, 281 and 438 nm consistent with the presence of a quinonoid chromophore. The IR spectrum of **1** showed absorption bands at 3444, 1653 and 1623 cm<sup>-1</sup> for OH, non-chelated and chelated carbonyl groups, respectively. The <sup>1</sup>H NMR spectrum of **1** showed four signals in the chelated hydroxyl region (*ca* 12 ppm), six aromatic proton signals, two methoxy, one methyl, and one hydroxy-methylene signals suggesting that **1** is a bianthraquinone.

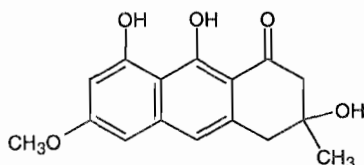
The chemical shifts for the protons of **1** were assigned by comparing the measured <sup>1</sup>H NMR spectrum with that of the closely related floribundone-1(**2**) [8] (see Table 1). In the spectra of both compounds, the signals attributable to H-5' and H-7 appear as non-coupled sharp singlets at δ 7.57 and 6.82, respectively, indicating that the two anthracene skeletons have a 5-7' internuclear bond in each of these compounds. An outstanding difference between the spectra of **1** and **2** is that the spectrum of **2** showed 2 x Ar-CH<sub>3</sub> signals at δ 2.45 and δ 2.35, whereas the spectrum of **1** revealed only one Ar-CH<sub>3</sub> at δ 2.36 in addition to a 2-proton signal at δ 4.85 that can be assigned to the methylene protons of a CH<sub>2</sub>-OH group. This led us to suspect that compound **1** might be a dimer based on physcion and fallacinol. EIMS showed a weak molecular ion at *m/z* 582 for [M<sup>+</sup>]. However, HRMS measurement to determine the exact mass of the ion failed repeatedly. The aromatic region displayed two sharp and four broad singlets. The two sharp singlets belong to H-5' and H-7 protons. The four broad singlets are assigned to H-2, H-2', H-4 and H-4' protons. The H-H COSY-45 spectrum of **1** showed cross peaks for the signals at δ 7.34, 7.82 and 4.85 (CH<sub>2</sub>OH). It is therefore concluded that the former two signals belong to H-2' and H-4'. The observed chemical shifts for these two protons are consistent with the deshielding effect of the -CH<sub>2</sub>OH group between the H-2' and H-4'



1, R' = CH<sub>3</sub>, R'' = CH<sub>2</sub>OH

2, R' = CH<sub>3</sub>, R'' = CH<sub>3</sub>

3



4

protons. The signals at  $\delta$  7.05 (H-2) and 7.42 (H-4) also showed cross peaks with each other and with the Ar-Me signal at  $\delta$  2.36. The alternative structure which would have the -CH<sub>2</sub>OH group at C-3 and the methyl group at C-3' is ruled out by comparing the <sup>1</sup>H NMR spectra of floribundone-1 (2) and 1. The <sup>1</sup>H NMR spectrum of floribundone-1 (2) showed that Me-3 and Me-3' resonate at  $\delta$  2.35 and 2.45, respectively. Due to the twisted conformation of the dimer, Me-3 falls in the shielding zone of the lower anthraquinone moiety and showed a small up-field shift compared to that of Me-3'. The <sup>1</sup>H NMR spectrum of 1 showed that the Ar-Me group signal appeared at 2.36 indicating that it is attached to C-3 and not to C-3'. If it were at C-3', the corresponding signal would have appeared at *ca.*  $\delta$  2.45. Compound 1 is optically active (see Experimental), though it has no chiral carbon. This is not unexpected, since such systems are known to exhibit axial dissymmetry due to hindered rotation about the internuclear bond between the two anthraquinone units [8, 13, 14].

## EXPERIMENTAL

*Plant material.* *Senna septemtrionalis* pods were collected from the experimental garden of the Department of Chemistry, Addis Ababa University (AAU), on April 20, 1995, and authenticated by

Dr. Sebsebe Demissew of the National Herbarium, AAU. Voucher specimen (voucher no. W-1) is deposited at the National Herbarium of AAU.

**Extraction and isolation.** The powdered pods of *S. septemtrionalis* (1.3 kg) were soaked in HOAc (5%) and defatted with cold petrol (9 L). The marc was then extracted with  $\text{CHCl}_3$  (7 L). The  $\text{CHCl}_3$  ext was then freed of solvent to give gummy residue (13 g, 1%). The  $\text{CHCl}_3$  ext was then subjected to flash CC using 250 mL of each of the following solvent mixtures successively: petrol-EtOAc 9:1 and 4:1, neat  $\text{CHCl}_3$ ,  $\text{CHCl}_3$ -MeOH 9:1 and 4:1. Fourteen frs of 75 mL each were collected. By TLC monitoring, the following frs were combined: 3-8 (Fr A) and 11-14 (Fr B). The rest of the frs (1, 2, 9, 10) contain no anthraquinones and were discarded. Fr A was subjected to silica gel CC using petrol-EtOAc 9:1 and 4:1 solvent systems (600 mL each). Ten frs of 100 mL each were collected. The first two frs were combined and subjected to Sephadex LH-20 column ( $\text{CHCl}_3$ -MeOH 2:1) and PTLC (petrol-EtOAc 9:1) to give chrysophanol and physcion. The ninth frn was introduced to a Sephadex LH-20 column ( $\text{CHCl}_3$ -MeOH 2:1) to give impure floribundone-1 (**2**) which was purified by PTLC (silica gel, petrol-EtOAc 4:1). The tenth frn was purified by PTLC (petrol-EtOAc 4:1) to yield emodin.

Fraction B was subjected to silica gel CC ( $\text{CHCl}_3$ -EtOAc 9:1) and Sephadex column ( $\text{CHCl}_3$ -MeOH 2:1) followed by PTLC ( $\text{CHCl}_3$ -EtOAc 4:1) to yield 5,7'-physcion-fallacinol (**1**) (9 mg,  $R_f$  0.51), torosanin-9',10'-quinone (**3**) ( $R_f$  0.46) and torosachryson (**4**) ( $R_f$  0.42).

1,1',8,8'-Tetrahydroxy-6,6'-dimethoxy-3-methyl-3'-hydroxymethylene-5,7'-bianthracene-9,9',10,10'-tetraone (**1**). A yellow pigment, mp 123-125 °C,  $[\alpha]_D^{22} = +164$  ( $c = 0.14$ ,  $\text{CHCl}_3$ ), UV-Vis  $\lambda_{\text{max}}$  (MeOH) nm (log  $\epsilon$ ): 438 (3.3), 281 (2.7), 245 (2.6), 203 (2.9). IR  $\nu_{\text{max}}$  (KBr)  $\text{cm}^{-1}$ : 3444, 2919, 1653, 1623, 1381, 1270.  $^1\text{H NMR}$ . See Table 1. EIMS 70 eV,  $m/z$  (rel. int. %) 582 [ $\text{M}^+$ ] (10%), 154 (82%), 136 (73%), 121 (45%), 107 (100%).

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