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MUKONAL, A PROBABLE BIOGENETIC INTERMEDIATE OF PYRANOCARBAZOLE ALKALOIDS FROM *MURRAYA KOENIGII*

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Key Word Index—*Murraya koenigii*; Rutaceae; mukonal; carbazole alkaloid.

Abstract—Mukonal, a carbazole alkaloid has been isolated from *Murraya koenigii*. The structure of the compound has been established as 2-hydroxy-3-formyl carbazole based on physical (UV, IR, ^{1}H NMR, ^{13}C NMR and mass spectrometry) and chemical transformations.

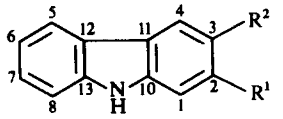
INTRODUCTION

Murraya koenigii is known to be the richest source of carbazole alkaloids so far reported [1]. The present investigation reveals the presence of a new carbazole alkaloid, mukonal, from the petrol extract of the stem bark of *M. koenigii*.

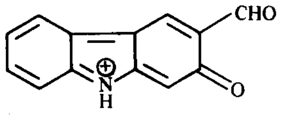
RESULTS AND DISCUSSIONS

Mukonal **1**, $C_{13}H_9NO_2$ $[M]^+$ *m/z* 211, mp 238° was homogeneous by TLC and mass spectrometry. It gave a 2,4-dinitrophenylhydrazone and reduced ammoniacal silver nitrate solution showing the presence of an aldehyde function. A deep blue colouration with ferric chloride indicated a chelated phenolic hydroxyl group. The UV spectrum of **1** ($\lambda_{\max}^{\text{EtOH}}$ nm: 234, 247, 278, 297 and 342 with log ε 4.42, 4.21, 4.54, 4.58 and 4.06) is characteristic of a 3-formyl carbazole [2]. The IR spectrum (KBr) showed absorption peaks at 3380 (OH or NH), 1640 (chelated aldehyde), 1610 and 1590 cm^{-1} (aromatic system).

The 100 MHz ^{1}H NMR spectrum (DMSO-d_6) displayed characteristic signals at δ 11.76 (1H, *s*, OH proton, exchangeable with D_2O), δ 11.0 (1H, *br s*, NH proton, exchangeable with D_2O), δ 10.16 (1H, *s*, CHO proton), δ 8.4 (1H, *s*, aromatic proton), δ 8.0–7.3 (4H, complex multiplet, aromatic proton) and δ 7.0 (1H, *s*, aromatic proton). The appearance of four protons in the region δ 8.0–7.3 as a complex multiplet suggests lack of substitution of one of the benzene rings of the carbazole moiety. The relatively deshielded singlet at δ 8.4 could be assigned to the C-4-H *ortho* to the aldehyde group. Since the C-4 proton is not *meta* coupled and the hydroxyl is chelated, the hydroxyl group could be located at C-2.



1 $R^1 = OH$, $R^2 = CHO$
2 $R^1 = H$, $R^2 = H$
4 $R^1 = OH$, $R^2 = H$
5 $R^1 = OAc$, $R^2 = CHO$
6 $R^1 = OH$, $R^2 = COOH$
7 $R^1 = OH$, $R^2 = COOMe$



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In the ^{13}C NMR of **1** (25.05 MHz; DMSO-d_6) (Table 1), the upfield shift of C-1 by 14.6 ppm and of C-11 by 5.6 ppm by comparison to the simple carbazole **2** is also suggestive of the presence of a hydroxyl group at position 2. The mass spectrum of **1** showed an $[M]^+$ at m/z 211. The base peak is at $[M-1]^+$ consistent with the presence of a phenolic hydroxyl group represented by the ionic species, **3**.

Mukonal, by decarbonylation [3] with Pd–C, forms 2-hydroxy carbazole (**4**), mp 278° [4]. On acetylation mukonal furnished an acetate **5**, mp 210°. Oxidation of **1** with active manganese dioxide furnished **6** mp 274°. Compound **6** on partial methylation furnished a compound **7** which was found to be identical with natural mukonidine [1]. The structure of mukonal has finally been confirmed by comparison with a synthetic specimen of 2-hydroxy-3-formyl carbazole prepared using our previous method [5]. The isolation of mukonal from *M. koenigii* is biogenetically significant. Popli and Kapil [6] suggested that 2-hydroxy-3-methyl carbazole plays a prominent role in the formation of pyranocarbazoles. Our isolation of mukonal provides strong circumstantial evidence for the above idea. The methyl group of 2-hydroxy-3-methyl carbazole has probably been oxidized to formyl in mukonal.

EXPERIMENTAL

All mps were uncorr. UV and IR spectra were recorded in EtOH and as KBr pellets, respectively.

Isolation of mukonal (**1**). Air dried finely powdered stem bark (1.5 kg) of *M. koenigii* Spreng were extracted with petrol (60–80°) in a Soxhlet for 36 hr. After extraction the solvent was distilled off and the residue taken up in C_6H_6 and chromatographed over silica gel. The column was eluted with petrol (60–80°), C_6H_6 and $CHCl_3$ in succession. From the C_6H_6 fraction a solid was obtained. This was recrystallized from C_6H_6–$CHCl_3$ yielding a homogeneous crystalline compound, mp 238°. It gave a red picrate on TLC (C_6H_6–$CHCl_3$, 1:1; R_f 0.31). Yield 0.001 %; (Found: C, 73.90; H, 4.27; N, 6.61 % Calculated for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63 %.)

2,4-Dinitrophenylhydrazone of **1**. Mukonal (20 mg) was dissolved in Me_2CO-free MeOH (10 ml) and to this was added a MeOH soln of 2,4-DNPH sulphate (0.25 %, 10 ml). An immediate red ppt was formed which was almost insoluble in all organic solvents. The compound did not melt even at 300°. (Found: C, 58.30; H, 3.31; N, 17.80 %. Calculated for $C_{19}H_{13}N_5O_5$: C, 58.31; H, 3.35; N, 17.90 %.)

Decarbonylation of mukonal and formation of **4**. Mukonal (40 mg) was mixed with Pd–C (20 mg) and heated in a sealed tube with 1 ml of dry EtOH for 15 min at 270° under vacuum. The residue obtained after removal of solvent from the EtOH extract of the reaction product, on crystallization from C_6H_6 furnished crystals of **4**, mp 278°. Yield 20 mg. The compound was soluble in alkali and gave a violet colour with alcoholic $FeCl_3$ soln. UV λ_{max}^{EtOH} nm (log ε): 235 (4.7), 258 (4.31), 303 (4.19); IR ν_{max}^{KBr} cm^{-1}: 3400, (OH), 3360, (NH) 1620, 1600 (aromatic). (Found: C, 78.61; H, 4.9; N, 7.59 %. Calculated for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65 %.)

Acetylation of mukonal and formation of **5**. To compound **1** (25 mg) Ac_2O (2 ml) and one drop of $HClO_4$ were added. It was kept in the dark overnight, then poured into crushed ice. The solid obtained was filtered and crystallized from C_6H_6. Yield 20 mg, mp 210°. UV λ_{max}^{EtOH} nm (log ε): 238 (4.45), 247 (4.29), 274 (4.50), 290 (4.56), 340 (4.16); IR ν_{max}^{KBr} cm^{-1}: 3380 (NH), 1750 (acetyl), 1650 (aldehyde), 1618, 1590 (aromatic). (Found: C, 71.10; H, 4.30; N, 5.48 %; Calculated for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53 %.)

Oxidation of **1** *to* **6**. A soln of **1** (50 mg) in CCl_4 with a suspension of freshly prepared active MnO_2 (500 mg) was stirred for 5 hr and filtered. On removal of solvent a solid was obtained, mp 274°. Yield 30 mg. (Found: C, 68.70; H, 3.91; N, 6.10 %; Calculated for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16 %.)

Partial methylation of **6** *to* **7**. Compound **6** (25 mg) in MeOH (5 ml) was refluxed in the presence of one drop of conc H_2SO_4 for 5 hr. The reaction mixture was poured into ice and treated with 5 % $NaHCO_3$ and extracted with Et_2O. After removal of solvent a solid residue was obtained which was recrystallized from C_6H_6, mp 244°. Yield 15 mg. It was found to be identical with natural mukonidine in all respects (mp, mmp, UV, IR).

Table 1. ^{13}C NMR of carbazole and mukonal

Carbazole		Mukonal	
Carbon no.	δ (ppm)	Carbon no.	δ (ppm)
1	110.9 (*d*)	1	96.3 (*d*)
2	118.4* (*d*)	2	160.0 (*s*)
3	120.1* (*d*)	3	115.7 (*s*)
4	125.4 (*d*)	4	124.9 (*d*)
10	139.7 (*s*)	5	125.5 (*d*)
		6	119.8* (*d*)
11	122.5 (*s*)	7	119.9* (*d*)
		8	111.1 (*d*)
		10	145.8 (*s*)
		11	116.9 (*s*)
		12	122.9 (*s*)
		13	140.7 (*s*)
		3-CHO	193.0 (*d*)

*Values interchangeable.

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