

## QUINONES OF *SENNA DIDYMOBOTRYA*

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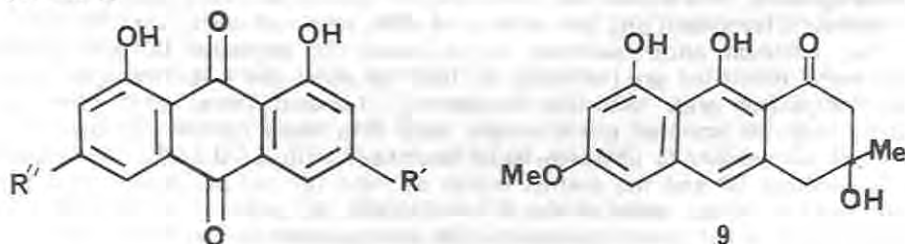
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**ABSTRACT.** Chrysophanol, physcion, aloë-emodin fallacinol rhein, parietinic acid and torosachryson have been isolated. Application of oxalic acid washed silica gel and Sephadex LH-20 successively enable the facile isolation of these quinones. New spectroscopic data are also generated for some of the anthraquinones.

### INTRODUCTION

The genus *Cassia* (Fabaceae) has been revised and regrouped recently by M. Thulin (1) into *Senna*, *Cassia* and *Chamaecrista*. *Cassia didymobotrya*, is now grouped under *Senna*. *S. Didymobotrya* is a bushy shrub found between altitudes of 1450 and 2400 meters and widespread in Eastern and Central Africa. This plant, as well as several species of the genus, are known for their medicinal properties, specially as purgative drugs (2). Chrysophanol, aloë-emodin and rhein have been reported from this plant by Egyptian workers (3). Our investigations of the leaves of *S. didymobotrya* resulted in the isolation and identification of chrysophanol, physcion, aloë-emodin fallacinol, rhein, parietinic acid and torosachryson. In this report we reveal a relatively simple procedure for the isolation of these, otherwise difficult to separate, pigments and also present, for the first time, <sup>1</sup>H NMR spectroscopic data for rhein and parietinic acid methyl esters.



- 1 R' = CH<sub>3</sub>, R'' = H (Chrysophanol)
- 2 R' = CH<sub>3</sub>, R'' = OCH<sub>3</sub> (Physcion)
- 3 R' = CH<sub>2</sub>OH R'' = H (Aloë-emodin)
- 4 R' = CH<sub>2</sub>OH R'' = OCH<sub>3</sub> (Fallacinol)
- 5 R' = COOH R'' = H (Rhein)
- 6 R' = CO<sub>2</sub>Me R'' = H (Rhein methyl ester)
- 7 R' = COOH R'' = OCH<sub>3</sub> (Parietic acid)
- 8 R' = CO<sub>2</sub>Me R'' = OCH<sub>3</sub> (Parietic acid methyl ester)

## RESULTS AND DISCUSSION

Eight anthraquinone (1-8) and one pre-anthraquinone (9) pigments are identified from the leaves of *S. didymobotrya*. The procedure of isolation employed in this study utilizes oxalic acid washed silica gel for column chromatography. Under such conditions the acidic anthraquinones such as rhein (5) and parietinic acid (7) are easily eluted from the column. The use of acidic silica gel has, however, the disadvantage of not offering good separation for torosachryson, aloemodin, fallacinal, rhein and parietinic acid. This difficulty was partially circumvented by passing the mixture through a column of Sephadex LH-20 and elution with dichloromethane. This led to the isolation of pure torosachryson, and mixtures of aloe-emodin-fallacinal and rhein-parietinic acid. The aloe-emodin-fallacinal mixture was separated by preparative layer

Table 1.  $^1\text{H}$  NMR spectra of aloe-emodin (3) fallacinal (4), rhein methyl ester (6), parietinic acid methyl ester (8) and torosachryson (9).

Proton	Aloemodin (3)	Fallacinal (4)	Rhein Me ester (6)	Parietic acid Me ester (8)	Torosachryson (9)
2H	7.36 brs	7.30 brs J=2 Hz	7.90 d J=2 Hz	7.88 d J=19 Hz	2.80 q
4H	7.79 brs	7.75 brs J=2 Hz	8.38 d J=2 Hz	8.32 d J=19 Hz	3.02 q
5H	7.82 dd J=8, 1 Hz	7.38 d J=2.6 Hz	7.84 d J=8.6 Hz	7.35 d J=2.8 Hz	6.50 d J=2.4 Hz
6H	7.68 t J=8.0 Hz	-	7.70 J=8.6 Hz	-	-
7H	7.30 dd J=8, 1 Hz	6.70 d J=2.6 Hz	7.30 d J=8.6 Hz	6.58 d J=2.8 Hz	6.45 d J=2.4 Hz
10H	-	-	-	-	6.85 brs
1-OH	12.00 s	12.18 s	11.92 s	12.12 s	-
8-OH	12.08 s	12.28 s	11.98 s	12.14 s	9.76
9-OH	-	-	-	-	16.04
6-OCH <sub>3</sub>	-	3.90 s	-	3.93 s	3.90 s
Other	4.80 s 3-CH <sub>2</sub> OH	4.80 s 3-CH <sub>2</sub> -OH	4.00 s 3-CO <sub>2</sub> Me	4.00 s 3-CO <sub>2</sub> Me	1.40 s 3-Me 3.20 brs 3-OH

chromatography (silica gel plates, petrol/EtOAc 4:1, multiple solvent development). The separation of the rhein-parietinic acid mixture was likewise achieved after esterifying the mixture of acids with methanol/sulphuric acid.

The common anthraquinones chrysophanol (1), physcion (2) and aloemodin (3) were identified on the basis of their physical and spectroscopic data and by comparison with authentic specimens. Torosachryson was identified by comparison of acquired spectroscopic data with those reported in the literature and by conversion to physcion upon treatment with KOH (4,5). The structures of fallacinal (4) and the methyl esters of rhein (6) and parietinic acid (7) were established on the basis of the UV,  $^1\text{H}$  NMR, IR and MS data. Since the  $^1\text{H}$  NMR spectra for these compounds are not reported in the literature they are given in Table 1 together with those of torosachryson and aloe-emodin. We are unable to find in the literature any data on the methyl ester of parietinic acid (8).

The anthraquinones chrysophanol and physcion are very common in higher plants including in the genus *Senna*. Aloe-emodin, and rhein, even though less common than the former two, are also found in several *Senna* species (3,6-8). The finding of fallacinal and parietinic acid in this plant is more significant since these compounds have been reported only from lichens and cultures of *Eurotium echinulatum* (9,10,11) and not from any higher plant. Torosachryson

has only been reported in two other *Senna* species, namely: *S. torosa* (4) and *S. singuana* (5).

### EXPERIMENTAL

**General.** NMR spectra were recorded on Bruker AM400 spectrometer (in  $\text{CDCl}_3$ , TMS  $\delta = 0$ ). Unless otherwise stated, tlc were carried out on silica gel impregnated with 0.5 N oxalic acid and developed with benzene/EtOAc 4:1.

**Plant material.** Leaves of *S. didymobotrya* were collected from Mojo, 70 km South-east of Addis Ababa. Voucher specimen of the plant is deposited at the National Herbarium, Addis Ababa University.

**Extraction and isolation.** The powdered leaves of *S. didymobotrya* (1 kg) were soaked in acetic acid (5%) and defatted with cold petroleum ether and the marc was subsequently extracted with methylene chloride (20 l, cold). Evaporation of the solvent gave a dark residue (31 g, 3.1%) which on tlc showed four coloured spots with  $R_f$  values of 0.47, 0.40, 0.26 and 0.18 respectively. The dark residue, 6 g, was applied on 100 g of acid washed (0.5 N oxalic acid) silica gel and eluted with methylene chloride. Two distinct bands were observed, which were collected as two fractions. The first fraction contained 12 mg (0.006%) of a two component mixture (tlc, silica gel, petrol/EtOAc 9:1). This mixture was applied on a micro column of silica gel and eluted with petrol/EtOAc (20:1) to yield the common anthraquinones physcion and chrysophanol which were identified by tlc comparison with authentic specimens and by UV, IR,  $^1\text{H}$  NMR and MS data. The second fraction was applied on Sephadex LH-20 and eluted with methylene chloride. Three bands were observed. The first band gave 8 mg (0.004%) of torosachryson. The second band yielded 10 mg (0.005%) as a mixture of rhein and parietinic acid. These acids were converted to the corresponding methyl esters (see below) and separated on preparative silica gel layers ( $R_f$  0.39 and 0.34 respectively) employing the above mentioned solvent system.

**Esterification of rhein-parietinic acid mixture.** The mixture of acids (6 mg) was dissolved in redistilled methanol (2 ml) and one drop of conc.  $\text{H}_2\text{SO}_4$  was added and the reaction mixture refluxed for 1 hr. The solvent was removed and the residue dissolved in methylene chloride and successively washed with aqueous  $\text{NaHCO}_3$  and water, dried with anhydrous  $\text{Na}_2\text{SO}_4$  and freed of solvent to give a mixture of the esters (4 mg).

Parietic acid methyl ester. M.p. 198-200°C; UV-vis  $\lambda_{\text{max}}$  nm ( $\text{CH}_3\text{CN}$ ): 227, 250, 435 (relative  $\epsilon$  2.2, 1.5, 1.0 respectively); IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr): 3450, 1730, 1680, 1630; HRMS: 328.0552 (calc. for  $\text{C}_{17}\text{H}_{12}\text{O}_7$ : 328.0583); MS  $m/z$  (rel. int.): 328 ( $\text{M}^+$ , 100), 297 (41), 269 (42), 241 (4), 213 (18), 185 (4);  $^1\text{H}$  NMR data see Table 1.

For  $^1\text{H}$  NMR data of all other compounds, also see Table 1. References for physical and other spectroscopic data of the other pigments are: aloemodin (12), (13) fallacinal (9), rhein methyl ester (6) and torosachryson (4, 5).

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