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A 1,4-ANTHRAQUINONE-DIHYDROANTHRACENONE DIMER FROM *SENNA SOPHERA*

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Key Word Index—*Senna sophera*; Leguminosae; seeds; bianthraquinone; preanthraquinone; presengulone.

Abstract—From the seeds of *Senna sophera*, a new hydroanthracene derivative named presengulone [9-(6′-methoxy-3′-methyl-3′,8′,9′-trihydroxy-1′-oxo-1′,2′,3′,4′-tetrahydro-anthracene-7′-yl)-5,10-dihydroxy-2-methoxy-7-methyl-1,4-anthraquinone] was isolated, together with physcion, physcion bianthrone, xanthorin, floribundone-1, isosengulone, sengulone, and anhydrophlegmacin-9,10-quinones A_2 and B_2.

INTRODUCTION

Senna sophera is one of the 18 *Senna* species occurring in Ethiopia [1]. It is well known for its medicinal value in the traditional health delivery system of India [2]. The roots, flowers and heart wood of *S. sophera* from India have been studied chemically resulting in the isolation of a number of unusual and common anthraquinones, flavonoids and sterols [3–7]. We have now examined the seeds of this species and found physcion, physcion bianthrone, xanthorin, floribundone-1 (**7**), isosengulone (**3**), sengulone (**2**), anhydrophlegmacin-9,10-quinones A_2 and B_2 (**5** and **6**) and a new compound, which we called presengulone (**1**). With the exception of physcion, the above mentioned compounds have not been reported from this plant.

RESULTS AND DISCUSSION

The chloroform extract of the seeds after repeated chromatography on silica gel, Sephadex LH-20 and preparative TLC yielded a number of pigments. Physcion and xanthorin were easily identified from their ^{1}H NMR spectra. Physcion bianthrone and anhydrophlegmacin-9,10-quinones A_2 and B_2 (**5** and **6**) were identified from their mass spectral data and by comparing their ^{1}H NMR spectra with those reported in the literature [8]. Floribundone-1 (**7**), isosengulone (**3**) and sengulone (**2**) were identified from their mass spectral ^{1}H NMR data and TLC comparison with authentic samples previously isolated from *S. multiglandulosa* [9, 10].

Presengulone (**1**) is a brown pigment. The UV–vis spectrum showed bands at 308, 335, 468 and 545 nm. Its colour and the base-induced bathochromic shift of its long wavelength absorption maximum in the UV–vis spectrum are indicative of a 1,4-anthraquinone structure. The IR spectrum showed absorptions at 1674 and 1627 cm^{-1} corresponding to unchelated and chelated carbonyl groups, respectively. The HR mass spectrum led to an exact mass of 570.1528 for the $[M]^+$ and it was possible to deduce the molecular formula as $C_{32}H_{26}O_{10}$ (calculated: 570.1518). It was assumed at this stage that **1** was a bianthracene dimer. The deduced molecular formula, with R+DB = 20, was suggestive of an anthraquinone linked to a preanthraquinone (R+DB = 11+9). Compound **1** exhibited strong optical rotation $[\alpha]_D$ +575° ($CHCl_3$, *c* 0.08) which indicated the possibility of an asymmetric centre and/or axial chirality. It was possible to recognize a group of signals in the ^{1}H NMR spectrum of **1** (Table 1) that were characteristic of a torosachrysone unit (**4**). These consisted of a very low field signal at δ 16.0 for the hydroxyl group at C-9, a second signal at δ 9.80 for the other hydroxyl group at C-8, a signal at δ 1.40 representing the methyl protons at C-3 and the two methylene protons at C-2 and C-4, giving rise to the characteristic signals at δ 2.90 and 3.10, respectively. Comparison between the ^{1}H NMR spectrum of **1** with that of torosachrysone (**4**), showed that the two doublets at δ 6.45 and 6.55 assigned to H-5 and H-7, respectively, of torosachrysone (**4**) [9] were lacking in **1**. The spectrum of **1**, however, showed

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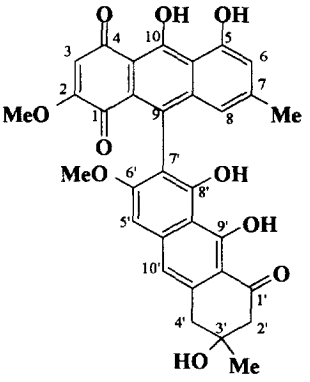
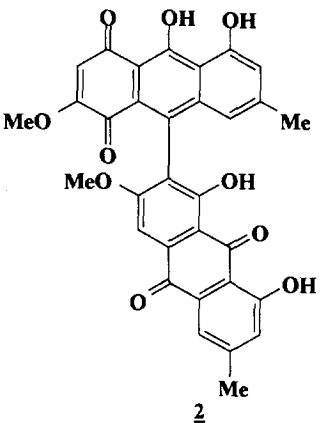


1



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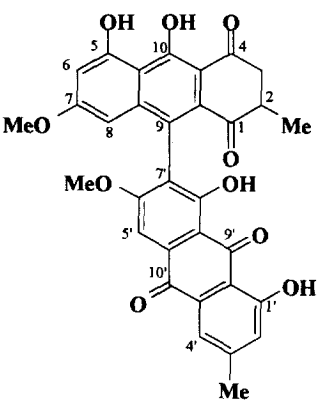

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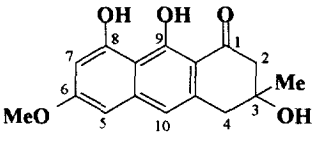

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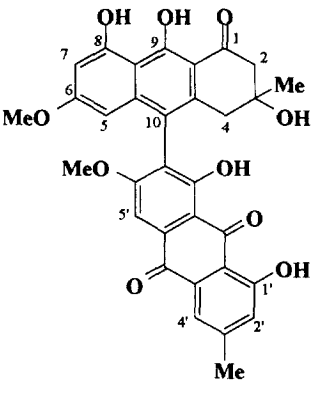

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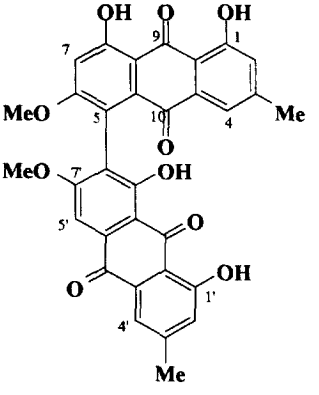

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a sharp singlet at δ 6.70 which could be assigned to either H-5′ or H-7′ suggesting that torosachrysone is connected to the other half of the molecule (**1**) either at position 5′ or 7′. In a NOE experiment, irradiation of the signal at δ 6.70 enhanced the signal at δ 7.00 (12%) and the methoxyl signal at δ 3.72 (16%). This is possible if the signal at δ 6.70 is assigned to H-5′ and the signal at δ 7.00 to H-10′, establishing that torosachrysone (**4**) is connected to the other half of the molecule at position 7′.

The remaining two hydroxyl group signals at δ 10.4 and 17.4 are indicative of a 1,4-anthraquinone skeleton [10], suggesting that **1** is a dimer of torosachrysone and a 1,4-anthraquinone. The nature and linkage pattern of the 1,4-anthraquinone moiety of **1** was readily established by comparing its ^{1}H NMR spectrum with those of sengulone (**2**) and isosengulone (**3**). Thus, the signals remaining after assigning those of torosachrysone (see above) showed a one-to-one correspondence to the signals of the 1,4-anthraquinone part of **2** [10] and not of isosengulone (**3**). Besides, NOE irradiation of the signal at δ 6.20 assigned to H-3 of **1** enhances the signal at δ 3.82, which is assigned to the 2-OMe group of the 1,4-anthraquinone. The structure of the new pigment was thus established as the mixed hydro- and anhydroanthracene compound **1**. The name presengulone is proposed on the assumption that it may very well be the biosynthetic precursor of sengulone (**2**).

EXPERIMENTAL

General

^{1}H NMR: 300 MHz; ^{13}C NMR: 75 MHz; $CDCl_3$ using the solvent peak as int. ref. EI/CIMS: direct inlet. IR: KBr disks; UV–vis: $CHCl_3$ soln. Prep. TLC: 0.50 or 0.75 mm thick layer silica gel. Flash CC: silica gel (particle size 40–63 μm) impregnated with 5% aq. oxalic acid.

Plant material

Senna sophera (L.) Roxb (synonym *Cassia sophera* L.) seeds were collected from Asebe Teferi, ca 320 km

Table 1. ^{1}H NMR spectral data of compounds **1–3** (300 MHz, $CDCl_3$)

H	1	2	3
2-OCH_3	3.82 *s*	3.82 *s*	—
2-CH_3	—	—	2.05 *d*, *J* = 1.4 Hz
3-H	6.20 *s*	6.20 *s*	6.91 *d*, *J* = 1.6 Hz
5-OH	10.40 *s*	10.32 *s*	10.99 *s*
6-H	6.92 *s*	6.95 *s*	6.38 *d*, *J* = 2.4 Hz
7-CH_3	2.30 *s*	2.32 *s*	—
7-OCH_3	—	—	3.72 *s*
8-H	6.85 *br s*	6.79 *s*	6.70 *d*, *J* = 2.4 Hz
10-OH	17.40 *s*	17.25 *s*	17.10 *s*
1′-OH	—	12.29* *s*	12.24* *s*
2′-H	—	7.09 *br s*	7.08 *br s*
2′-CH_2	3.10 *br s*	—	—
3′-CH_3	1.40 *s*	2.49 *s*	2.47 *br s*
4′-H	—	7.70 *s*	7.67 *br s*
4′-CH_2	2.90 *br s*	—	—
5′-H	6.70 *s*	7.59 *s*	7.58 *s*
6′-OCH_3	3.72 *s*	3.88 *s*	3.84 *s*
8′-OH	9.80 *s*	12.04* *s*	12.03* *s*
10′-H	7.00 *s*	—	—

* Signals in the same column may be interchanged.

east of Addis Ababa in March 1996 and identified by Dr Ensermu Kelbessa of the National Herbarium, Addis Ababa University, where a voucher specimen is deposited (Voucher No. Z. Asfaw 212).

Extraction and isolation

Dried and ground seeds (800 g) were soaked in 5% HOAc for 24 h and dried in air; defatted with petrol and subsequently extracted with $CHCl_3$. The $CHCl_3$ extract was freed of solvent to give 45 g of residue, which was subjected to flash CC on silica gel and eluted successively with $CHCl_3$ and $CHCl_3$–EtOAc (20:1). A total of 33 × 250 ml frs were collected. Frs 1–6 (Fr. A) eluted with $CHCl_3$ were combined and frs 17–33 (Fr. B) eluted with $CHCl_3$–EtOAc (20:1) were also combined. Fr. A was subjected to silica gel CC and eluted with 1 l each of petrol–$CHCl_3$ (4:1), petrol–$CHCl_3$ (2:1) and $CHCl_3$. A total of 24 × 125 ml frs were collected. By TLC monitoring, frs 2–7 (Fr. C), frs 8–15 (Fr. D), frs 16 and 17 (Fr. E), and frs 18–24 (Fr. F) were combined. Fr. C gave physcion. Fr. D, upon silica gel column chromatography (petrol–EtOAc, 20:1) followed by purification on Sephadex LH-20 (MeOH) yielded physcionbianthrone, xanthorin and floribundone-1 (**7**). Fr. E was subjected to prep. TLC ($CHCl_3$) and Sephadex LH-20 ($CHCl_3$–MeOH, 2:1) to yield isosengulone (**3**). Fr. F was purified using a microsilica gel column ($CHCl_3$), prep. TLC ($CHCl_3$) and Sephadex LH-20 ($CHCl_3$–MeOH, 2:1) to give sengulone (**2**).

Fr. B was separated by silica gel CC and eluted with $CHCl_3$–EtOAc (20:1); 13 frs of 200 ml each were collected. By TLC monitoring, frs 1–9 (Fr. G) and frs 10–13 (Fr. H) were combined. Fr. H was subjected to silica gel CC and eluted with $CHCl_3$; 23 frs. of 200 ml each were collected. Frs 1–6 (Fr. 1), frs 7–11 (Fr. J) and frs 12–13 (Fr. K) were combined based on TLC similarity. Fr. J was subjected to Sephadex LH-20 CC ($CHCl_3$–MeOH, 2:1) and prep. TLC ($CHCl_3$–EtOAc, 9:1) to give anhydrophlegmacin-9,10-quinones A_2 and B_2 (**5** and **6**). Fr. K was separated on Sephadex LH-20 ($CHCl_3$–MeOH, 2:1) and prep. TLC ($CHCl_3$–EtOAc, 9:1) to yield presengulone (**1**) (7 mg).

Presengulone (**1**). Brown pigment. $[\alpha]_D$ +575° ($CHCl_3$, *c* 0.08). M.p. 193–195°. UV–vis λ_{max} nm (log ε): 308 (3.4), 335 (3.2), 468 (3.0), 545 (2.9). IR ν_{max} KBr cm^{-1}: 3437, 2845, 1729, 1674, 1627, 1454. ^{1}H NMR: Table 1. HRMS 570.1528, calculated for $C_{32}H_{26}O_{10}$ 570.1518; EIMS (probe) 70 eV, *m/z* (rel. int.): 570 (10), 552 (14), 284 (16), 270 (100).

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REFERENCES

1. Thulin, M., *Flora of Ethiopia*, Vol. 3, ed. I. Hedberg and S. Edwards, Addis Ababa University,

Addis Ababa, Ethiopia; Uppsala, Sweden, 1989, pp. 57–64.
2. Kirtikar, K. R. and Basu, B. D., *Indian Medicinal Plants*, Vol. 3, Leader Press, Allahabad, 1940, p. 863.
3. Tiwari, R. D. and Misra, G., *Planta Medica*, 1975, **28**, 182.
4. Malhotra, S. and Misra, K., *Planta Medica*, 1982, **46**, 247.
5. Malhotra, S. and Misra, K., *Phytochemistry*, 1982, **21**, 197.
6. Dass, A., Joshi, T. and Shukla, S., *Phytochemistry*, 1984, **23**, 2689.
7. Ghosh, P., Thakur, S., Itoh, T. and Matsumoto, T., *Indian J. Chem.*, 1982, **21B**, 796.
8. Kitanaka, S. and Takido, M., *Phytochemistry*, 1982, **21**, 2103.
9. Alemayehu, G. and Abegaz, B. M., *Phytochemistry*, 1996, **41**, 919.
10. Abegaz, B. M., Bezabeh, M., Alemayehu, G. and Duddeck, H., *Phytochemistry*, 1994, **35**, 465.