



SHORT REPORTS

DESMOSINE, AN ARTEFACT ALKALOID FROM *DESMOS DUMOSUS**

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Key Word Index—*Desmos dumosus*; Annonaceae; flavonoid derived alkaloid.

Abstract—The alkaloid, desmosine, an artefact resulting probably from the action of NH_4OH on a flavone, was isolated from the bark of *Desmos dumosus*. Its structure was elucidated by 2D NMR experiments.
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INTRODUCTION

In the course of our research on Malaysian plants, particularly on alkaloids [1–4], we have investigated the alkaloidal extract of the bark of a species of the genus *Desmos* (Annonaceae), which is well known for its isoquinoline alkaloid content: *D. dumosus* (Roxb.) Safford. The plant material was collected from Air Hitam Reserve Forest in the Peninsula of Malaya. A novel alkaloid, desmosine (**1**), was isolated using the conventional alkaloid extraction method.

RESULTS AND DISCUSSION

Desmosine (**1**) exhibited a $[\text{M} + \text{H}]^+$ peak in the HRCI mass spectrum at m/z 298.1062 (Δ , –1.76 mmu) corresponding to the molecular formula $\text{C}_{17}\text{H}_{15}\text{NO}_4$. The orange colour of the alkaloid and the profile of the UV spectrum, which shows four maxima at 222, 256, 297 and 410 nm, suggested a highly conjugated system. In the IR spectrum, a band characteristic of a conjugated carbonyl function at 1646 cm^{-1} was observed. The ^1H NMR in $\text{DMSO}-d_6$ (Table 1) revealed two aromatic methoxyl singlets at δ 3.62 and 3.81, multiplets

representing five protons of a monosubstituted aromatic ring at δ 7.60 and 7.93 and two aromatic proton singlets at δ 6.26 and 6.84. In addition, two doublets ($J = 1\text{ Hz}$) at low field (δ 9.23 and 12.71) corresponded to an NH_2 group having one of the protons (NHb , δ 12.71) chelated by an hydrogen bond to the $\text{C}=\text{O}$ group. The ^{13}C NMR (Table 1) exhibited the resonances of the aromatic ring at δ 125.9, δ 129.1 (4CH) and 130.5, 131.8 (2C). The signal for the carbonyl appeared at δ 167.6 and those of the two methoxyl groups at δ 55.6 and δ 59.4. The two aromatic methines resonated at δ 82.9 (δ_{H} 6.26) and δ 96.6 (δ_{H} 6.84) as deduced from a HMQC spectrum. Four additional quaternary carbon signals appeared at low field, each bonded to a nitrogen or an oxygen atom at δ 135.2, 151.8, 160.3 and 160.6. Careful analysis of the HMBC spectrum (Fig. 1) led to structure **1** for desmosine. Particularly diagnostic were the correlations from H-8 to C-4, C-5, C-6, C-7, C-10 and from H-3 to C-2, C-4, C-10. The two NH_2 protons also correlated with their neighbouring carbons. Finally, the NOE correlations $\text{NHa}/\text{H}-3$, $\text{H}-3/\text{H}-2'$ and $7\text{-OMe}/8$ further confirmed the structure of desmosine **1**.

Due to its unusual structure, we suspected that alkaloid **1** was an artefact. Effectively, it was not obtained when ammonia, which was used in the alkaloid extraction method, was replaced by sodium carbonate. The structure of the alkaloid **1** appears to be derived from the known 5-hydroxy-6,7-dimethoxy-flavone (**2**) [5], which has been isolated

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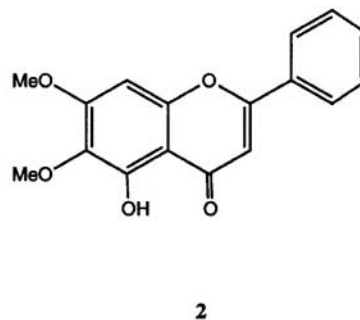
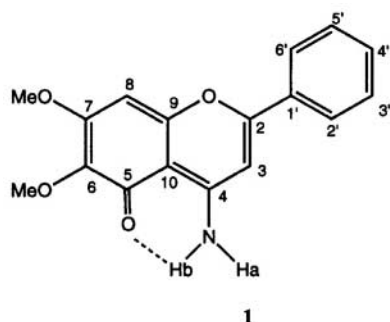


Table 1. ^{13}C (62.5 MHz) and ^1H (400 MHz) data for desmosine (**1**) in $\text{DMSO}-d_6$

Position	δC	δH (J, Hz)
2	160.3	
3	96.6	6.84 s
4	160.6	
5	167.6	
6	135.2	
7	157.9	
8	82.9	6.26 s
9	151.8	
10	100.1	
1'	130.5	
2', 6'	125.9	7.93 m
3', 5'	129.1	7.58 m
4'	131.8	7.60 m
6-OMe	59.4	3.62 s
7-OMe	55.6	3.81 s
NHa		9.23 d (1)
NHb		12.71 d (1)

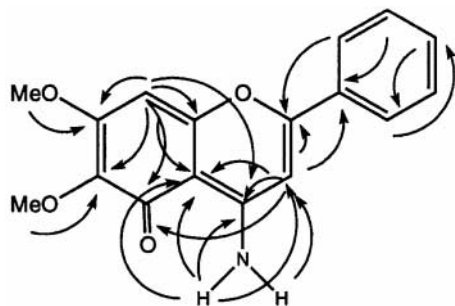


Fig. 1. HMBC correlations for desmosine (**1**).

in the neutral extract of the plant. Treatment of compound **2** with NH_4OH in a mixture of CH_2Cl_2 and methanol or with pure NH_4OH did not afford **1**. However, the exact conditions of the extraction complex medium, which have led to the formation of compound **1** from compound **2**, cannot be exactly reproduced, thus explaining the observed failure.

EXPERIMENTAL

General

UV: MeOH. IR: CHCl_3 . ^1H NMR: 250 or 400 MHz. ^{13}C NMR: 62.5 MHz. 2D experiments: 400 MHz. CC: Merck silica gel H 60.

Plant material

Bark of *D. dumosus* (Roxb.) Safford was collected from the Air Hitam Reserve Forest, Selangor (Malaysia). Voucher specimens (KL 3715) are deposited at the Herbarium of Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia and at the Herbarium of the Forest Research Institute, Kepong, Malaysia.

Extraction and isolation

Alkaloids were extracted by the classical method after alkanisation of the plant material with NH_4OH . A total of 2.38 g of crude alkaloids was obtained from the bark (250 g). The crude product (1 g) was subjected to cc on silica gel with CH_2Cl_2 containing increasing amounts of MeOH, yielding desmosine (**1**) (CH_2Cl_2 -MeOH 9:1, 25 mg). Cc of the neutral portion of the alkaloid extraction gave 5-hydroxy-6,7-dimethoxy-flavone (**2**) [5] (3 mg, eluent CH_2Cl_2).

Desmosine (**1**)

Orange crystals, m.p. 240°C (dec). UV λ_{max} nm (log ϵ) 222 (4.43), 256 (4.07), 297 (4.38), 410 (3.53). IR ν cm^{-1} 3450, 1646, 1600. HRCIMS m/z 298.1062 $[\text{M} + \text{H}]^+$ ($\text{C}_{17}\text{H}_{16}\text{NO}_4$, Δ , -1.76). ^1H and ^{13}C NMR: Table 1.

REFERENCES

- Awang, K., Païs, M., Sévenet, T., Schaller, H., Nasir, A. M. and Hamid, A. H. A., *Phytochemistry*, 1991, **30**, 3164.
- Awang, K., Sévenet, T., Hamid, A. H. A., David, D. and Païs, M., *Tetrahedron Letters*, 1992, **33**, 2493.
- Awang, K., Sévenet, T., Hamid, A. H. A. and Païs, M., *Journal Natural Products*, 1993, **55**, 1134.
- Awang, K., Thoison, O., Hamid, A. H. A., Païs, M. and Sévenet, T., *Natural Products Letters*, 1993, **3**, 283.
- Harborne, J. B., *The Flavonoids*. Chapman and Hall Publishers, London, 1992.