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MUKONICINE, A CARBAZOLE ALKALOID FROM LEAVES OF *MURRAYA KOENIGII*

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

Abstract—A new carbazole alkaloid, mukonicine, was isolated from the leaves of *Murraya koenigii*. From physical methods coupled with chemical evidence its structure was determined as 1,2-[2:2-dimethyl-Δ^3-pyrano]-3-methyl-6,8-dimethoxycarbazole.

In continuation of our investigations on the chemistry of carbazole alkaloids [1–4], we now wish to report the isolation and structural elucidation of a new carbazole alkaloid, mukonicine, from the leaves of *Murraya koenigii* Spreng.

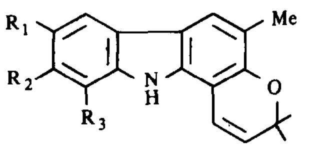
Mukonicine (**1**), $C_{20}H_{21}NO_3$, mp 233–234° was isolated from an alcoholic extract of the leaves of *M. koenigii* by column chromatography over alumina. The homogeneity of mukonicine was confirmed by TLC using various solvent systems. Its UV spectrum in EtOH with λ_{max} at 226 (log ε4.70), 240 (4.67) 300 (4.59) and 342 nm (4.26) was strikingly similar to that of koenimbine [5]. The IR spectrum of mukonicine showed absorption peaks at ν_{max}^{KBr} 3440 (–NH–), 1648 (–OMe), 1630, 1560, 1460 (aromatic residue), 1385 (C–Me) and 765, 745 cm^{-1} (substituted benzene derivative). The ^1H NMR spectrum of mukonicine (90 MHz in $CDCl_3$) showed signals for one indolic proton (*s*, δ7.81, confirmed by D_2O exchange), three aromatic protons at δ7.56 (*s*), 7.40 (*s*) and 6.88 (*s*), two olefinic protons 6.55 and 5.65 (pair of doublets), six protons of two aromatic OMe (*s*, δ3.9) and three protons of an aromatic C-Me group (*s*, δ2.3). The appearance of one of the aromatic protons as a singlet (δ7.56) clearly indicated that the position of the aromatic Me was at C-3 [5]. The signal for a C-5 proton at a higher field (δ7.40. shielded) showed that one of the two OMe groups was at C-6, similar to that of koenimbine [5]. The position of the second OMe group was fixed at C-8 on the basis that the C-7 proton appeared at a much higher field (δ6.88) than that of the C-5 proton. The signal for the six-proton singlet at δ1.44 together with symmetrical doublets at δ6.55 and 5.65 ($J = 9$ Hz each) suggested the presence of a 2:2-dimethyl-Δ^3-pyran ring fused with a carbazole skeleton.

Mukonicine showed a $[M]^+$ at *m/z* 323. The most important peak appeared at *m/z* 308 $[M-15]^+$, which is the base peak. The peak at *m/z* 308 was very similar to that of mahanimbine and girinimbine and can be represented by species **2**. This also supports the presence of a 2:2-dimethyl-Δ^3-pyran system in mukonicine. The 3-methyl carbazole skeleton of mukonicine was confirmed by the isolation of a 3-methyl carbazole after zinc dust distillation of mukonicine. Further proof for the presence of a 2:2-dimethyl-Δ^3-pyran ring was provided by chromic acid oxidation, when acetone was obtained.

On the basis of the above evidence the structure of mukonicine can be represented by **1**. Moreover, mukonicine was found to be quite different from koenigicine (**3**) [6, 7].

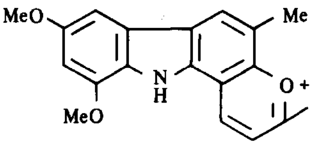
EXPERIMENTAL

All mps are uncorr. UV and IR spectra were recorded in EtOH and as KBr pellets, respectively. ^1H NMR were measured at



1 $R_1 = R_3 = -OMe, R_2 = H$

3 $R_1 = R_2 = -OMe, R_3 = H$



2

90 MHz in $CDCl_3$ with TMS as int. standard.

Isolation of mukonicine. Defatted leaves were extracted with EtOH. The conc. extract was digested with 10% HCl for 3 hr, the soln filtered, the residue washed with H_2O until acid-free and then dried. The dark green residue was extracted with C_6H_6 and the extract concd and chromatographed over Al_2O_3. The column was successively eluted with petrol, C_6H_6 and $CHCl_3$. Mukonicine was obtained from the C_6H_6 eluate and crystallized from C_6H_6–$CHCl_3$, mp 233–234°. TLC on Si gel G and C_6H_6–$CHCl_3$ (1:1), R_f 0.46 (Found: C, 74.18; H, 6.62; N, 4.62. Calc. for $C_{20}H_{21}NO_3$: C, 74.23; H, 6.55; N, 4.33%.)

Zn *dust distillation.* The product was obtained from mukonicine on distillation with Zn dust and subsequent crystallization from petrol–C_6H_6 (1:1) mp 206–207°. It was identical with 3-methyl carbazole in all respects (mp, mmp., UV and TLC). (Found: C, 86.06; H, 6.21; N, 7.68. Calc. for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73%.)

Chromic acid oxidation. Mukonicine (25 mg) dissolved in HOAc (10 ml) was treated with CrO_3 in HOAc (0.1 g in 5 ml) with constant stirring. The reaction mixture was kept at room temp. for 72 hr. It was then neutralized with 50% aq. NaOH soln and steam-distilled. The distillate was collected in a flask containing a freshly prepared aq. soln of 2,4-dinitrophenyl hydrazine sulphate, when a flocculent ppt. appeared. It was then extracted with CCl_4, the extract washed with H_2O and dried (Na_2SO_4). On removing the solvent, yellow crystals were obtained which were dissolved in C_6H_6 and chromatographed over Al_2O_3. The column was successively eluted with petrol, petrol–C_6H_6 (1:1) and C_6H_6. In the petrol–C_6H_6 eluate, a yellow solid was obtained which was crystallized from MeOH, mp 125–126°. This compound was found to be identical with an authentic sample of the 2,4-dinitrophenyl hydrazone of Me_2CO.

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