

STRUCTURE OF THE CARBAZOLE ALKALOID ISOMURRAYAZOLINE FROM *MURRAYA KOENIGII*

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(Revised received 26 February 1982)

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

Abstract—The structure of a new hexacyclic carbazole alkaloid from *Murraya koenigii* has been shown to be 9a,10,11,12,13a-hexahydro-5,9,9,12-tetramethyl-1,12-epoxy-9H-indolo-(3,2,1-de)phenanthridine.

In connection with our studies on molecular ecology in relation to secondary plant constituents, we were further interested to examine the stem bark of *Murraya koenigii*. We now report the structure of a new carbazole alkaloid isomurrayazoline. Isomurrayazoline (**1a**), $C_{23}H_{25}NO$ (M^+ 331), mp 269–270° is an optically active, $[\alpha]_D^{CHCl_3} - 7.33^\circ$, neutral, homogeneous compound with a carbazole skeleton. The UV spectrum of **1a** (λ_{max}^{EtOH} nm: 240, 253, 258, 303 and 330 nm with $\log \epsilon$ 4.65, 4.15, 4.08, 3.85 and 3.47) showed the presence of a 2-oxygenated carbazole chromophore [1]. Since the IR spectrum of **1a** ($\nu_{max} cm^{-1}$: 1605, 1645, 1380, 1375, 888 and 810) showed the lack of a NH function, this functional group on the carbazole skeleton was substituted.

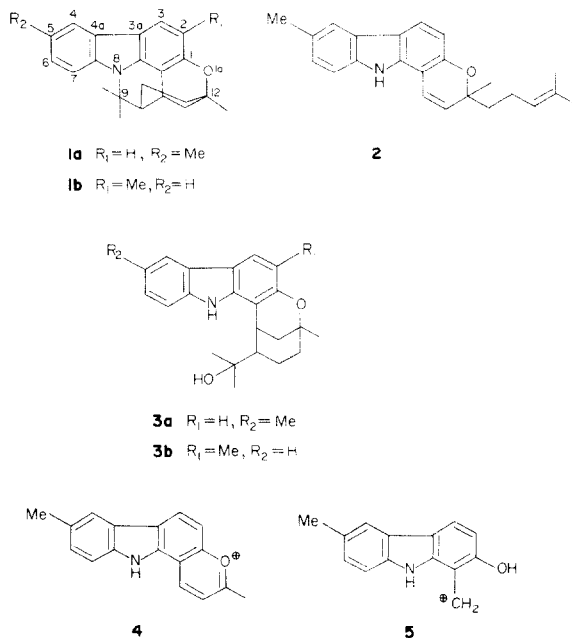
The 1H NMR spectrum of **1a** (90 MHz in $CDCl_3$) showed signals for five aromatic protons [δ 7.95 (1H, *m*), 7.55 (2H, unresolved doublet), 7.13–7.33 (2H, *m*)] very similar to those of isomahanimbine [2] (**2**). The 1H NMR spectrum also showed signals for one benzylic proton [δ 3.3 (1H, *m*)], one aromatic methyl group [δ 2.35 (3H, *s*)], one *gem*-dimethyl group [δ 1.92 (6H, *s*)], one aliphatic methyl group [δ 1.29 (3H, *s*) and a seven proton multiplet at δ 1.47 for six methylene protons plus the cyclohexane ring methine proton. The 1H NMR data thus indicated the presence of a 6-methylcarbazole skeleton similar to that of isomahanimbine (**2**) together with a fused monoterpene system similar to murrayazoline [3] (**1b**).

The mass spectrum of **1a** showed a strong M^+ at m/z 331 [M] $^+$ (100) and another at 316 [$M - 15$] $^+$ (79.26). The peaks at m/z 248 (51.22) and 210 (7.31) could be represented by the carbazopyrylium ion (**4**) and the ionic species (**5**), respectively. Evidently the mass spectra of **1a** and murrayazoline (**1b**) are very similar.

Like **1b**, **1a** under acid-catalysed (80% aq. acetic acid) hydration [4] gave a hydroxy derivative (**3a**) which we have named isomurrayazolinine. This compound (**3a**), $C_{23}H_{27}NO_2$, M^+ 349, mp 159°, showed IR absorption bands at 3550 and 3290 cm^{-1} (originally absent in isomurrayazoline) indicating the presence of OH and NH functions, respectively, which in turn

indicated the addition of the elements of water to **1a**. The UV spectrum of **3a** (λ_{max}^{EtOH} nm: 240, 253, 258, 304 and 330 with $\log \epsilon$ 4.60, 4.12, 4.07, 3.87 and 3.52) still indicated the presence of a 2-oxygenated carbazole chromophore.

The 1H NMR spectrum of **3a** (90 MHz in $CDCl_3$) showed signals for five aromatic protons [δ 7.75 (1H, *m*), 7.2–7.5 (4H, *m*)] similar to **1a**. The appearance of a NH signal at δ 8.00 (1H, *m*) and an OH signal at δ 1.68 (1H, *s*), which disappeared on D_2O exchange, confirmed the breaking of the C–N bond. Other signals were located for one benzylic proton [δ 3.83 (1H, *m*)], one aromatic methyl group [δ 2.35 (3H, *s*)], six methylene protons plus the cyclohexane ring methine proton [δ 1.48 (7H, *m*)] and one aliphatic methyl group [δ 1.31 (3H, *s*)]. The three proton singlets at δ 1.90 were attributed to one of the methyl groups of the *gem*-dimethyl function, while the signal at δ 0.53 (3H, *s*)



was attributed to the other methyl group of the *gem*-dimethyl function. This methyl group is highly shielded probably by the aromatic ring current effect. Similar shielding is well known, e.g. the central methylene groups of (1, 8)-paracyclophane [5] are shielded by δ 1 more than ordinary methylene groups because they are held rigidly above the plane of the benzene rings. The benzylic proton signals of **1a** have experienced a downfield shift (δ 0.53) after hydration. A similar downfield shift (δ 0.38) was observed when **1b** was hydrated to **3b**. Such shifts are indeed observed in chromenes carrying a OH function at C-5 [6]. In the present case the downfield shift was explained by placing the carbazole nitrogen in a similar position with respect to the benzylic CH group. The hydration is also supported by the mass spectrum of **3a** 349 $[M]^+$ (100), which showed peaks at m/z 331 $[M - 18]^+$ (43.77), 316 $[M - 18 - 15]^+$ (75.9), 248 (69.88), 210 (65.06) and 59 $(\text{C}^+ = \text{OH})$ (6.02).

Considering the close similarity of the physical properties of isomurrayazoline (**1a**) with those of murrayazoline (**1b**) and the same for isomurrayazolinine (**3a**) and murrayazolinine (**3b**) [7], structure **1a** is assigned to isomurrayazoline.

EXPERIMENTAL

Isolation of 1a. 2 kg air-dried finely powdered stem bark of *M. koenigii* Spreng. were Soxhlet extracted for 24 hr with C_6H_6 . The solvent was distilled off and the residue dissolved in C_6H_6 and chromatographed over neutral Al_2O_3 . The petrol (60–80°) eluent on repeated crystallization gave a solid. This was recrystallized from $\text{C}_6\text{H}_6\text{-CHCl}_3$ yielding homogeneous colourless crystals, mp 269–270° which gave a red picrate on

TLC ($\text{C}_6\text{H}_6\text{-CHCl}_3$, 1:1; R_f 0.91). (Found: C, 83.40; H, 7.65; N, 4.21%. Calc. for $\text{C}_{23}\text{H}_{25}\text{NO}$: C, 83.34; H, 7.6; N, 4.23%.)

Isomurrayazolinine (3a). Isomurrayazoline (50 mg) in 80% aq. HOAc (30 ml) was heated at 100° for 10 hr. HOAc was then removed by heating at 100° keeping the vol. constant by adding H_2O . Finally H_2O was removed and the residue dried in a vacuum oven at 50°. The dried residue was dissolved in CHCl_3 , which on prep. TLC gave pure crystals of isomurrayazolinine, $\text{C}_{23}\text{H}_{27}\text{NO}_2$, M^+ 349, mp 159°. Yield 27 mg. (Found: C, 79.00; H, 7.76; N, 4.00%. Calc. for $\text{C}_{23}\text{H}_{27}\text{NO}_2$: C, 79.05; H, 7.80; N, 4.05%.)

Acknowledgements—We express our thanks to Professor S. C. Bhattacharyya, Director and to Professor A. Sen, Head of the Dept. of Chemistry, Bose Institute, for their interest in this work. Partial financial assistance from DST, India is gratefully acknowledged.

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