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BIANTHRAQUINONES FROM THE SEEDS OF *SENNA MULTIGLANDULOSA*

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Key Word Index—*Senna multiglandulosa*; Leguminosae; bianthraquinones; physcion; floribundone; torosachrysone; anhydrophlegmacin-9′,10′-quinone; 9-(physcion-7′-yl)-5,10-dihydroxy-2-methyl-7-methoxy-1,4-anthraquinone.

Abstract—Torosachrysone, physcion, floribundone-1, anhydrophlegmacin and a new bianthraquinone, 9-(physcion-7′-yl)-5,10-dihydroxy-2-methyl-7-methoxy-1,4-anthraquinone, named isosengulone, are reported from the seeds of *Senna multiglandulosa*. The compounds were identified on the basis of spectroscopic and other physical data.

INTRODUCTION

Plants belonging to *Cassia* and *Senna* yield a large number of polyketide-derived anthraquinones and bianthraquinones in addition to their glycosides [1]. In some cases simple isoquinoline and piperidine alkaloids have been reported [2, 3]. *Senna multiglandulosa* Jack (synonyms: *Cassia tomentosa* l.f., *C. multiglandulosa*) is one of the 18 *Senna* species growing in Ethiopia [4]. Earlier reports on this plant dealt with the isolation of common constituents and four bianthraquinones from the leaves and stems [5, 6]. Our findings, based on the investigation of the the seeds of *S. multiglandulosa*, are presented in this report.

RESULTS AND DISCUSSION

The chloroform extract of the seeds of *S. multiglandulosa*, after repeated chromatography on silica gel and Sephadex (LH-20), gave physcion, the three bianthraquinones **1–3** and the preanthraquinone **4**. Floribundone-1 (**1**) and anhydrophlegmacin (**2**) were identified on the basis of their ^{1}H NMR spectra (Table 1) and by direct comparison with authentic samples previously obtained from the leaves of *S. multiglandulosa* [6] and *C. floribunda* (synonym: *S. septemtrionalis*) [7]. Physcion and torosachrysone (**4**) were also identified from their ^{1}H NMR data and by direct comparison with authentic samples previously obtained from the leaves of *S. didymobotrya* [8].

Isosengulone (**3**) is an optically inactive, brown pigment. HRMS showed an exact mass of 566.1217, consistent with the molecular formula $C_{32}H_{22}O_{10}$ (calculated 566.1212). The UV–visible spectrum showed bands at 226, 300, 370, 447 and 537 nm suggesting a quinonoid chromophore. This natural product was suspected to be a 1,4-anthraquinones from the bathochromic shift of its long wavelength absorption maximum. The infrared spectrum of **3** showed absorptions at 1672 (sh) and 1639 cm^{-1}, suggesting the presence of two carbonyl groups one of which is chelated. The ^{1}H NMR

Table 1. ^{1}H NMR spectral data of compounds **1**, **2** and **4** (90 MHz, $CDCl_3$)

H	1	2	4
1-OH	12.34* *s*	–	–
2-H	7.10 *br s*	–	–
2-CH_2	–	2.70	2.80 *br s*
3-Me	2.35 *s*	1.40	1.40 *s*
3-OH	–	3.00	2.00 *br s*
4-H	7.40 *br s*	–	–
4-CH_2	–	2.85	3.00 *br s*
5-H	–	6.05 *d*, $J = 2.5$	6.45 *d*, $J = 2.5$
6-OMe	3.80† *s*	3.70* *s*	3.90
7-H	6.80 *s*	6.50 *d*, $J = 2.5$	6.55 *d*, $J = 2.5$
8-OH	12.40* *s*	10.20 *s*	9.80 *s*
9-OH	–	16.70 *s*	16.10 *s*
10-H	–	–	6.85 *s*
1′-OH	12.05 *s*	12.40† *s*	–
2′-OH	7.05 *br s*	7.10 *br s*	–
3′-Me	2.45 *br s*	2.50 *br s*	
4′-H	7.65 *br s*	7.70 *br s*	
5′-H	7.55 *s*	7.60 *s*	
6′-OMe	3.90† *s*	3.85* *s*	
7′-H	–	–	
8′-OH	13.05* *s*	12.01† *s*	

*†Signals with the same symbol in the same column may be interchanged.

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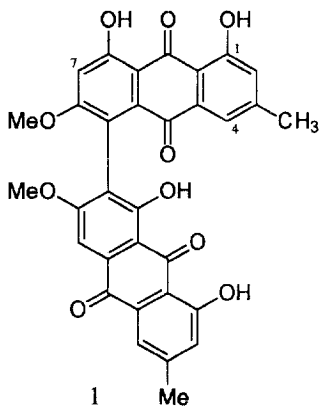

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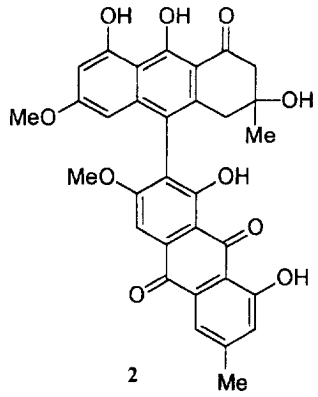

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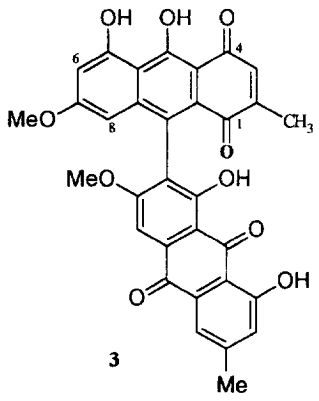

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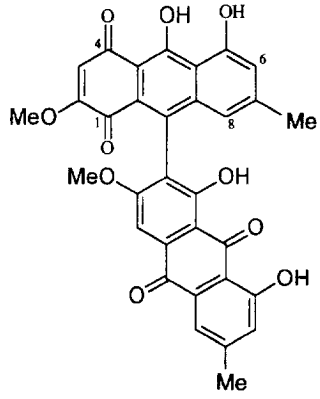

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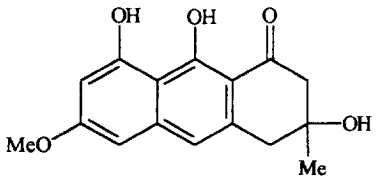

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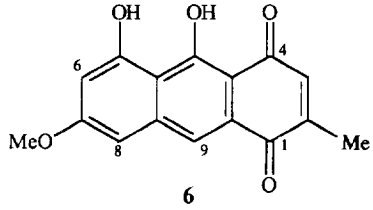

6

spectrum of **3** (Table 2) showed four signals that could be assigned to four chelated hydroxyl groups, two methoxy and two aryl-methyl resonances and six signals that could be assigned to six aromatic protons. These observations, together with the molecular formula suggested from the HRMS data, led to the conclusion that **3** was a bianthraquinone. Two of the hydroxyl (δ12.26 and 12.05), and three of the aromatic proton resonances could be assigned to one physcion moiety of a bianthraquinone system. The observation that the signal assignable to H-5 of the physcion portion was a sharp singlet, not broadened by even allylic or 1,4-couplings established position 7 as the point of linkage to the other unit of the bianthraquinone.

The conclusion that **3** was different from the isomeric sengulone (**5**) [6] was easily reached from the differences in melting points and by TLC (silica gel, benzene–ethyl acetate, 19:1) where R_f values of 0.16 and 0.32 were observed for **3** and **5**, respectively. Further spectroscopic differences were also observed. Comparison of the ^{1}H NMR spectra of **3** and **5** showed that the signals attributed to the protons of the physcion moieties of the two compounds were very similar whereas those of the non-physcion portion of the two molecules exhibited quite different signals. The most striking difference was that the methyl signals which appeared as a broad singlet at δ2.32 in **5** appeared as a doublet at δ2.07 in **3**. This led us to suspect that the methyl group, which resonates as a doublet at δ2.07, may be at position 2 of the 1,4-anthraquinone moiety, as in **6** [9]. Decoupling experiments and examination of the H–H COSY spectrum of **3** were most useful in clearly establishing the assignments of the aromatic protons of isosengulone. Irradiation of the signal at δ6.94 resulted in the collapse of the methyl doublet resonance at δ2.07. Similar irradiation of the methyl doublet affected only what was presumed to be the Q–H proton signal at δ6.94 which changed into a sharp singlet. The H–H COSY spectrum showed that the signal at δ 6.94 (H-3) showed only one cross-peak with the methyl signal at δ2.07. In contrast to this, the signal at δ7.11 showed two cross-peaks with the aromatic proton signals at δ7.69 and the methyl resonance at

Table 2. ^{1}H NMR data of compounds **3**, **5** and **6** (300 MHz, $CDCl_3$)

H	3	6	H	5
7-OMe	3.72* *s*	3.95 *s*	2-OMe	3.82* *s*
3-H	6.91 *d*, $J = 1.6$	6.91 *q*, $J = 1.5$	3-H	6.20 *s*
5-OH	10.99 *s*	10.32 *s*	5-OH	10.32 *s*
6-H	6.38 *d*, $J = 2.4$	6.67 *d*, $J = 2.3$	6-H	6.95 *br s*
2-Me	2.05 *d*, $J = 1.4$	2.21 *d*, $J = 1.5$	7-Me	2.32 *br s*
8-H	6.70 *d*, $J = 2.4$	6.86 *d*, $J = 2.3$	8-H	6.79 *br s*
10-OH	17.10 *s*	16.20 *s*	10-OH	17.25 *s*
9-H	–	7.86 *s*	1′-OH	12.25† *s*
1′-OH	12.24† *s*		2′-H	7.99 *s*
2′-H	7.08 *br s*		3′-Me	2.49 *br s*
3′-Me	2.47 *br s*		4′-H	7.70 *br s*
4′-H	7.67 *br s*		5′-H	7.59 *s*
5′-H	7.58 *s*		6′-OMe	3.88* *s*
6′-OMe	3.84* *s*		8′-OH	12.04† *s*
8′-OH	12.03† *s*			

*†Signals with the same symbol in the same column may be interchanged.

δ2.49. Comparison of the ^{1}H NMR spectra of **3** and **6** [9] showed that signals that could be assigned to H-3, H-6 and H-8 were present in both spectra. However, the signal that appeared at δ7.86 as a singlet in the spectrum of **6** was absent from the spectrum of **3**. This established the coupling position to be at 9 of **6** and the structure of the new compound, which we called isosengulone, must be **3**. The methyl group at position 2 which resonates at δ2.21 (*d*) in **6** appeared at δ2.07 (*d*) in **3** probably owing to the shielding effect of the ring current of the physcion moiety. The H-3, which resonates as a quartet at δ6.91 ppm in **6**, resonates as a broad doublet with the same chemical shift in **3**.

EXPERIMENTAL

Plant material. Senna multiglandulosa seeds were collected along the Addis Ababa–Ambo road *ca* 80 km west of Addis Ababa in December 1990. Voucher specimens are deposited in the National Herbarium at Addis Ababa University (Voucher No. MB-2).

Extraction and isolation. The dried and ground seeds (1 kg) of *S. multiglandulosa* were soaked in 5% HOAc for 24 hr and dried in air; defatted with petrol and subsequently extracted with $CHCl_3$. The $CHCl_3$ extract was freed of solvent to give 14 g of residue, which was subjected to flash chromatography on 4% oxalic acid-impregnated silica gel and eluted with $CHCl_3$. A total of 30×250 ml frs was collected by eluting with $CHCl_3$–petrol (1:1). Frs 1–11 gave physcion, frs 12–16 contained floribundone-1, frs 17–25 contained a mixture of anthraquinones in small quantities. Frs 26–30 were subjected to prep. TLC to yield **2** (5 mg) and **4** (5 mg). The residue from frs 17–25 was applied to a silica gel column deactivated with oxalic acid and eluted with $CHCl_3$–petrol (1:1); 15×250 ml frs were collected. Frs 6–10 (monitored by TLC) were combined and the solvent removed to give 600 mg of residue. The MeOH-soluble portion of the residue, which showed one major spot on TLC, was subjected to Sepahdex (LH-20) CC and eluted with MeOH to yield pure **3** (10 mg).

9-(*physcion-7′-yl*)-5,10-*dihydroxy-2-methyl-7-methoxy-1,4-anthraquinone* (Isosengulone, **3**). Dark brown pigment, mp 152–154°, UV-VIS $\lambda_{max}^{CHCl_3}$ (log ε): 577 (3.8), 537 (4.0), 447 (4.2), 370 (3.9), 300 (4.3), 226 nm (4.5); IR ν_{max} cm^{-1} (KBr) 3400, 2950, 1680, 1640, 1370, 1280, 1205, 1120; ^{1}H NMR: Table 2; HRMS 566.1217, calculated for $C_{32}H_{22}O_{10}$ 566.1212; EIMS *m/z* (rel. int.): 566 (23), 535 (30), 284 (12), 96 (100).

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