Synthesis of Doryanine and Related Isoquinolones and Isocoumarins

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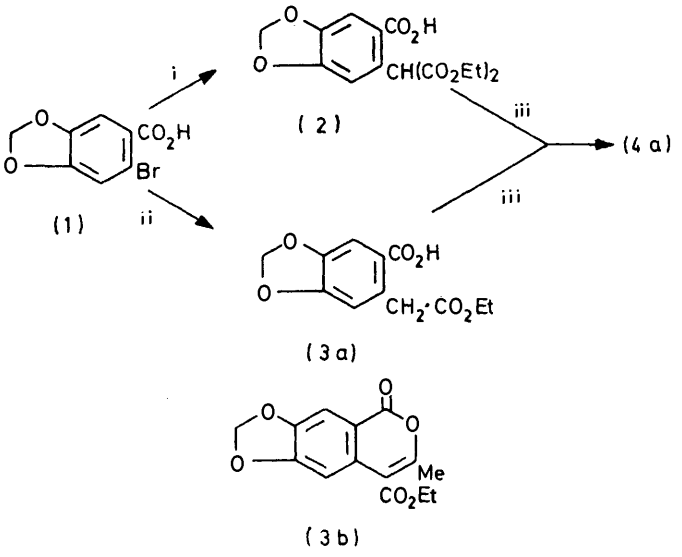
4,5-Methylenedioxyhomophthalic acid, which was synthesised in two steps from 2-bromopiperonylic acid, on treatment with dimethylformamide–phosphoric trichloride at 100 °C furnished doryanine-4-carboxylic acid. Decarboxylation afforded doryanine[2-methyl-6,7-methylenedioxy-1(2*H*)-isoquinolone]. The same reaction at 0 °C gave an intermediate isochromandione (8a), an alcoholic solution of which on treatment with hydrogen chloride gas furnished a 6,7-methylenedioxyisocoumarin-4-carboxylate acid ester; this also gave doryanine-4-carboxylic acid on heating with aqueous methylamine. The same series of reactions with 4-methoxyhomophthalic acid furnished the corresponding 7-methoxyisoquinolones and isocoumarins.

We have briefly reported the reaction of homophthalic acid with dimethylformamide–phosphoric trichloride (DMF–$POCl_3$) at *ca.* 100 °C to give 1,2-dihydro-2-methyl-1-oxoisoquinoline-4-carboxylic acid in one step.[1] A modification of this reaction [2] gave an isocoumarin-4-carboxylate, by isolation of an intermediate isochroman-1,3-dione from the same reaction at 0 °C and treating its alcoholic solution with hydrogen chloride gas. We now

[1] V. H. Belgaonkar and R. N. Usgaonkar, *Tetrahedron Letters*, 1975, 3849.

[2] V. H. Belgaonkar and R. N. Usgaonkar, *Chem. and Ind.*, 1976, 954.

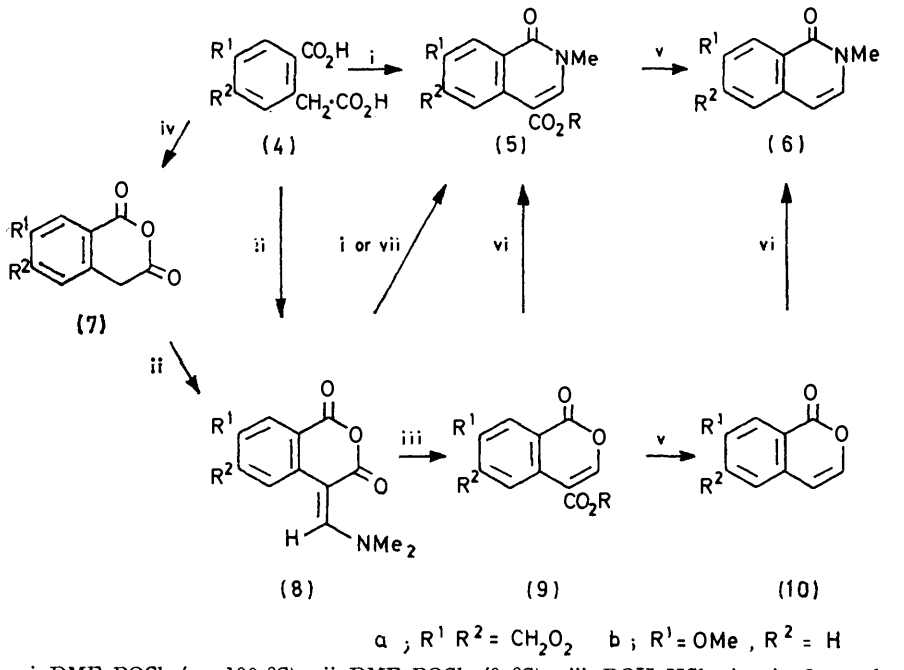
report a synthesis of the isoquinoline alkaloid doryanine [isolated [3] from *Doryphora sassafras* Endlicher (*Moni-*



SCHEME 1 Reagents: i, $H_2C(CO_2Et)_2$,NaH–Cu_2Br_2; ii, $AcCH_2CO_2Et$,NaH–Cu_2Br_2; iii, aq. NaOH

miaceae)] in high yield by direct application of the reaction to 4,5-methylenedioxyhomophthalic acid (4a) reaction *via* the intermediate (8a) furnished in moderate yield the isocoumarin (9a) (R = Me or Et), which gave doryanine (6a) *via* the acid (5a; R = H). Scheme 2 also shows other routes by which doryanine (6a) was obtained. Yields in all the reactions depicted were satisfactory. Doryanine (6) was identified by comparison (m.p. and spectral data) with data reported for the natural alkaloid.[3] I.r. and n.m.r. spectra confirmed all structures assigned. Then n.m.r. signals of H-3, -5, and -8 of compounds (5a; R = H) and (9a) were not assigned unambiguously because of their closeness. However, the signals of (5a), at δ 8.53, 8.35, and 7.85, are tentatively assigned, by comparison with those of (6a), to H-3, -8, and -5, respectively, in view of the expected deshielding of H-3 by CO_2R. The twin i.r. bands (1 710 and 1 660 cm^{-1}) for the anhydride carbonyl groups of (8a) are at low frequency; this may be attributed to conjugation with NMe_2.

The isocoumarin acids and esters (9a and b) with aqueous methylamine gave the corresponding *N*-methylisoquinolone acids (5a and b; R = H). This type of conversion is known, and was explained in an earlier paper.[4] However, the conversion of the acids (9a and b; R = H), which have no 3-substituent, was not by accompanied decarboxylation as was found with 3-methyl- and 3-benzyl-isocoumarin-4-carboxylic acids.[4,5]



SCHEME 2 Reagents: i, DMF–$POCl_3$ (*ca.* 100 °C); ii, DMF–$POCl_3$ (0 °C); iii, ROH–HCl; iv, Ac_2O; v, heat (R = H); vi, aq. $MeNH_2$; vii, $POCl_3$

(Scheme 2). Scheme 1 outlines a new synthesis of (4a) from 2-bromopiperonylic acid (1) in two steps

Doryanine (6a) was thus synthesised in two simple steps from (4a) by reaction with DMF–$POCl_3$. The same This could be because of the conformation of the intermediate [4] which undergoes elimination.

6,7-Methylenedioxyisocoumarin (10a) was prepared

[3] S. A. Gharbo, J. L. Beal, R. H. Schlessinger, M. P. Cava, and G. Svoboda, *Lloydia*, 1965, **28**, 237 (*Chem. Abs.*, 1966, **64**, 2135c).

[4] R. B. Tirodkar and R. N. Usgaonkar, *Indian J. Chem.*, 1972, **10**, 1062.

[5] V. H. Belgaonkar and R. N. Usgaonkar, *Indian J. Chem.*, 1975, **13**, 336.

earlier [6,7] in an elaborate way in very low yield. 7-Methoxyisocoumarin (10b) and the corresponding 4-carboxylic acid (9b; R = H) and methyl ester (9b; R = Me) were obtained in low yield by a synthesis that involved a Claisen condensation of diethyl 4-methoxyhomophthalate with methyl formate.[8,9] The present synthesis of these compounds is much simpler, and proceeds in high yield. Conditions for maximum yield in the hydrolysis of the ester (9; R = Me or Et) to the acid (9; R = H) were established.

The new synthesis of (4a) (Scheme 1) is shorter, with high yields at all stages, than the earlier [10] procedure from 3,4-methylenedioxycinnamic acid *via* the corresponding indanone. The yield of the final product (4a) is practically the same whether diethyl malonate or ethyl acetoacetate is used for condensation. However, the latter method gave, as a by-product, a small amount of an isocoumarin (3b). This must have resulted from acidic hydrolysis *in situ* of the primary condensation product to give 2-carboxybenzyl methyl ketone, which gave a lactone on acidification. The major product (3a), however, arose *in situ* by ketonic hydrolysis. The constitution of (3b) followed from i.r. and n.m.r. spectral data.

EXPERIMENTAL

Microanalyses were carried out by Mrs. J. A. Patankar. U.v. spectra were recorded by Dr. P. M. Dhadke with a Zeiss VSU2P spectrophotometer. N.m.r. spectra were measured with Varian A60 and T60 spectrometers. The purity of compounds was tested by t.l.c.

2-Ethoxycarbonylmethyl-4,5-methylenedioxybenzoic Acid (3a) *and Ethyl 3-Methyl-6,7-methylenedioxyisocoumarin-4-carboxylate* (3b).—A solution of 2-bromopiperonylic acid (1)[11] (5 g, 0.024 mol) in tetrahydrofuran (THF) (30 ml) and ethyl acetoacetate (15.9 ml, 0.12 mol) was added dropwise to a stirred ice-cold (*ca.* 0 °C) solution of sodium hydride (2.9 g, 0.12 mol) in THF (10 ml). Copper(I) bromide (0.35 g, 0.001 2 mol) was then added, and the mixture was heated at 75—80 °C for 4 h and poured on crushed ice (after filtration if necessary). The mixture was shaken with ether. The aqueous layer was then acidified with hydrochloric acid; compound (3a) separated and was immediately filtered off, and the filtrate was left in a refrigerator overnight. Compound (3a) crystallised from benzene as *needles* (3.8 g), m.p. 153—155° (Found: C, 57.5; H, 4.5. $C_{12}H_{12}O_6$ requires C, 57.15; H, 4.8%). From the filtrate, compound (3b) slowly separated. It crystallised from n-hexane as *needles* (1.0 g), m.p. 119—120° (Found: C, 60.5; H, 4.2. $C_{14}H_{12}O_6$ requires C, 60.87; H, 4.35%); $\lambda_{max.}$ (MeOH) 245 (log ε 4.54), 300 (3.64), and 330 nm (3.60); $\nu_{max.}$ (KBr) 1 740 and 1 715 (C=O of ester and of lactone), 1 620, and 1 490 cm^{-1} (aromatic); δ (60 MHz; $CDCl_3$) 1.43 (3 H, t, $CH_2{\cdot}CH_3$), 2.45 (3 H, s, CH_3), 4.5 (2 H, m, $CH_2{\cdot}CH_3$), 6.18 (2 H, s, $O{\cdot}CH_2{\cdot}O$), 7.3 (1 H, s, H-5), and 7.67 (1 H, s, H-8).

2-(Bisethoxycarbonylmethyl)-4,5-methylenedioxybenzoic Acid (2).—The reaction was carried out and the product worked up as above, with diethyl malonate (19.6 ml, 0.12 mol) in place of ethyl acetoacetate. Acidification of the solution gave a solid which crystallised from n-hexane–acetone as *plates* (4.0 g), m.p. 108–109° (Found: C, 56.1; H, 5.0. $C_{15}H_{16}O_8$ requires C, 55.55; H, 4.9%); δ (60 MHz; $CDCl_3$) 1.26 (6 H, t, $CH_2{\cdot}CH_3$), 4.26 (4 H, m, $CH_2{\cdot}CH_3$), 5.88 (1 H, s, CH), 6.06 (2 H, s, $O{\cdot}CH_2{\cdot}O$), 6.98 (1 H, s, H-6), 7.58 (1 H, s, H-3), and 9.42 (1 H, s, CO_2H).

4,5-Methylenedioxyhomophthalic Acid (4a).—This was obtained by heating either compound (2) or (3a) (4 g) with aqueous sodium hydroxide (10%; 40 ml) on a boiling water bath for 1 h and acidifying the resulting solution. It crystallised from ethanol as prisms (3.2 g), m.p. 225—228° (decomp.) [lit.,[10] 236° (decomp.)] (Found: C, 53.8; H, 4.0. Calc. for $C_{10}H_8O_6$: C, 53.6; H, 3.6%). When the product (4a) was refluxed with acetic anhydride (4 ml) and the solution cooled, the anhydride (7a) crystallised out. It crystallised from benzene–acetone as needles (2 g), m.p. 173—174° (hydrolysed readily on exposure to air). On refluxing with ethanol for 1.5 h it gave the acid (3a), m.p. and mixed m.p. 153—155°.

4-(Dimethylaminomethylene)-6,7-methylenedioxyisochroman-1,3-dione (8a).—Phosphoric trichloride (1.82 ml, 0.01 mol) was added dropwise to a stirred solution of the acid (4a) (2.2 g, 0.01 mol) in DMF (7.3 ml, 0.1 mol) cooled in ice. Stirring was continued for 45 min at 0 °C and then at room temperature for 1 h, with separation of solid. Crushed ice was added; the solid crystallised from benzene–acetone as yellow *needles* (2 g), m.p. 237—238° (decomp.) (Found: C, 59.75; H, 4.3; N, 5.4. $C_{13}H_{11}NO_5$ requires C, 59.75; H, 4.2; N, 5.35%); $\lambda_{max.}$ (dioxan) 225 (log ε 4.39), 270 (4.34), and 380 nm (4.25); $\nu_{max.}$ (Nujol) 1 710 and 1 660 (C=O of anhydride), and 1 610 and 1 580 cm^{-1} (aromatic); δ [60 MHz; $(CD_3)_2SO$] 3.3 (6H , s, NMe_2), 6.12 (2 H, s, $O{\cdot}CH_2{\cdot}O$), 7.16 (1 H, s, H-5), 7.28 (1 H, s, $CH{\cdot}NMe_2$), and 8.32 (1 H, s, H-8). Compound (8a) (2 g) was also obtained from the anhydride (7a) (2.2 g) in place of the acid (4a).

4-(Dimethylaminomethylene)-7-methoxyisochroman-1,3-dione (8b).—The reaction of DMF–$POCl_3$ with (4b) (2.1 g) or (7b) (2 g) was performed as above. The product crystallised from benzene as yellow *needles* (2 g), m.p. 125—128° (Found: C, 62.7; H, 5.6; N, 5.6. $C_{13}H_{13}NO_4$ requires C, 63.2; H, 5.6; N, 5.7%).

Methyl 6,7-Methylenedioxyisocoumarin-4-carboxylate (9a; R = Me).—Dry hydrogen chloride was bubbled through a methanolic solution of the dione (8a) (2 g; 100 ml) for 4 h at room temperature and the solution was then refluxed for 2 h and cooled. The solid that separated crystallised from ethanol as *needles* (1.6 g), m.p. 215—216° (Found: C, 58.1; H, 3.4. $C_{12}H_8O_6$ requires C, 58.05; H, 3.2%); $\lambda_{max.}$ (MeOH) 245 (log ε 4.49), 290 (4.55), and 320 nm (3.77); $\nu_{max.}$ (Nujol) 1 720 (C=O of ester and lactone) and 1 620 cm^{-1} (aromatic); δ (60 MHz; $CF_3{\cdot}CO_2H$) 4.13 (3 H, s, $CO_2{\cdot}CH_3$), 6.2 (2 H, s, $O{\cdot}CH_2{\cdot}O$), and 7.75, 8.13, and 8.35 (each 1 H, s, H-5, -8, and -3).

Ethyl 6,7-Methylenedioxyisocoumarin-4-carboxylate (9a; R = Et).—This was made by using an ethanolic solution of (8a) (2 g; 100 ml) in the above reaction. It crystallised from ethanol as *needles* (1.3 g), m.p. 162—164° (Found: C, 59.6; H, 3.4. $C_{13}H_{10}O_6$ requires C, 59.5; H, 3.8%).

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[7] N. K. Bose and D. N. Chaudhary, *J. Indian Chem. Soc.*, 1966, **43**, 411.
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[9] A. Kamal, A. Robertson, and E. Tittensor, *J. Chem. Soc.*, 1950, 3375.
[10] W. H. Perkin, jun., and R. Robinson, *J. Chem. Soc.*, 1907, **91**, 1084.
[11] F. Dallacker, *Annalen*, 1960, **633**, 14.

Methyl 7-Methoxyisocoumarin-4-carboxylate (9b; R = Me).—The reaction was carried out as above with a methanolic solution of (8b) (2.25 g; 100 ml). The product crystallised from methanol as *needles* (1.5 g), m.p. 124—125° (lit.,[8,9] 124—125°) (Found: C, 61.6; H, 4.1. Calc. for $C_{12}H_{10}O_5$: C, 61.6; H, 4.25%); $\nu_{max.}$ (KBr) 1 750 and 1 720 (C=O of lactone and ester), and 1 600 and 1 490 cm^{-1} (aromatic).

Ethyl 7-Methoxyisocoumarin-4-carboxylate (9b; R = Et).—Use of an ethanolic solution of (8b) (2 g; 100 ml) in the above reaction gave the *product* as *needles* (1.2 g), m.p. 125—126° (from ethanol) (Found: C, 62.5; H, 4.9. $C_{13}H_{12}O_5$ requires C, 62.9; H, 4.85%).

6,7-Methylenedioxyisocoumarin-4-carboxylic Acid (9a; R = H).—The ethyl or methyl ester (9; R = Me or Et) (1 g) was refluxed with glacial acetic acid (20 ml), concentrated hydrochloric acid (30 ml), and water (10 ml) for 4 h. The solid which separated crystallised from ethanol as *prisms* (0.7 g), m.p. 276—278° (Found: C, 56.4; H, 2.6. $C_{11}H_6O_6$ requires C, 56.4; H, 2.7%); $\lambda_{max.}$ (MeOH) 245 (log ε 4.52), 290 (3.5), and 330 nm (3.66); $\nu_{max.}$ (Nujol) *ca.* 1 700br (C=O of lactone and acid), and 1 610 and 1 570 cm^{-1} (aromatic); δ (60 MHz; $CF_3{\cdot}CO_2H$) 6.25 (2 H, s, O·CH_2·O), and 7.8, 8.28 and 8.53 (each 1 H, s, H-5, -8, and -3).

7-Methoxyisocoumarin-4-carboxylic Acid (9b; R = H).—The reaction as above with (9b; R = Me or Et) (1.3 g) gave the product as cream coloured needles (1.0 g), m.p. 245—246° (from ethanol) (lit.,[8,9] 255°) (Found: C, 59.6; H, 3.8. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.6%); $\nu_{max.}$ (KBr) 1 730br (C=O of lactone and acid), and 1 610 and 1 500 cm^{-1} (aromatic).

6,7-Methylenedioxyisocoumarin (10a).—The acid (9a; R = H) (0.3 g) was decarboxylated by heating in a metal bath for 0.5 h with a pinch of copper-bronze (275—280 °C) until evolution of carbon dioxide ceased. The product was sublimed under reduced pressure, and crystallised from ethyl acetate–methanol as pale yellow needles (0.15 g), m.p. 168° (lit.,[6,7] 168—169°) (Found: C, 63.6; H, 3.05. Calc. for $C_{10}H_6O_4$: C 63.15; H, 3.2%); $\lambda_{max.}$ (MeOH) 240 (log ε 4.63), 280 (3.70), and 330 nm (3.72); $\nu_{max.}$ (Nujol) 1 690 (C=O of lactone), 1 630, 1 600, and 1 580 cm^{-1} (aromatic); δ (60 MHz; $CF_3{\cdot}CO_2H$) 6.2 (2 H, s, O·CH_2·O), 6.8 (1 H, d, *J* 7 Hz, C*H*:CH·O), 7.01 (1 H, s, H-5), 7.46 (1 H, d, *J* 6 Hz, CH:C*H*·O), and 7.68 (1 H, s, H-8).

7-Methoxyisocoumarin (10b).—Decarboxylation of (9b; R = H) (0.7 g) as above, sublimation of the product under reduced pressure, and crystallisation from n-hexane gave needles (0.3 g), m.p. 109—110° (lit.,[9] 108—109°) (Found: C, 68.6; H, 5.0. $C_{10}H_8O_3$ requires C, 68.2; H 4.6%); $\nu_{max.}$ (KBr) 1 700 (C=O of lactone), 1 630, 1 600, and 1 490 cm^{-1} (aromatic). This product was also obtained by refluxing the ester (9b; R = Me) (0.5 g) with glacial acetic acid (7 ml), concentrated hydrochloric acid (20 ml), and water (10 ml) for 4 h; m.p. and mixed m.p. 109—110°.

1,2-Dihydro-2-methyl-6,7-methylenedioxy-1-oxoisoquinoline-4-carboxylic Acid (5a; R = H).—(i) *Action* of DMF–$POCl_3$ *at* 100 °C *on compounds* (4a) *and* (7a). The reaction was initially carried out at 0 °C as described for the preparation of (8a), and the mixture was then heated with addition of DMF (7.3 ml 0.1 mol) on a boiling water bath for 4 h; the solid slowly went into solution and a new substance crystallised out. After adding crushed ice, the product was filtered off and crystallised from glacial acetic acid as *needles* (2 g), m.p. 321—322° (decomp.) (Found: C, 57.75; H, 3.5; N, 5.9. $C_{12}H_9NO_5$ requires C, 58.3; H, 3.65; N, 5.65%); $\lambda_{max.}$ (dioxan) 255 (log ε 4.61), 310 (4.06), and 340 nm (4.05); $\nu_{max.}$ (Nujol) 1 710 and 1 630 (C=O of acid and lactam) and 1 580 cm^{-1} (aromatic); δ (60 MHz; $CF_3{\cdot}CO_2H$) 3.98 (3 H, s, NCH_3), 6.23 (2 H, s, O·CH_2·O), and 7.85, 8.35, and 8.53 (each 1 H, s, H-5, -8, and -3). The anhydride (7a) (2 g) could be used in place of (4a) in the above reaction.

(ii) *Action of* $POCl_3$ *on the dione* (8a). A mixture of (8a) (1.5 g) and phosphoric trichloride (6 ml) was heated on a boiling water bath for 3 h and poured on crushed ice. The product crystallised as before (0.5 g); m.p. and mixed m.p. 321—322° (decomp.).

(iii) *Action of aqueous methylamine on the isocoumarin ester and acid* (9a; R = Me, Et, *or* H). A mixture of (9a; R = Me or Et) (0.3 g) or (9a; R = H) (0.7 g) and aqueous methylamine (30 ml) was heated on a boiling water bath for 3 h, and the solid that separated after acidification was crystallised as before (0.2 g and 0.6 g); m.p. and mixed m.p. 320—321° (decomp.).

1,2-Dihydro-7-methoxy-2-methyl-1-oxoisoquinoline-4-carboxylic Acid (5b; R = H).—This was obtained by reactions (i)—(iii) above in the 'b' series. It crystallised from ethanol as cream-coloured *needles* (1.5 g), m.p. 263—264° (decomp.) (Found: C, 61.4; H, 5.2; N, 5.7. $C_{12}H_{11}NO$ requires C, 61.8; H, 4.7; N, 6.0%); $\lambda_{max.}$ (MeOH) 220 (log ε 4.56), 295 (3.99), and 340 nm (3.77); $\nu_{max.}$ (KBr) 1 720 and 1 680 (C=O of acid and lactam), 1 650, 1 615, 1 555, and 1 500 cm^{-1} (aromatic). The *methyl ester* (5b; R = Me), prepared by refluxing a methanolic solution of the acid (5b; R = H) (0.6 g in 70 ml) with concentrated sulphuric acid (1 ml) for 18 h, crystallised from methanol as *needles* (0.8 g), m.p. 147—148° (Found: C, 63.4; H, 5.5; N, 5.8. $C_{13}H_{13}NO_4$ requires C, 63.2; H, 5.25, N, 5.65%); $\nu_{max.}$ (KBr) 1 715 and 1 660 (C=O of ester and lactam), 1 625, 1 610, 1 555, and 1 500 cm^{-1} (aromatic). The *ethyl ester* (5b; R = Et), prepared similarly, crystallised from aqueous ethanol as *needles* (0.8 g), m.p. 145—146° (Found: C, 64.0; H, 5.7; N, 5.4. $C_{14}H_{15}NO_4$ requires C, 64.4; H, 5.75; N, 5.35%).

2-Methyl-6,7-methylenedioxy-1(2H)-isoquinolone (6a) (*Doryanine*).—(i) *Decarboxylation of the acid* (5a; R = H). The acid (0.5 g) was heated in a metal-bath above its m.p. until evolution of carbon dioxide ceased (0.5 h). The product was sublimed under reduced pressure and crystallised from benzene–n-hexane as *needles* (0.2 g), m.p. 159—160° (lit.,[3] m.p. 160—162°) (Found: C, 64.6; H, 4.2; N, 6.5. $C_{11}H_9NO_3$ requires C, 65.15; H, 4.4; N, 6.9%); $\lambda_{max.}$ (MeOH) 230 (log ε 4.45), 250 (4.51), 285 (3.85), 295 (3.91), and 325 nm (3.67); $\nu_{max.}$ (Nujol) 1 658 (C=O of lactam), and 1 610 and 1 580 cm^{-1} (aromatic); δ (60 MHz; $CF_3{\cdot}CO_2H$) 4.18 (3 H, s, NCH_3), 6.31 (2 H, s, O·CH_2·O), 7.35 (1 H, s, H-5), 7.5 (1 H, d, *J* 7.5 Hz C*H*=CH·N), 7.7 (1 H, d, *J* 7.5 Hz CH=C*H*·N), and 7.9 (1 H, s, H-8).

(ii) *Action of aqueous methylamine on the isocoumarin* (10a). Compound (10a) (0.2 g) was heated with aqueous methylamine (10 ml) on a boiling water bath for 3 h and then acidified. The product crystallised as above; m.p. and mixed m.p. 159—160°.

7-Methoxy-2-methyl-1(2H)-isoquinolone (6b).—This was obtained (i) by decarboxylation of the acid (9b; R = H) and (ii) by action of aqueous methylamine on (10b) (procedure detailed above). Its crystallised from n-hexane as *plates* (0.5 g), m.p. 78—79° (Found: C, 69.8; H, 5.5; N, 7.3. $C_{11}H_{11}NO_2$ requires C, 69.85; H, 5.8; N, 7.4%); $\lambda_{max.}$ (MeOH) 220 (log ε 4.51), 280 (4.04), 290 (4.02), and 340 nm (3.68); $\nu_{max.}$ (KBr) 1 640 (C=O of lactam), 1 620, 1 600, 1 545, and 1 500 cm^{-1} (aromatic); δ (60 MHz; $CDCl_3$) 3.63 (3 H, s, NCH_3), 3.96 (3 H, s, OCH_3), 6.52 (1 H, d, *J* 7.5 Hz, C*H*:CH·N),

7.06 (1 H, d, *J* 7.5 Hz CH:C*H*·N), and 7.7 (3 H, m, H-5, -6, and -8).

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