

AN ALKALOID FROM LEAVES OF *MELODINUS SCANDENS*

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Key Word Index—*Melodinus scandens*; Apocynaceae; 9-hydroxyepimelosine; 9-methoxyepimelosine.**Abstract**—A new alkaloid, 9-hydroxyepimelosine, was isolated by chromatography of the mother liquor after recrystallization of scandomelonine.

INTRODUCTION

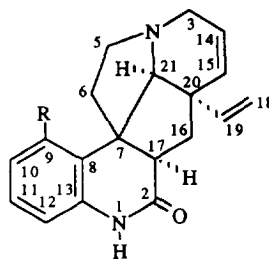
The isolation and structural determination of some monomeric and dimeric alkaloids from the leaves of *Melodinus scandens* Forst has been reported previously [1-6]. The mother liquor from the recrystallization of scandomelonine [3] was submitted to preparative TLC on Silica gel 60 and eluted with CH_2Cl_2 -MeOH (19:1) to give the new alkaloid, 9-hydroxyepimelosine (1).

The mass spectrum of 1 showed a $[\text{M}]^+$ at m/z 308 (found $[\text{M}]^+$ 308.3981) compatible with the empirical formula, $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$. The $[\alpha]_D$ was $+206^\circ$, (CHCl_3 , c 1) and its UV spectrum (EtOH) was analogous to that of epimelosine (2) [7], viz: λ_{max} : nm (log ϵ): 210 (4.34), 252 (4.01), 290 (3.6), but unlike 2, an important bathochromic shift was observed in a basic medium (24 nm). The IR, ^1H NMR and mass spectral data for 1 and 2 were compared. The IR spectrum of 1 showed a supplementary band at 3200 cm^{-1} , which could be assigned to the presence of an OH group. In its mass spectrum, peaks corresponding to the aromatic moiety were shifted up by 16 mu (Table 1), while other signals remain unchanged. In the ^1H NMR spectrum of 1, the signal of an aromatic proton (7.45 ppm, $J_1 = 7\text{ Hz}$, $J_2 = 2\text{ Hz}$ in 2) was missing, while a broad peak at 3.6 ppm (s), disappearing after D_2O exchange, was observed. These data are consistent with the presence of an OH group on the aromatic ring of epimelosine.

To support this hypothesis, 1 was methylated with CH_2N_2 in CH_2Cl_2 to give methoxyepimelosine (3). The ^1H NMR spectrum of 3 showed three adjacent aromatic protons at 6.78 (dd, $J_1 = 8\text{ Hz}$, $J_2 = 2.5\text{ Hz}$, 1H), 7.02 (t, $J = 8\text{ Hz}$, 1H) and 7.17 ppm (dd, $J_1 = 8\text{ Hz}$, $J_2 = 2.5\text{ Hz}$, 1H), respectively. This allows only two possibilities for the location of the group OH: C-9 or C-12.

Table 1. Mass spectral fragmentation pattern of compounds 1 and 2

	1	2
$[\text{M}]^+$	308	292
	279	263
	215	199
m/z	188	172
	175	159
Peaks in common: 134, 91, 77		



	R
1	OH
2	H
3	OCH ₃

Comparison of the ^{13}C NMR data for 3 and 2 [7, 8] (Table 2) led to the assignment of the OH group to C-9. In the ^{13}C NMR spectrum of 3, the signal at 116 ppm is assigned to C-12, as in 2 [8]. Accordingly, the C-9 signal at 112.3 ppm in 2 undergoes a downfield shift at 146.5 ppm in 3 due to the OH substitution and is now quaternary. Concomitantly, a β -effect of 11 and 13 ppm, respectively, is observable on C-8 and C-10. Until now,

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Table 2. Comparative ^{13}C NMR data for compounds 2 and 3

Carbon No.	Epimelosine (2)	Methoxy-9 epimelosine (3)
C-2	173 s	169 s
C-3	45.7 t	45.3 t
C-5	51.7 t	51.5 t
C-6	35.4 t	34.3 t
C-7	55.3 s	56.4 s
C-8	135.8 s	124.8 s
C-9	122.3 d	146.5 s
C-10	123.2 d	109.8 d
C-11	126.7 d	124.3 d
C-12	116.2 d	116 d
C-13	136.5 s	132.7 s
C-14	120.8 d	115.9 d
C-15	130.9 d	131.6 d
C-16	47.9 t	48 t
C-17	34.2 d	33.78 d
C-18	121.1 t	114.78 t
C-19	144.3 d	141.1 d
C-20	44.9 s	46.6 s
C-21	71.5 d	69 d
OCH ₃	—	55.7 q

only one phenolic alkaloid belonging to the quinolinone group has been reported, 10-hydroxyscandine [9].

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