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ON THE STRUCTURES OF GIRINIMBINE, MAHANIMBINE, ISOMAHANIMBINE, KOENIMBIDINE AND MURRAYACINE*

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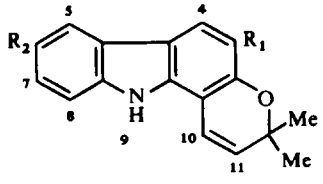
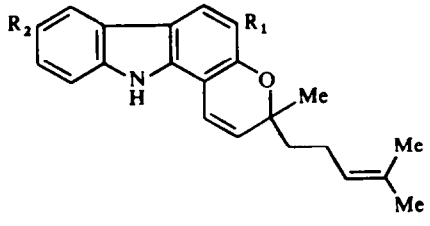
Abstract—The isolation of mahanimbine, girinimbine and two new carbazole alkaloids isomahanimbine and koenimbidine from the leaves and roots of *Murraya koenigii* Spreng. is reported. Spectroscopic and degradative evidence has been presented supporting structures for girinimbine (**3**), mahanimbine (**4**), isomahanimbine (**13**), koenimbidine (**17**) and murrayacine (**12**).

THE isolation of the carbazole alkaloids girinimbine,[1] mahanimbine[2] and murrayacine[3] from *Murraya koenigii* Spreng., has been reported by Chakraborty *et al.* They proposed the structure **1** for girinimbine,[4,5] **2** for murrayacine,[3] and a partial structure for mahanimbine.[2] Dutta and Quassim[6] have proposed a different structure **3** for girinimbine and Narasimhan *et al.*[7] have formulated mahanimbine as **4**.





1: R_1 = H; R_2 = Me
2: R_1 = H; R_2 = CHO
3: R_1 = Me; R_2 = H
12: R_1 = CHO; R_2 = H
16: R_1 = Me; R_2 = OMe

4: R_1 = Me; R_2 = H
13: R_1 = H; R_2 = Me

The present work deals with the isolation and structure elucidation of the two previously described alkaloids mahanimbine, girinimbine and two new alkaloids designated as isomahanimbine and koenimbidine. Mahanimbine, isomahanimbine $C_{23}H_{25}NO$ m.p. 142°, koenimbin[7] and koenimbidine $C_{20}H_{21}NO_3$ m.p. 225° were isolated by chromatographic separation of the hexane extract of the leaves of *Murraya koenigii* Spreng. and girinimbine was isolated from the roots. Dutta's structure for girinimbine (**3**) was solely based on NMR spectral evidence whereas Chakraborty *et al.* proposed the structure **1** mainly on the following degradative evidence.[4] Girinimbine on ozonolysis gave a methyl hydroxycarbazole-1-carbaldehyde $C_{14}H_{11}NO_2$ m.p. 193° which on decarbonylation provided the corresponding methyl hydroxy-

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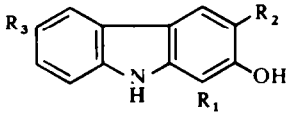
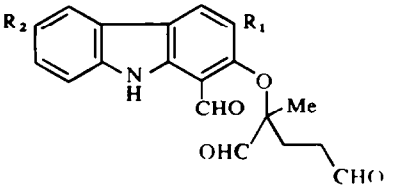
carbazole m.p. 242°. These compounds were assigned the structures **5** and **6** respectively, although no proof was given for the position of the Me group. Narasimhan's structure for mahanimbine was based on NMR spectral evidence and ozonoloysis of **4** to give a phenolic aldehyde $C_{14}H_{11}NO_2$, m.p. 193–194°.





5: R_1 = CHO; R_2 = H; R_3 = Me
6: R_1 = H; R_2 = H; R_3 = Me
7: R_1 = H; R_2 = Me; R_3 = H

8; $R_1 = CH_2—N(Me)(Me)$; R_2 = H; R_3 = H

9: R_1 = Me; R_2 = H; R_3 = H
10: R_1 = CHO; R_2 = Me; R_3 = H

11: R_1 = Me; R_2 = H
15: R_1 = H; R_2 = Me

By the ozonolysis of mahanimbine, we obtained a phenolic aldehyde m.p. 195° along with a neutral compound $C_{20}H_{19}NO_4$ m.p. 215°. The phenolic compound showed typical UV spectrum of carbazole-1-carbaldehyde[8] and showed in its NMR spectrum an aldehyde proton at δ 10·6 (s), a chelated OH at δ 11·6 (s), three aromatic protons in the region δ 7·0–7·5 due to H-6, H-7, H-8 and two downfield protons due to H-4 at δ 7·98 (s), H-5 at δ 7·8 (m) and an aromatic Me group at δ 2·3. The phenolic aldehyde on decarbonylation by heating with Pd/C[9, 10] gave methyl hydroxycarbazole m.p. 243° identical with an authentic sample of 2-hydroxy-3-methyl carbazole (**7**) in its mixed m.p. TLC and IR spectra. Since compound **7** has not been reported, attempts were made to prepare the same from 2-hydroxycarbazole. The Mannich reaction with formaldehyde and dimethylamine gave the compound (**8**) which on catalytic reduction provided **9**. The structures **8** and **9** were supported by the NMR spectrum which exhibited an AB spectrum at δ 6·7 and 7·65 (J = 8 c/s) due to H-3 and H-4 protons. The Vilsmeier-Haak reaction on 2-hydroxycarbazole gave apart from 2-hydroxycarbazole-1-carbaldehyde and 2-hydroxycarbazole-3-carbaldehyde which have been described earlier,[11, 12] another isomer m.p. 210°. 2-Hydroxycarbazole-3-carbaldehyde on Huang-Minlon reduction gave 2-hydroxy-3-methyl carbazole (**7**). This confirms the formulation of mahanimbine as **4**, and the phenolic aldehyde as **10**. The neutral compound has been assigned the structure **11** on the basis of elemental analysis, UV, IR and NMR spectra. The NMR spectrum shows an aromatic Me at δ 2·45, a tertiary Me at δ 1·48 and three aldehydic protons at δ 9·7 (s), 9·6 (s) and 10·6 (m). A sample of the phenolic aldehyde obtained by the ozonolysis of girinimbine* was found to be identical in its mixed m.p., TLC and IR spectra with the aldehyde (**10**) obtained from mahanimbine. Girinimbine should therefore be formulated as **3**. The structure **2** for murrayacine was based on the conversion of dihydromurrayacine with LAH to give a compound identical with dihydrogirinimbine. Since the structure of girinimbine needs revision from **1** to **3**, it would follow that murrayacine should be constituted as **12**.

* Kindly furnished by Dr. D. P. Chakraborty to whom our thanks are due.

The UV spectrum of isomahanimbine shows close resemblance to that of mahanimbine, indicative of a carbazole skeleton. It showed an NH group (ν – 3440 cm^{-1}) and formed an N-Me derivative. Reduction with Pd/C gave a tetrahydro derivative which exhibited a UV spectrum similar to 2-methoxycarbazole.[13] This allows the placement of the only oxygen function in isomahanimbine at the 2-position. The NMR spectrum (Fig. 1) revealed the attachment of a geranyl side chain oxidatively cyclized

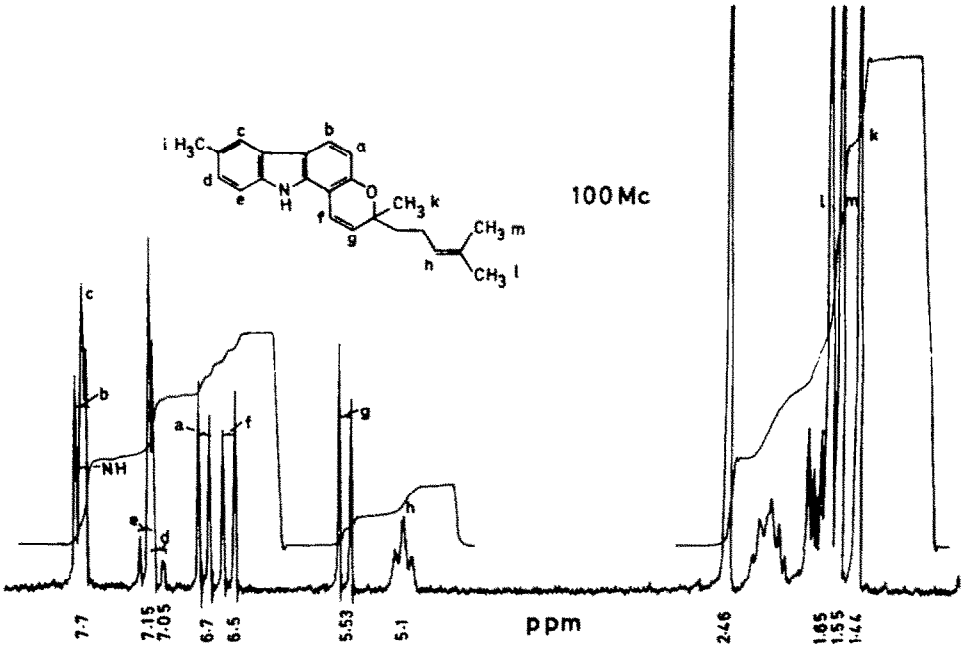


FIG. 1 NMR Spectrum of isomahanimbine.

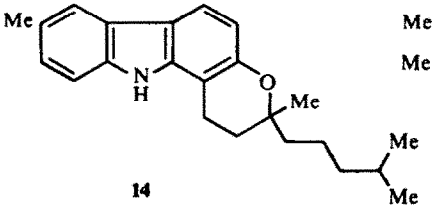
through the oxygen function at the 2-position of the carbazole nucleus as in mahanimbine. The Me region of the spectrum showed an aromatic Me at δ 2·46, *gem* dimethyls on a double bound at δ 1·55, 1·65 and a tertiary Me adjacent to the other oxygen as a sharp singlet at δ 1·44. Four protons due to two methylene groups appeared as a complex multiplet between δ 1·7–2·4 and the olefinic proton was a triplet at δ 5·1. In mahanimbine and isomahanimbine the NMR spectrum of the C-10 residue closely resembles the chromene ring and the isoprenic chain of Flemingins A, B and C,[14] gambogic acid[15] and cannabichromene.[16,17] The N-Me derivatives of girinimbine and mahanimbine showed a downfield shift of the N-Me group by about 0·3 ppm as compared to N-methylcarbazole as well as the C_{10} proton by approximately 0·6 ppm (Table 1). In both these compounds, the Δ^3-pyran is angularly attached to the carbazole nucleus. The mutual low field shifts could be attributed to Van der Waals deshielding effect[18] and appeared to be diagnostic in determining the angular fusion of the Δ^3-pyran ring to the carbazole nucleus. N-Methylisomahanimbine similarly showed a deshielding of the N-Me group as well as the C-10 proton. The C-3 and C-4 protons appeared as an AB quartet at δ 6·7 and 7·7 (J = 8·5 c/s). The C-5 proton appeared as a slightly broad singlet at δ 7·68 and the NH proton at δ 7·65 was masked by the other protons. However, on addition of benzene, this showed an upfield shift.

The AB spectrum at δ 7·05 (J = 8 c/s and 1 c/s) and δ 7·15 (J = 8 c/s) could be assigned to the C-7 and C-8 protons respectively. The above evidence indicates structure **13** for isomahanimbine.

TABLE 1.

Compound	Chemical shift (δ)		
	C-10 proton doublet; J = 10 c/s	C-11 proton doublet; J = 10 c/s	N—CH_3
Mahanimbine (**4**)	6·46	5·51	
N-Methylmahanimbine	7·11	5·58	3·9
N-Ethylmahanimbine	7·05	5·65	
Girinimbine (**3**)	6·5	5·6	
N-Methylgirinimbine	7·1	5·6	3·9
Isomahanimbine (**13**)	6·5	5·53	
N-Methyl isomahanimbine	7·11	5·58	3·9
Koenimbidine (**17**)	6·78	5·63	
N-Methylkoenimbidine	7·22	5·7	3·9

NMR spectrum of tetrahydroisomahanimbine (**14**) supported the above formulation. The signals due to C-10, C-11 protons and the olefinic proton had disappeared.



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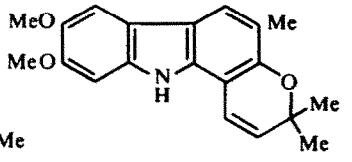

17

A triplet due to the benzylic methylene appeared at δ 2·7, and the AB spectrum due to C-7, C-8 protons showed a better resolved quartet centred at δ 7·15.

Ozonolysis of isomahanimbine provided a phenolic compound m.p. 198–200° showing characteristic UV spectrum of 1-formyl carbazole. A comparison of its TLC, mixed m.p. and IR spectra with the phenolic aldehyde (**10**) obtained from mahanimbine showed it to be different. This aldehyde should therefore be formulated as **5**. A neutral compound m.p. 294–295° isolated from the ozonolysis has been assigned the structure **15**.

Koenimbidine exhibited a UV spectrum closely similar to that of koenimbin (**16**).[7] It formed a dihydro derivative m.p. 237°, the UV spectrum of which resembled dihydrokoenimbin indicating the reduction of the pyran double bond. The NMR spectrum shows the following peaks: A sharp singlet at δ 1·49 (6H) and the doublets at δ 5·63 and 6·78 (each 1H: J = 10 c/s) are typical of a 2,2-Dimethyl chromene system.[19,20] The sharp singlet at δ 2·3 (3H) is due to the aromatic Me group. Two OMe's appeared at δ 3·9 and the presence of three aromatic singlet protons at δ 7·53, 7·4 and 6·9 could be assigned to the C-4, C-5 and C-8 protons respectively. As in the case of other angularly fused Δ^3 pyranocarbazoles, N-methylkoenimbidine showed deshielding of the N-Me and the C-10 proton (Table 1). Koenimbidine should therefore be formulated as **17**.

EXPERIMENTAL

UV and IR spectra were determined on Beckman DK-2A and Perkin–Elmer infracord spectrophotometers. NMR were taken on Varian A-60 or HA-100 spectrophotometers in $CDCl_3$ solution with TMS as internal reference. M.ps are uncorrected.

Isolation of mahanimbine (**4**), *isomahanimbine* (**13**) *koenimbine* (**16**) *and koenimbidine* (**17**). The dried, powdered leaves collected in the local market (9·5 kg) were extracted with hexane (30 l. × 3) at room temp. The extracts were combined and the solvent was removed under reduced press. The waxy residue (200 g) was dissolved in benzene (1 l.) and chromatographed on Sigel (2 kg; 0·2–0·5 mm) in benzene. The eluted fractions (100 ml) were collected and the progress of the chromatogram followed by TLC.

Fractions 19–25 (eluent: benzene) were combined and the solvent distilled off. The residue on crystallization from hexane gave mahanimbine (4 g), m.p. 93°; $[\alpha]_D$ +40·6° (*c*, 2·1; $CHCl_3$) UV (EtOH) λ_{max} 223, 239, 288, 330 and 343 mμ (log ε 4·55, 4·66, 4·61, 3·90 and 3·42); IR (Nujol): 3320, 1640, 1600, 1325, 1250, 1220, 1200, 1155, 1140, 1110, 1080, 1055, 1025, 900, 890, 878, 840, 750 and 745 cm^{-1}. (Found: C, 83·9; H, 7·7. Mol. wt. by mass spectrum 331. Calc. for $C_{23}H_{25}NO$: C, 83·3; H, 7·6%; Mol. wt. 331).

Fractions 26–34 (eluent: benzene) gave **13** which crystallized from CH_2Cl_2–hexane (900 mg) m.p. 142°; $[\alpha]_D$ −6° (*c*, 2·1; $CHCl_3$) UV (EtOH) λ_{max} 225, 238, 281, 290, 335 and 354 mμ (log ε 4·54, 4·69, 4·39, 4·72, 3·89 and 3·87); IR (Nujol); 3440, 3410, 1638, 1600, 1580, 1338, 1300, 1230, 1210, 1195, 1170, 1095, 1040, 910, 885, 820, 805, 800, 745 and 718 cm^{-1}. (Found: C, 83·4; H, 7·8; N, 4·5. Mol. Wt. by mass spectrum 331. $C_{23}H_{25}NO$ requires: C, 83·3; H, 7·6; N, 4·2%. Mol. wt. 331).

Fractions 51–60 (eluent: benzene–$CHCl_3$ 1:1) gave a residue which on crystallization from $CHCl_3$–hexane gave **16** (75 mg), m.p. 193°; UV (EtOH) λ_{max} 230, 237, 297, and 336 mμ (log ε 4·61, 4·62, 4·43 and 3·87); IR (KBr): 3410, 2970, 2910, 1640, 1610, 1580, 1490, 1460, 1420, 1400, 1380, 1360, 1340, 1295, 1285, 1260, 1250, 1210, 1188, 1140, 1125, 1110, 1055, 1020, 975, 930, 890, 875, 845, 805, 775, 765, 745, 720 and 680 cm^{-1}.

Fractions 124–220 (eluent: $CHCl_3$) gave **17** which crystallized from EtOH (900 mg), m.p. 225°; UV (EtOH) λ_{max} 223, 238, 290, 299 and 342 mμ (log ε 4·61, 4·59, 4·38, 4·54 and 3·99); IR (Nujol): 3420, 1640, 1620, 1600, 1480, 1400, 1340, 1290, 1270, 1240, 1205, 1190, 1180, 1155, 1125, 1115, 1055, 1030, 990, 875, 863, 820, 780, 765, 740 and 720 cm^{-1}. (Found: C, 74·2; H, 6·7; N, 4·4. Mol. wt. by mass spectrum 323. $C_{20}H_{21}NO_3$ requires: C, 74·3; H, 6·6; N, 4·3%. Mol. wt. 323).

Isolation of girinimbine (**3**). The dried, powdered roots (5 kg) were extracted by percolation with cold hexane (45 l). The residue (65 g) obtained on evaporation of the solvent was dissolved in hexane (100 ml) and chromatographed on Sigel (0·05–0·2 mm, 300 g) in hexane. 100 ml fractions were collected and the progress of the chromatogram followed by TLC.

Fractions 7–10 (eluent: benzene) gave an oily residue, which on crystallization from $CHCl_3$–hexane gave **3** (1 g), m.p. 175°; UV (EtOH) λ_{max} 222, 237, 278(∼), 287, 314(∼), 328, 242, and 358 mμ (log ε 4·54, 4·65, 4·37, 4·59, 3·76, 3·87, 3·89 and 3·84); IR (Nujol): 3290, 1620, 1580, 1480, 1380, 1315, 1305, 1235, 1220, 1200, 1185, 1170, 1150, 1140, 1115, 1050, 1020, 975, 950, 935, 920, 895, 875, 865, 805, 780, 750, 735, 720 and 680 cm^{-1}. (Found: C, 81·8; H, 6·5; N, 5·5. Calc. for $C_{18}H_{17}NO$: C, 82·1; H, 6·5; N, 5·3%).

N-Methylgirinimbine. A soln of girinimbine (260 mg) in acetone (5 ml) was shaken for 15 min with NaOH (0·5 g/1 ml H_2O), and then for a further 15 min after the addition of Me_2SO_4 (1 ml). The reaction mixture was allowed to stand at room temp overnight and then diluted with ice. The ppt so obtained was filtered, washed, dried and crystallized from EtOH (140 mg), m.p. 150°; UV (EtOH): λ_{max} 239, 290, 328, 345 and 360 mμ (log ε 4·70, 4·68, 3·87, 3·86 and 3·84; IR (Nujol); 1620, 1600, 1580, 1560, 1460, 1390, 1340, 1320, 1280, 1240, 1210, 1195, 1160, 1150, 1125, 1060, 1050, 1020, 1010, 975, 940, 910, 900, 865, 750, 740, 715, 660 and 620 cm^{-1}. (Found: C, 82·3; H, 7·1; N, 5·2. $C_{19}H_{19}NO$ requires: C, 82·2; H, 6·9; N, 5·0%).

Tetrahydromahanimbine. Mahanimbine (331 mg) was dissolved in EtOH (40 ml) and hydrogenated at 29° using 5% Pd/C 0·4 g) as catalyst. The reaction was stopped when there was no more absorption of H_2. After filtration, the solvent was removed and the residual gum crystallized from pentane (120 mg) m.p. 110°; UV (EtOH) λ_{max} 215, 241, 253, 304, and 330 mμ (log ε 4·49, 4·65, 4·38, 4·21 and 3·64); IR (Nujol): 3420, 1620, 1310, 1220, 1160, 1055, 900, 875, 805, 765 and 750 cm^{-1}. (Found: C, 82·6; H, 8·9. Calc. for $C_{23}H_{29}NO$: C, 82·3; H, 8·7%).

N-Methylmahanimbine. A soln of mahanimbine (500 mg) in acetone (7 ml) was shaken with NaOH (0·8 g in 1·5 ml H_2O) for 15 min and then for a further 15 min after the addition of Me_2SO_4 (1 ml). After allowing it to stand at room temp for 2 hr the reaction mixture was diluted with ice. The ppt thus obtained was collected by filtration, washed, dried and crystallized from EtOH to give colourless needles (225 mg), m.p. 120°; UV (EtOH) λ_{max} 239, 291, 330, 346 and 360 mμ (log ε 4·59, 4·50, 3·68, 3·69 and 3·68); IR (Nujol):

1630, 1605, 1590, 1400, 1320, 1270, 1225, 1210, 1165, 1135, 1120, 1090, 1070, 1050, 1020, 980, 930, 910, 878, 850, 822, 742, 718, 685 and 660 cm^{-1}. (Found: C, 83·4; H, 8·0; N, 3·9. $C_{24}H_{27}NO$ requires: C, 83·4; H, 7·8; N, 4·0%).

N-Ethylmahanimbine. A soln of mahanimbine (660 mg) in acetone (20 ml) was shaken with NaOH (1 g in 2 ml H_2O) for 15 min and then refluxed with EtI (2 ml) for 12 hr. The reaction mixture was diluted with ice and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over anhyd Na_2SO_4 and the solvent distilled off. The resulting gummy residue was twice crystallized from EtOH (70 mg), m.p. 96°; UV (EtOH): λ_{max} 240, 292, 330, 347 and 360 mμ (log ε 4·64, 4·63, 3·80, 3·82 and 3·77); IR (Nujol): 1620, 1600, 1580, 1560, 1320, 1300, 1210, 1195, 1195, 1175, 1150, 1130, 1110, 1085, 1060, 1050, 1020, 980, 940, 910, 880, 775, 740, 710, 685 and 665 cm^{-1}. (Found: C, 83·8; H, 8·3; N, 4·0. $C_{25}H_{29}NO$ requires: C, 83·5; H, 8·1; N, 3·9%).

Ozonolysis of mahanimbine to obtain the compounds **10** *and* **11**

Mahanimbine (2·5 g) dissolved in $CHCl_3$ (100 ml) was ozonised at 0° until a positive test with KI-starch paper was just obtained. The solvent was removed under reduced press. Water (100 ml), AcOH (4 ml) and a small amount of Zn dust were added to the residue and the mixture heated in a water-bath for 45 min. It was cooled, extracted with ether and the ether soln worked up into (1) phenolic (300 mg) and (ii) neutral (1·6 g) fractions.

(i) The phenolic product was carefully chromatographed on Sigel (0·05–0·2 mm). Elution with benzene–$CHCl_3$ (1 : 1) gave a yellow crystalline ($CHCl_3$–hexane) compound **10** (90 mg), m.p. 195°. This was identical with the phenolic aldehyde obtained from girinimbine by Dr. D. P. Chakraborty (TLC, superimposable IR spectra and mixed m.p. undepressed); UV (EtOH) λ_{max} 225, 234, 287, 296 and 395 mμ (log 4·60, 4·60, 4·19, 4·21 and 3·81); IR (KBr): 3440, 2920, 1630, 1460, 1445, 1405, 1378, 1355, 1320, 1210, 1170, 1150, 1050, 1015, 975, 905, 785, 768, 730, 700 and 685 cm^{-1}. (Found: C, 74·4; H, 5·2; N, 6·3. Calc. for $C_{14}H_{11}NO_2$: C, 74·6; H, 4·9; N, 6·2%).

An intimate mixture of **10** (10 mg) and 10% Pd/C (50 mg), was heated in a sublimation tube at 180–190° for 15 min in an atmosphere of N_2. It was then sublimed at 210°/2 × 10^{-3} mm to yield a colourless sublimate, m.p. 242–243°. This was identical in its mixed m.p., TLC, UV, IR with a synthetic sample of **7**.

(ii) The natural product was chromatographed on Sigal (0·05–0·2 mm). Elution with $CHCl_3$: 1% MeOH yielded a gum which crystallized from $CHCl_3$–hexane (**11**; 100 mg), m.p. 215°; UV (EtOH) λ_{max} 239, 298, 307 and 385 mμ (log ε 4·66, 4·16, 4·42 and 4·09); IR (KBr): 3330, 1750, 1660, 1615, 1500, 1480, 1450, 1440, 1420, 1340, 1315, 1245, 1210, 1185, 1090, 1060, 900, 870, 775, 745, and 730 cm^{-1}. (Found: C, 71·5; H, 5·4; N, 4·2. Mol. wt. by mass spectrum 337. $C_{20}H_{19}NO_4$ requires: C, 71·2; H, 5·6; N, 4·1% Mol. wt. 337).

2-Hydroxy-3-methylcarbazole (**7**). A mixture of 2-hydroxy-3-formyl carbazole (1·5 g), KOH pellets (1·5 g), hydrazine hydrate (90% soln, 2·2 ml) and ethylene glycol (7·5 ml) was heated in an open flask at 160° for 1 hr and then at 195–200° for another 2 hr. The reaction mixture was cooled, diluted with ice and carefully acidified with conc HCl. The ppt so formed was isolated by filtration, washed free from acid, dried and extracted with $CHCl_3$ in a soxhlet apparatus. The extract was evaporated to dryness to give a brownish residue (1 g). This was purified by repeated (thrice) sublimation at 210°/2 × 10^{-3} mm, m.p. 243°; UV (EtOH): λ_{max} 210, 237, 254, 259, 304 and 333 mμ log ε 4·51, 4·66, 4·25, 4·26, 4·18 and 3·66); IR (KBr): 3520, 3400, 3060, 2940, 2920, 2860, 1635, 1610, 1475, 1460, 1390, 1380, 1355, 1335, 1315, 1290, 1265, 1250, 1225, 1215, 1185, 1150, 1130, 1105, 1035, 1020, 930, 890, 860, 830, 765, 750 and 725 cm^{-1}. (Found: C, 78·5; H, 5·7; N, 7·6. Mol. wt. by mass spectrum 197. $C_{13}H_{11}NO$ requires: C, 79·2; H, 5·6; N, 8·1%. Mol. wt. 197).

1-Dimethylaminomethyl-2-hydroxyca-bazole (**8**). To a stirred soln of 2-hydroxycarbazole (5 g) in EtOH (70 ml), Me_2NH (5·5 g) and subsequently formaldehyde (38%; 3·5 g) were added. The reaction mixture was stirred at 38° for 2 hr. The solvent was removed under reduced press and the solid crystallized from EtOH (1·5 g) m.p. 178°; UV (EtOH) λ_{max} 213, 237, 260 and 303 mμ (log ε, 4·5, 4·65, 4·38 and 4·13); NMR signals

δ 2·32 (S; 6H; $-N\begin{matrix}CH_3\\CH_3\end{matrix}$); 3·91 (S; 2H, $-CH_2$) 6·71 (d; 1H; J = 8 c/s; H-3); 7·76 (d, 1H, J = 8 c/s; H-4); 7·8 (m, 1H, H–5); 7·0–7·5 (m, 3H, H-6, 7, 8). (Found: C, 75·3; H, 7·0; N, 11·7. $C_{15}H_{16}N_2O$ requires: C, 75·0; H, 6·7; N, 11·7%).

2-Hydroxy-1-methylcarbazole (**9**). A soln of **8** (0·5 g) in EtOH (50 ml) was hydrogenated over 10% Pd/C (250 mg). After removal of the catalyst the solvent was removed under reduced press and the residue crystallized from 45% MeOH as colorless needles m.p. 217–218°; UV (EtOH) λ_{max} 215, 239, 252, and 301 mμ (log ε, 4·46, 4·6, 4·45 and 4·12). IR (KBr) 3420, 1615, 1490, 1460, 1420, 1360, 1330, 1310, 1225, 1211, 1160,

1120, 1082, 1070, 1010, 940, 925, 890, 800, 765, 750 and 730 cm^{-1}; NMR signals at δ 2·4 (s, 3H, $-CH_3$), 6·75 (d, J = 9 c/s, 1H, H-3), 7·6 (d, J = 9 c/s, 1H, H-4), 7·8 (m, 1H, H-5), 7·0–7·5 (m, 4H, H-6, 7, 8, NH). (Found: C, 79·2; H, 5·0; N, 7·0. $C_{13}H_{11}NO$ requires: C, 79·2; H, 5·6; N, 7·1%).

Tetrahydroisomahanimbine (**14**). Isomahanimbine (165 mg) was dissolved in EtOH (40 ml) and hydrogenated at 29° using 5% Pd/C (0·2 g) as catalyst till there was no more absorption of H_2. After filtration of the catalyst, the solvent was distilled off and the residue crystallized from pentane (65 mg) m.p. 166–167°; UV (EtOH): λ_{max} 220, 241, 255, 260, 306 and 320 mμ (log ε 4·49, 4·64, 4·47, 4·47, 4·23 and 3·97); IR (Nujol): 3410, 1620, 1480, 1310, 1300, 1230, 1215, 1160, 1130, 1100, 1080, 910, 875 and 810 cm^{-1}. (Found: C, 82·8; H, 8·9. Mol. wt. by mass spectrum 335. $C_{23}H_{29}NO$ requires: C, 82·3; H, 8·7%, mol. wt. 335).

N-*Methylisomahanimbine*. A soln of isomahanimbine (350 mg) in acetone (5 ml) was shaken for 15 min with NaOH (0·5 g in 1 ml H_2O), and then for a further 15 min after the addition of Me_2SO_4 (1 ml). The reaction mixture was allowed to stand at room temp overnight and then diluted with ice. The ppt was filtered, washed, dried and crystallized from EtOH (200 mg), m.p. 94°; UV (EtOH): λ_{max} 240, 293, 332, 345 and 358 mμ (log ε 4·64, 4·66, 3·77, 3·78 and 3·80). IR (Nujol): 1630, 1580, 1485, 1390, 1340, 1320, 1250, 1210, 1190, 1180, 1125, 1110, 1080, 1045, 1020, 1010, 885, 805, 795, 790, 745 and 720 cm^{-1}. (Found: C, 83·4; H, 8·0; N, 4·2. $C_{24}H_{27}NO$ requires: C, 83·4; H, 7·8; N, 4·0%).

Ozonolysis of isomahanimbine to obtain the compounds **5** *and* **15**. Isomahanimbine (600 mg) was dissolved in $CHCl_3$ (50 ml), ozonised and worked up as in mahanimbine.

The phenolic fraction (30 mg), after chromatography on Sigel yielded a yellow crystalline compound (**5**) m.p. 198–200°; UV (EtOH): λ_{max} 230, 290, 298, and 380 mμ (log ε 4·60, 4·12, 4·20 and 3·87); IR (KBr): 3440, 2920, 2840, 1640, 1600, 1455, 1390, 1340, 1330, 1290, 1220, 1160, 1070, 1020 and 790 cm^{-1}, mol. wt. by mass spectrum 225.

The neutral fraction (500 mg), after chromatography on neutral alumina, yielded the crystalline compound (**15**), m.p. 294–295°; UV (EtOH): λ_{max} 240, 290, 311 and 390 mμ (log ε 4·32, 3·88, 4·06 and 3·68); IR (KBr): 2920, 1740, 1660, 1620, 1490, 1415, 1335, 1330, 1210, 1160, 1150, 1090, 1025, 820 and 800 cm^{-1}, mol. wt. by mass spectrum 337.

N-*Methylkoenimbidine*. A soln of koenimbidine (160 mg) in acetone (25 ml) was treated and worked up as in the case of isomahanimbine. The product crystallized from EtOH (125 mg) m.p. 190–191°; UV (EtOH): λ_{max} 225, 239, 302 and 343 mμ (log ε 4·40, 4·44, 4·48 and 3·86); IR (Nujol): 1610, 1590, 1490, 1398, 1300, 1250, 1230, 1210, 1195, 1158, 1125, 1050, 1015, 975, 875, 865, 835, 810, 795, 775, 765, 740, 730, 710, 695 cm^{-1}. (Found: C, 74·7; H, 7·0; N, 4·3. $C_{21}H_{23}NO_3$ requires: C, 74·7; H, 6·8; N, 4·1%).

Dihydrokoenimbidine. Koenimbidine (161 mg) was dissolved in EtOH (40 mg) and hydrogenated at 29° using 5% Pd/C (0·2 g) till no more H_2 was absorbed. The catalyst was filtered off, the filtrate concentrated and the residue crystallized from hexane (70 mg), m.p. 237°; UV (EtOH): λ_{max} 215, 235, 267, 315 and 323 mμ (log ε 4·47, 4·61, 4·17, 4·23 and 4·23); IR (Nujol): 3410, 1610, 1305, 1280, 1260, 1245, 1215, 1200, 1180, 1160, 1120, 1060, 1040, 1000, 900, 885, 870, 850, 770, 760, 745, 720 cm^{-1}. (Found: C, 74·0; H, 7·2. Mol. wt. by mass spectrum 325. $C_{20}H_{23}NO_3$ requires: C, 73·8; H, 7·1%. Mol. wt. 325).

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