

## Synthesis of Gambirtannine† Derivatives by Photocyclization of Enamine Intermediates

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The synthesis of several gambirtannine derivatives by photochemical cyclization of enamine intermediates, prepared from harmaline and suitably substituted benzyl halides, is described.

**HARMALINE** (4,9-dihydro-7-methoxy-1-methyl-3*H*-pyrido[3,4-*b*]indole) (1) is a simple indole alkaloid occurring in the seeds of *Peganum harmala*.<sup>1-3</sup> Our earlier studies on its chemistry led to the observation of a mobile imine-enamine equilibrium,<sup>4</sup> which was exploited for the synthesis of a number of novel indoloquinolizidines,<sup>5,6</sup> reserpine analogues,<sup>7,8</sup> 11-methoxy-nauclefine and 11-methoxyrutaecarpine.<sup>9</sup>

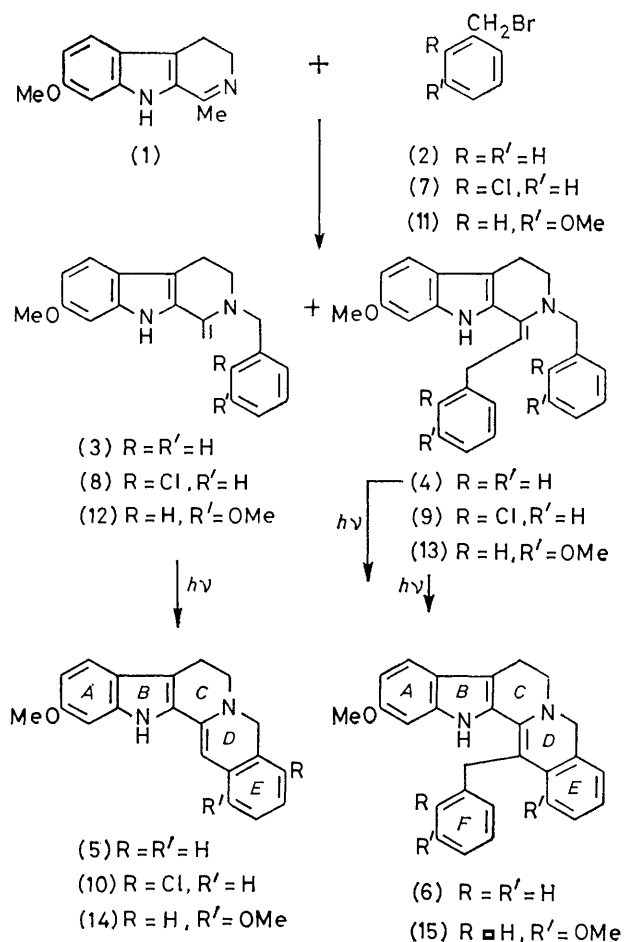
Much work has been carried out recently on the photocyclization of dienamides to afford complex heterocyclic systems,<sup>10-24</sup> including alkaloids of the benzylisoquinoline, amaryllidaceae, and indole types.<sup>25-27</sup> Examples of photoadditions of enamines to olefinic carbon atoms with the generation of new ring systems are encountered rarely, however.<sup>28-30</sup> The ready availability of harmaline, and our interest in synthesizing 11-methoxy-gambirtannine derivatives of potential pharmacological importance, have led us to develop facile photoannulations of suitably substituted *N*<sub>b</sub>-benzylharmalines to give the corresponding gambirtannine derivatives.

When harmaline was refluxed for 15 h with an excess of benzyl bromide in 1:1 methanol-benzene, it was converted into two products. The one moving closer to harmaline on t.l.c. possessed a greenish fluorescence and was formed first; the faster-running material, possessing a bright green fluorescence, was formed later. The molecular weight of the slower-running compound (*m/z* 304.1593) agreed with the molecular formula of the mono-alkylated product (3). The presence of the benzyl moiety was confirmed by peaks at *m/z* 91 ( $C_7H_7^+$ ) and 213 ( $M^+ - C_7H_7$ ). I.r. absorption at 1630  $cm^{-1}$  indicated the presence of the olefinic double bond, and u.v. absorption at 327 nm reflected the presence of extended conjugation. The olefinic <sup>1</sup>H n.m.r. peak at δ 5.11 indicated that *N*-alkylation had occurred rather than *C*-alkylation, in agreement with our earlier observation at elevated temperatures.<sup>5</sup> The methoxy singlet occurred at δ 3.8.

The faster running material showed *m/z* 394.2042 ( $M^+$ ,  $C_{27}H_{26}N_2O$ ), 303 ( $C_{20}H_{19}N_2O^+$ ), 291, 168, 91 ( $C_7H_7^+$ ), and 77 ( $C_6H_5^+$ ). The u.v. absorptions indicated the presence of a highly conjugated system, and the n.m.r. spectrum showed the presence of one olefinic proton (δ 5.9). These data are consistent with the dialkylated product (4).

Irradiation of the *N*-monoalkylated product (3) in

† Methyl 3,14,15,16,17,18,19,20-octadehydrohimban-16-carboxylate.



SCHEME 1

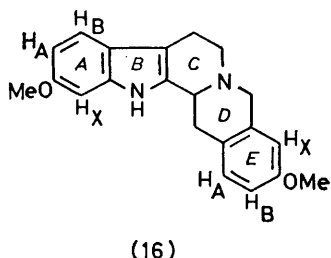
dichloromethane with a medium-pressure mercury lamp for 7 h gave a product having a violet fluorescence in u.v. light (254 nm). The mass spectrum agreed with the molecular formula  $C_{20}H_{18}N_2O$  expected for the cyclized product. The n.m.r. spectrum showed one olefinic proton singlet at δ 5.95, in agreement with structure (5).

A solution of the dialkylated product (4) was similarly irradiated to give the dialkylated cyclized product (6).

Similar reactions of harmaline with *o*-chloro- and *m*-methoxy-benzyl bromide in each case gave a monoalkylated [(8) or (12)] and a dialkylated product [(9) or (13), respectively].

Attempts to cyclize compound (8) to form ring *D* via

benzyne, using freshly prepared phenyl-lithium or sodium in liquid ammonia, were unsuccessful. However u.v. irradiation in dichloromethane for 5 h gave a chlorine-containing product ( $M^+$  336/338). The n.m.r. spectrum showed a methoxy singlet at  $\delta$  3.5 and a singlet for one olefinic proton at  $\delta$  6.06. These and other spectral data were consistent with structure (10). Similar irradiation of the enamine (12) gave the cyclized product (14). The n.m.r. spectrum confirmed that cyclization had occurred, showing only one olefinic proton signal at  $\delta$  5.0. An ABC-type coupling pattern for the aromatic protons in ring *E* confirmed that cyclization had occurred *ortho* to the aromatic methoxy-group. The alternative structure (16) would be expected



to exhibit two ABX patterns for rings *A* and *E* with the X portions appearing as high-field one-proton signals showing small *meta*- and *para*-couplings. This result is consistent with the observation of a higher partial rate factor for *ortho*-arylation of anisoles as compared with *para*-arylation.<sup>31</sup>

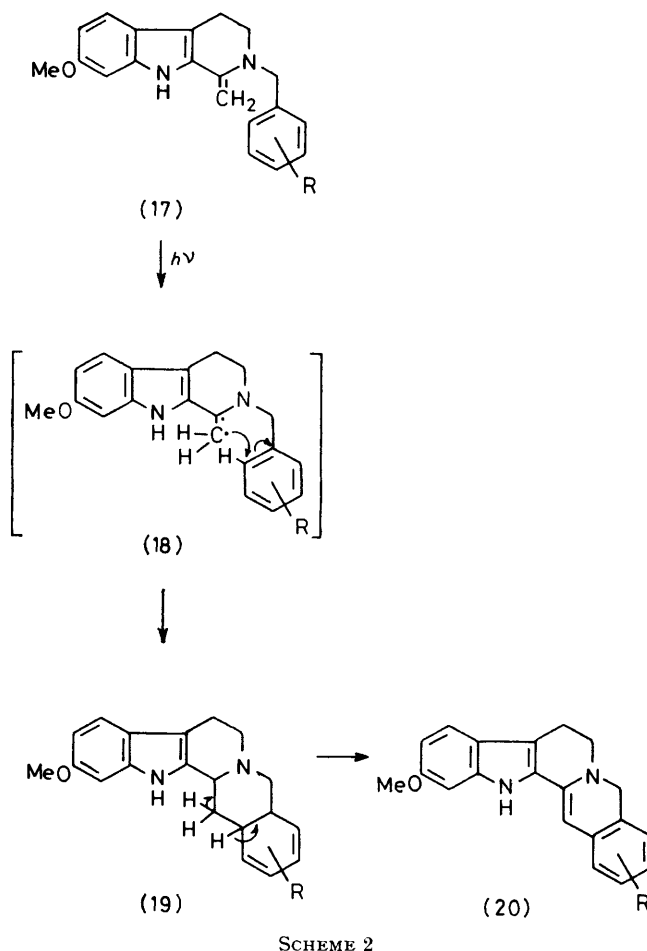
Irradiation of the dialkylated product (13) for 2 h resulted in cyclization to (15). The n.m.r. spectrum showed no olefinic protons, and the aromatic protons showed only one ABX system (ring *A* protons); the remaining aromatic proton signals appeared as complex overlapping ABC multiplets. The alternative structure involving cyclization *ortho* to the methoxy-group would be expected to exhibit two ABX patterns (for rings *A* and *E*).

Treatment of harmaline directly with *o*-chlorobenzyl alcohol in the presence of catalytic quantities of toluene-*p*-sulphonic acid in various solvents and at different temperatures showed no reaction.

A mechanism for the reaction is suggested in Scheme 2. A similar mechanism has been invoked for the photocyclization of stilbene derivatives.<sup>32,33</sup> The loss of hydrogen may be assisted by the presence of dissolved oxygen in the solvent or by the solvent itself acting as the hydrogen scavenger. As no products at a lower oxidation level were formed, the possibility of the starting materials or the products acting as hydrogen scavengers could be ruled out. Precedent for such reactions exists.<sup>34-38</sup>

#### EXPERIMENTAL

2-Benzyl-1,2,3,4-tetrahydro-7-methoxy-1-methylene- $\beta$ -carboline (3) and 2-Benzyl-1,2,3,4-tetrahydro-1-phenethylidene- $\beta$ -carboline (4).—Harmaline (1) (500 mg, 2.3 mmol) was dissolved in 1:1 methanol-benzene (40 ml) with stirring



at 40 °C. Benzyl bromide (2) (3 ml, 25 mmol) was then added over 30 min. The mixture was refluxed and stirred for 15 h; the solution developed a dark green colour and turned viscous. T.l.c. (9:1 chloroform-methanol) showed a gradual conversion into two faster-running products, which were observed in u.v. light as green and bright green fluorescent spots. The solvent was evaporated to afford a gum, which was dissolved in chloroform and chromatographed on silica. Elution with chloroform afforded the products along with some unchanged harmaline. The benzyl derivative (3) was obtained as yellow crystals (355 mg, 50%), m.p. 110 °C,  $m/z$  304 ( $M^+$ , 21%), 303 (11), 291 (18), 289 (6), 120 (25), 119 (18), 85 (100), and 83 (96) (Found:  $M^+$  304.1593.  $C_{20}H_{20}N_2O$  requires  $M$  304.1575);  $\nu_{\max}$  (KBr) 3 340 (indole NH) and 1 630  $cm^{-1}$  (olefinic C=C);  $\lambda_{\max}$  (MeOH) 215, 261, 288, 314, and 327 nm;  $\delta$ ( $CDCl_3$ ) 3.05 (m, 4 H,  $CH_2$ -indole,  $CH_2$ N), 3.80 (s, 3 H,  $OCH_3$ ), 5.11 (br, s, 2 H,  $CH_2$ ), and 6.5–7.2 (m, aromatic).

The green semi-solid obtained from the column was dissolved in chloroform and filtered through silica to give yellow crystals of the dibenzyl derivative (4) (184 mg, 20%), m.p. 106–110 °C;  $m/z$  394 ( $M^+$ , 17%), 303 (29), 302 (23), 301 (20), 291 (53), 110 (18), 109 (44), 108 (9), 107 (13), 105 (9), 101 (32), 100 (29), 99 (26), 98 (17), 97 (70), 96 (26), 95 (57), 94 (14), 93 (15), 111 (56), 85 (100), 84 (53), and 83 (96) (Found:  $M^+$ , 394.2042.  $C_{27}H_{26}N_2O$  requires  $M$ , 394.2045);  $\nu_{\max}$  (KBr) 1 630  $cm^{-1}$  (C=C str.),  $\lambda_{\max}$  (MeOH)

217, 262, and 404 nm;  $\delta[(\text{CD}_3)_2\text{SO}]$  3.95 (s, 3 H,  $\text{OCH}_3$ ), 5.98 (br, s, 1 H, CH), and 7.1—8.9 (m, aromatic).

11-Methoxy-16-de(methoxycarbonyl)gambirtannine (5).—A solution of compound (3) (150 mg, 0.49 mmol) in chloroform (400 ml) was irradiated in a Pyrex vessel at room temperature with a medium-pressure mercury lamp for 7 h. T.l.c. showed complete conversion of the starting material into a faster-running product. Evaporation left a residue, which after repeated crystallization from methanol afforded the *product* as pale brown crystals (119 mg, 80%), m.p. 150—152 °C;  $m/z$  302 ( $M^+$ , 31%), 214 (14), 213 (12), 212 (56), 211 (17), 197 (21), 129 (67), 128 (33), 127 (26), 126 (28), 120 (59), 119 (39), 118 (58), 91 (94), 88 (15), 87 (94), 86 (40), 85 (100), 84 (88), and 83 (93) (Found:  $M^+$  302.1442.  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}$  requires  $M$ , 302.1419);  $\nu_{\text{max}}$  (KBr) 3 420 (indole NH) and 1 635  $\text{cm}^{-1}$  (C=C);  $\lambda_{\text{max}}$  (MeOH) 214, 255, and 337 nm;  $\delta[(\text{CD}_3)_2\text{SO}]$  3.9 (s, 2 H,  $\text{OCH}_3$ ), 5.95 (s, 1 H, CH), and 6.8—7.4 (m, aromatic).

14-Benzyl-11-methoxy-16-de(methoxycarbonyl)gambirtannine (6).—Irradiation of a solution of compound (4) (50 mg, 0.17 mmol) in chloroform (200 ml) with a medium-pressure mercury lamp for 5 h resulted in complete conversion of the starting material (t.l.c.). Evaporation left a dark residue, which was dissolved in chloroform and filtered through silica; evaporation then gave pale yellow crystals which were recrystallized from methanol–chloroform; m.p. 234—238 °C; yield 35 mg (70%);  $m/z$  392 ( $M^+$ , 28%), 303 (13), 302 (100), 301 (90), 225 (48), and 211 (10) (Found:  $M^+$ , 392.1895.  $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}$  requires  $M$ , 392.1888);  $\nu_{\text{max}}$  (KBr) 3 400 (NH indole) and 1 630  $\text{cm}^{-1}$  (C=O);  $\lambda_{\text{max}}$  (MeOH) 213, 257, and 338 nm;  $\delta[(\text{CD}_3)_2\text{SO}]$  3.95 (s, 3 H,  $\text{OCH}_3$ ).

2-(*o*-Chlorobenzyl)-1,2,3,4-tetrahydro-7-methoxy-1-methylene- $\beta$ -carboline (8) and 2-(*o*-Chlorobenzyl)-1-(*o*-chlorophenethylidene)-1,2,3,4-tetrahydro-7-methoxy- $\beta$ -carboline (9).—Harmaline (300 mg, 1.4 mmol) was dissolved in warm 1 : 1 methanol–benzene (30 ml). The stirred solution was refluxed with *o*-chlorobenzyl bromide (7) (2 ml) for 15 h. T.l.c. (9 : 1 chloroform–methanol) showed gradual conversion into two faster-running products. The solution was cooled and evaporated; the residue was dissolved in chloroform–methanol and chromatographed on a silica PF<sub>254</sub> column to afford the products and unchanged harmaline. The *monoalkyl derivative* (8) was obtained on evaporation of the eluates as yellow crystals (263 mg, 50%), m.p. 112—114 °C;  $m/z$  340 (isotopic peak, 9%), 338 ( $M^+$ , 25), 324 (6), 323 (5), 304 (22), 303 (77), 288 (6), 281 (5), 279 (12), 169 (20), 167 (14), 155 (17), 149 (48), 137 (13), 127 (27), 125 (27), 91 (15), 87 (78), 86 (13), 85 (100), 84 (44), 83 (92), 82 (42), and 81 (40) (Found:  $M^+$  338.1184.  $\text{C}_{20}\text{H}_{18}\text{ClN}_2\text{O}$  requires  $M$ , 338.1185);  $\nu_{\text{max}}$  (KBr) 3 420 (indole NH) and 1 630  $\text{cm}^{-1}$  (C=C str.);  $\lambda_{\text{max}}$  (MeOH) 220, 262, and 400 nm;  $\delta(\text{CDCl}_3)$  3.1 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 3.85 (s, 5 H,  $\text{OCH}_3$ ,  $\text{PhCH}_2\text{N}$ ), 5.2 (s, 2 H, = $\text{CH}_2$ ), and 6.3—7.3 (m, aromatic).

The *dialkyl derivative* (9) obtained from the column was crystallized from chloroform–methanol; m.p. 226 °C, yield 19 mg (3%);  $m/z$  427 ( $M - \text{Cl}$ , 20%), 337 (19), 327 (5), 325 (47), 303 (14), 302 (11), and 301 (100) (Found:  $M^+ - \text{Cl}$ , 427.1562.  $\text{C}_{27}\text{H}_{24}\text{Cl}_2\text{N}_2\text{O}$  requires  $M$ , 462.187),  $\nu_{\text{max}}$  (KBr) 1 630  $\text{cm}^{-1}$  (C=C str.);  $\lambda_{\text{max}}$  (MeOH) 221, 261, and 406 nm.

19-Chloro-11-methoxy-16-de(methoxycarbonyl)gambirtannine (10).—A solution of compound (8) (200 mg, 0.59 mmol) in chloroform (200 ml) under nitrogen was exposed in a

Pyrex vessel to a medium-pressure mercury lamp. T.l.c. showed complete conversion into a faster-running product after 5 h. The solvent was evaporated at 40 °C and the residue, after repeated crystallization from chloroform–methanol, gave the *product* (10), m.p. 178 °C, yield 159 mg (80%);  $m/z$  336 ( $M^+$ , 5%), 213 (5), 212 (51), 197 (7), 169 (17), 127 (32), and 125 (100) (Found:  $M^+$  336.1026.  $\text{C}_{20}\text{H}_{17}\text{ClN}_2\text{O}$  requires 336.1025);  $\nu_{\text{max}}$  (KBr) 3 400 (indole NH) and 1 623  $\text{cm}^{-1}$  (C=C str.);  $\delta[(\text{CD}_3)_2\text{SO}]$  3.5 (s, 3 H,  $\text{OCH}_3$ ), 6.06 (s, 1 H, =CH), and 6.6—7.9 (m, aromatic).

1,2,3,4-Tetrahydro-7-methoxy-2-(3-methoxybenzyl)-1-methylene- $\beta$ -carboline (12) and 1,2,3,4-Tetrahydro-7-methoxy-2-(3-methoxybenzyl)-1-(3-methoxyphenethylidene)- $\beta$ -carboline (13).—Harmaline (400 mg, 2.3 mmol) in 1 : 1 methanol–benzene (35 ml) was stirred at 40 °C until a homogenous solution was obtained. 3-Methoxybenzyl bromide (11) (3 ml) was then added over 30 min. The mixture was refluxed for 15 h. T.l.c. showed a gradual conversion into two faster-running products, which were observed in u.v. light as green and bright green fluorescent spots. Evaporation left a dark residue which was chromatographed on a silica column with chloroform (98%) and methanol (2%). Evaporation of the eluate afforded the *monoalkyl derivative* (12) as bright yellow, glass-like crystals, m.p. 90 °C, yield 343 mg (55%);  $m/z$  334 ( $M^+$ , 11%), 333 (5), 332 (32), 321 (100), 214 (10), 187 (32), 121 (64), 91 (19), and 82 (22) (Found:  $M^+$ , 334.1682.  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$  requires  $M$ , 334.1681);  $\nu_{\text{max}}$  (KBr) 3 378 (indole NH) and 1 640  $\text{cm}^{-1}$  (C=C str.);  $\lambda_{\text{max}}$  (MeOH) 220, 263, and 298 nm;  $\delta(\text{CDCl}_3)$  3.09 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{N}$ ), 3.85 (s, 6 H, 2  $\text{OCH}_3$ ), 3.88 (s, 2 H,  $\text{PhCH}_2\text{N}$ ), and 5.1 (br, s, 2 H, = $\text{CH}_2$ ).

The *dialkyl derivative* (13) was obtained as a green residue, which was dissolved in chloroform and filtered through silica gel; the filtrate was evaporated to give yellow crystals, which were recrystallized from chloroform–methanol; m.p. 100—103 °C, yield 254 mg (30%);  $m/z$  333 [ $M^+ - (3\text{-methoxybenzyl})$ , 37%], 332 (11), 331 (8), 322 (26), 312 (96), 307 (4), 303 (14), 302 (11), 301 (10), 240 (5), 225 (21), 200 (18), 199 (30), 187 (17), 186 (10), 122 (20), 121 (100), and 115 (6);  $\nu_{\text{max}}$  (KBr) 1 628  $\text{cm}^{-1}$  (C=C str.);  $\lambda_{\text{max}}$  (MeOH) 220, 265, and 295 nm;  $\delta(\text{CDCl}_3)$  3.8 (s, 9 H, 3  $\text{OCH}_3$ ), 4.6 (s, 1 H, C=CH), and 6.5—7 (m, aromatic).

11,16-Dimethoxy-16-de(methoxycarbonyl)gambirtannine (14).—A solution of compound (12) (200 mg, 0.59 mmol) in dichloromethane (200 ml) was irradiated in a Pyrex vessel with a medium-pressure mercury lamp for 3 h. T.l.c. then showed complete conversion into a major slow-running product (a few other unidentified products were formed in traces). The major product was isolated by column chromatography on silica with chloroform. Recrystallization from chloroform–methanol afforded yellow crystals, m.p. 98 °C, yield 159 mg (80%);  $m/z$  332 ( $M^+$ , 30%), 212 (54), 169 (10), 122 (10), 121 (100), 91 (22), 77 (6), and 69 (7) (Found:  $M^+$ , 332.1527.  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}$  requires  $M$ , 332.1525);  $\nu_{\text{max}}$  (KBr) 3 378 (NH indole) and 1 640  $\text{cm}^{-1}$  (C=C olefinic);  $\lambda_{\text{max}}$  (MeOH) 212, 227, 255, and 336 nm;  $\delta(\text{CDCl}_3)$  3.76 (s, 6 H, 2  $\text{OCH}_3$ ) and 5.0 (s, 1 H, =CH).

11,16-Dimethoxy-14-(13-methoxybenzyl)-16-de(methoxycarbonyl)gambirtannine (15).—A solution of compound (13) (100 mg, 0.22 mmol) in dichloromethane (200 ml) was irradiated at room temperature with a Hanovia medium-pressure mercury lamp. T.l.c. showed complete conversion into faster-running products after 2 h. The solution was then evaporated and the major *product* isolated by preparative t.l.c. on silica gel PF<sub>254</sub> (30 g plates; yield 70

mg (70%); m.p. 94—100 °C;  $m/z$  452 ( $M^+$ , 2%), 332 (25), 331 (21), 241 (6), 226 (5), 225 (23), and 212 (20);  $\nu_{\max}$  (KBr) 1624  $\text{cm}^{-1}$  (C=C);  $\lambda_{\max}$  (MeOH) 213, 256, and 240 nm;  $\delta$ ( $\text{CDCl}_3$ ) 3.8 (s, 9 H, 3  $\text{OCH}_3$ ), 3.94 (s, 2 H,  $\text{PhCH}_2\text{N}$ ), 6.3—7.1 (m, aromatic), and 8.01 (s, 1 H, indole NH).

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