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A 7-HYDROXYAPORPHINE ALKALOID FROM *DESMOS DASYMACHALUS*

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Key Word Index—*Desmos dasymachalus*; Annonaceae; leaves; alkaloids; 7-hydroxyaporphine; dicentrinone; dasymachaline.

Abstract—A new 7-hydroxyaporphine, dasymachaline, having the *cis* H-6a and H-7 configuration has been isolated from the leaves *Desmos dasymachalus* together with the known alkaloid dicentrinone.

INTRODUCTION

Although alkaloids have been found to occur in many genera of the Annonaceae [1], phytochemical studies of the genus *Desmos* are scarce. However, a recent paper [2] on *D. tiebaghiensis* reported the isolation of 13 alkaloids belonging to five different classes. During our survey of the Annonaceae of peninsular Malaysia we have isolated two aporphinoids, one of which is a new compound, from *D. dasymachalus*.

RESULTS AND DISCUSSION

The first alkaloid was identified as dicentrinone (**1**) [3] from its characteristic blood red colour in an acid medium and by its physical and spectral properties. The second compound, named dasymachaline (**2**), was found to be a 7-hydroxyaporphine. Compound **2** was found to be somewhat unstable decomposing slowly to a dark brown mixture. A small amount of **1** was isolated from this mixture, thus establishing that the structure of **2** was closely related to **1**. Its mass spectrum exhibited a strong $[M]^+$ at m/z 355 (base peak) and its IR spectrum showed a broad hydroxyl absorption at 3500 cm^{-1}. The presence of 1,2-methylenedioxy and 9,10-dimethoxy groups was indicated by its ^1H NMR spectrum which showed a singlet at $\delta 3.94$ for the two methoxyl groups and the typical double doublets pattern of methylenedioxy protons at $\delta 5.94$ and 6.09. The singlets at $\delta 6.52$, 6.96, and 7.74 were assigned to H-3, H-8 and H-11. The *cis* H-6a, H-7 configuration was shown by the small coupling constant ($J = 2.6$ Hz) of the two doublets at $\delta 3.23$ (H-6a) and 4.83 (H-7). The doublet at $\delta 4.83$ became a singlet upon irradiation at $\delta 3.23$ thus confirming their 1,2-*cis* relationship.

On the basis of the above data structure **1** was assigned to dasymachaline. 7-Hydroxyaporphines having the *trans* H-6a, H-7 configuration are more commonly encountered [4–6] than the corresponding *cis*-isomers. The discovery of **2** adds one more to the short list of this group of compounds.

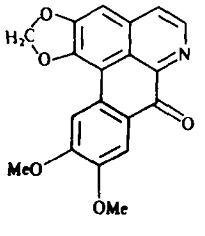
EXPERIMENTAL

^1H NMR were recorded in $CDCl_3$ at 100 MHz with TMS as int. standard. Chromatography was carried out using the following materials: Merck Kieselgel 60 (230–400 mesh) (flash); Merck pre-coated plates (silica gel 60 F-254) (TLC); Merck Al_2O_3 F-254 Type T (prep. TLC); Waters Associates Radial Pak μPorasil (8 × 100 mm) column (HPLC).

Plant material. Leaves of *D. dasymachalus* (B.P./Safford) were collected and identified by J. R. Deverre (CNRS, Gif-sur-Yvette, France) near Kluang in the State of Johore, Malaysia in September 1983.

Extraction and isolation. Leaves (550 g) were air dried and ground to small pieces. The plant material was moistened with 20% NH_4OH and then Soxhlet extracted with $CHCl_3$ (3 l.) for 24 hr. The $CHCl_3$ extract was concd to *ca* 1 l. and then extracted with 3 × 300 ml 5% HCl, giving a clear blood red aq. layer. This aq. layer was adjusted to *ca* pH 11 by addition of NH_4OH. The alkaloids liberated were extracted with 3 × 300 ml $CHCl_3$ to yield a crude alkaloid mixture (2.3 g). Flash chromatography (1% MeOH in $CHCl_3$) of this mixture afforded a fraction (0.9 g) which contained two partially overlapping spots on TLC (5% MeOH in $CHCl_3$). Prep. TLC on Al_2O_3 ($CHCl_3$) followed by HPLC (2% MeOH in $CHCl_3$) separated **1** and **2** in pure form. It should be noted here that on keeping in a stoppered flask for a couple of weeks, even in a refrigerator, a freshly purified sample of **2** (by HPLC) gradually turned to a dark brown mixture containing a small amount of **1** and other unidentifiable polar materials.

Dicentrinone (**1**). Crystallized from $CHCl_3$ as yellow needles, mp 297–299° (dec.); $C_{19}H_{13}O_5N$; MS m/z 335 $[M]^+$ (100), 310 (23), 304 (21), 292 (16), 277 (13), 264 (13); UV λ_{max}^{EtOH} nm (log ε):



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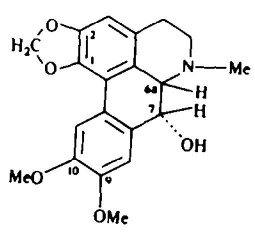

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211 (4.40), 249 (4.26), 271 (4.18), 308 (3.76), 349 (3.77), 388 (3.66), 433 (3.57); IR ν_{max}^{nujol} cm^{-1}: 1635 (s), 1590 (s), 1570 (s), 1510 (s), 1300 (s), 1270 (m), 1210 (m), 1130 (m), 1050 (s), 1020 (w), 1000 (m), 960 (s), 900 (w), 880 (m), 850 (m), 815 (w), 775 (m); ^{1}H NMR (CF_3COOH): δ4.16 (3H, *s*, OMe), 4.22 (3H, *s*, OMe), 6.71 (2H, *s*, OCH_2O), 7.56 (1H, *s*, H-3), 8.03 (1H, *s*, H-8), 8.29 (1H, *s*, H-11), 8.47 (1H, *d*, J = 6.4 Hz, H-4), 8.78 (1H, *d*, J = 6.4 Hz, H-5).

Dasymachaline (2). Amorphous; $C_{20}H_{21}O_5N$; $[\alpha]_D^{26}$ −47° ($CHCl_3$; *c* 0.34); MS *m/z*: 355 $[M]^+$ (100), 340 (33), 326 (16), 312 (44), 296 (14), 281 (9), 266 (9), 254 (13), 190 (53); UV λ_{max}^{EtOH} nm (log ε): 221 (4.37), 285 (4.12), 297 (4.07); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (br OH), 1605 (m), 1515 (s), 1460 (s), 1400 (m), 1380 (m), 1340 (m), 1300 (w), 1270 (s), 1245 (s), 1220 (s), 1090 (vs), 1050 (m), 1035 (w), 970 (w), 940 (m), 865 (m), 820 (w); ^{1}H NMR: δ2.17 (*br s*, exch. D_2O), 2.63 (3H, *s*, N–Me), 2.67–3.17 (4H, *m*, 2H-4, 2H-5), 3.23 (1H, *d*, J = 2.6 Hz, H-6a), 3.94 (6H, *s*, 2 × OMe), 4.83 (1H, *d*, J = 2.6 Hz, H-7, *s* on irradiation at 3.23), 5.94 and 6.09 (each 1H, *d*, J = 1.5 Hz, OCH_2O), 6.52 (1H, *s*, H-3), 6.96 (1H, *s*, H-8), 7.74 (1H, *s*, H-11).

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(+)-11-OXOCYTISINE, A LUPIN ALKALOID FROM LEAVES OF *SOPHORA SECUNDIFLORA*

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Key Word Index—*Sophora secundiflora*; Leguminosae; leaves; lupin alkaloid; quinolizidine alkaloid; (+)-11-oxocytisine; (−)-cytisine; (−)-*N*-methylcytisine; (−)-anagyrine; (−)-baptifoline.

Abstract—A new lupin alkaloid, (+)-11-oxocytisine (1), was isolated from the leaves of *Sophora secundiflora* together with (−)-anagyrine, (−)-*N*-methylcytisine, (−)-baptifoline, (−)-*N*-formylcytisine, (−)-*N*-acetylcytisine and (−)-cytisine. The structure of the new alkaloid (1) was presumed to be (+)-11-oxocytisine on the basis of its spectroscopic data.

INTRODUCTION

The seeds of *Sophora secundiflora* are commonly referred to as 'mescal beans', 'red beans' or 'dry whisky', and have been utilized as a divinatory medium for various ceremonial purposes by Indians of the Southwest United States and adjacent Mexico because of their purported hallucinogenic activity [1–3]. Previous phytochemical investigations on lupin alkaloids reveal that seeds harvested in America contain seven quinolizidine alkaloids, cytisine, *N*-methylcytisine, anagyrine, thermopsine, sparteine, Δ^5-dehydrolupanine and epilupinine [4–8]. Bourn *et al.* reported recently that the major alkaloids of the seeds, cytisine, *N*-methylcytisine and sparteine produced responses similar to those of the known hallucinogenic