Studies on the Syntheses of Heterocyclic Compounds. Part 676.† Synthesis of 1-Substituted 7-Methoxymitosenes

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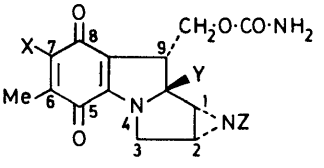
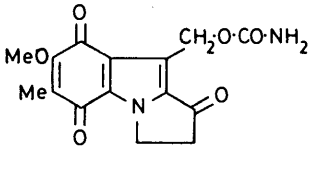
On treatment with lead tetra-acetate in acetic acid, the 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indoles (4)—(8) were selectively acetoxylated at C-1 to give the acetates (13)—(17). The acetates (16) and (17) and 1-acetoxy-2,3-dihydro-7-methoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carbaldehyde (27) were hydrolysed to the corresponding alcohols (20), (21), and (28). The alcohols (20) and (21) were oxidised to the 1-ketones (22) and (23), and (28) was chlorinated with methanesulphonyl chloride and lithium chloride in dimethylformamide to give 1-chloro-2,3-dihydro-7-methoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carbaldehyde(29). On heating the acetates (13), (14), and (17) in acetic acid, elimination of acetic acid occurred to yield the 3*H*-pyrrolo[1,2-*a*]indoles (24)—(26).

RECENTLY, we reported a convenient synthesis of 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indoles, required for a synthetic approach to the mitomycins (1).[1] We now report a method for introduction of a functional group at C-1 in these compounds, an important step in the envisaged synthesis. Our work provides an alternative route to the intermediate (16), used by Remers and his co-workers [2] for the synthesis of desammonoapomitomycin A (2),[3] and also an alternative synthesis of (26), which has been transformed into the tetracyclic compound (3) by Matsui *et al.*[4]

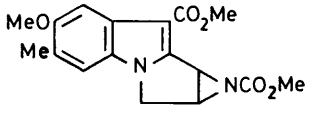


(1)

	X	Y	Z
Mitomycin A	MeO	MeO	H
Mitomycin B	MeO	HO	Me
Mitomycin C	NH_2	MeO	H
Porfiromycin	NH_2	MeO	Me



(2)



(3)

First, oxidative reactions of the 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitriles (4) and (5) [1] were examined under several conditions. On treatment with 2 mol. equiv. of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in methanol at room temperature [5] (4) was unaffected but (5) gave 6-formyl-2,3-dihydro-7-methoxy-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (9) in 71% yield. Treatment of (4) or (5) with *N*-bromosuccinimide in carbon tetrachloride yielded no bromination product. On the other hand, treatment of (5) with *N*-bromosuccinimide in methanol at room temperature yielded 8-bromo-2,3-dihydro-7-methoxy-6-methyl-1*H*-pyrrolo-[1,2-*a*]indole-9-carbonitrile (10) and 8-bromo-2,3-dihydro-5,7-dimethoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (11) in 29 and 31% yield, respectively. Bromine is presumably introduced first at C-8 (having a higher electron density than C-5), and compound (11) would then be formed through the adduct (12), by oxidation.

Introduction of a substituent at C-1 was achieved by using lead tetra-acetate. Thus stirring compound (4) or (5) with 1 mol. equiv. of lead tetra-acetate in acetic acid at room temperature [6] afforded the 1-acetoxy-compounds (13) and (14) in 76 and 74% yield, respectively. However, reactions with 2 mol. equiv. of lead tetra-acetate in acetic acid at 90—100 °C furnished tarry products, from which 1,8-diacetoxy-2,3-dihydro-6,7-dimethoxy-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (18) and 1-acetoxy-6-acetoxymethyl-2,3-dihydro-7-methoxy-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (19) were isolated in 11 and 18% yield, respectively.

The 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carbaldehydes (6) and (7) [1] were then acetoxylated to give compounds (15) and (16) in 65 and 74% yield, respectively, by treatment with 1 mol. equiv. of lead tetra-acetate in acetic acid at room temperature. The acetate (16) was hydrolysed with hot methanolic 10% potassium hydroxide to afford the alcohol (20) in 86% yield. Oxidation of the alcohol (20) with activated manganese dioxide in methylene chloride yielded 2,3-dihydro-7-methoxy-6-methyl-1-oxo-1*H*-pyrrolo[1,2-*a*]-indole-9-carbaldehyde (22) in 74% yield. Refluxing (13) and (14) in glacial acetic acid under nitrogen gave the 3*H*-pyrrolo[1,2-*a*]indoles (24) and (25), identified from spectra (see Experimental section). Similar treatment of (16) gave no olefinic compound but only tarry material. The acetate (16) has already been converted into desammonoapomitomycin A (2) in eight steps by Remers and his co-workers.[3] Heating 1-acetoxy-2,3-

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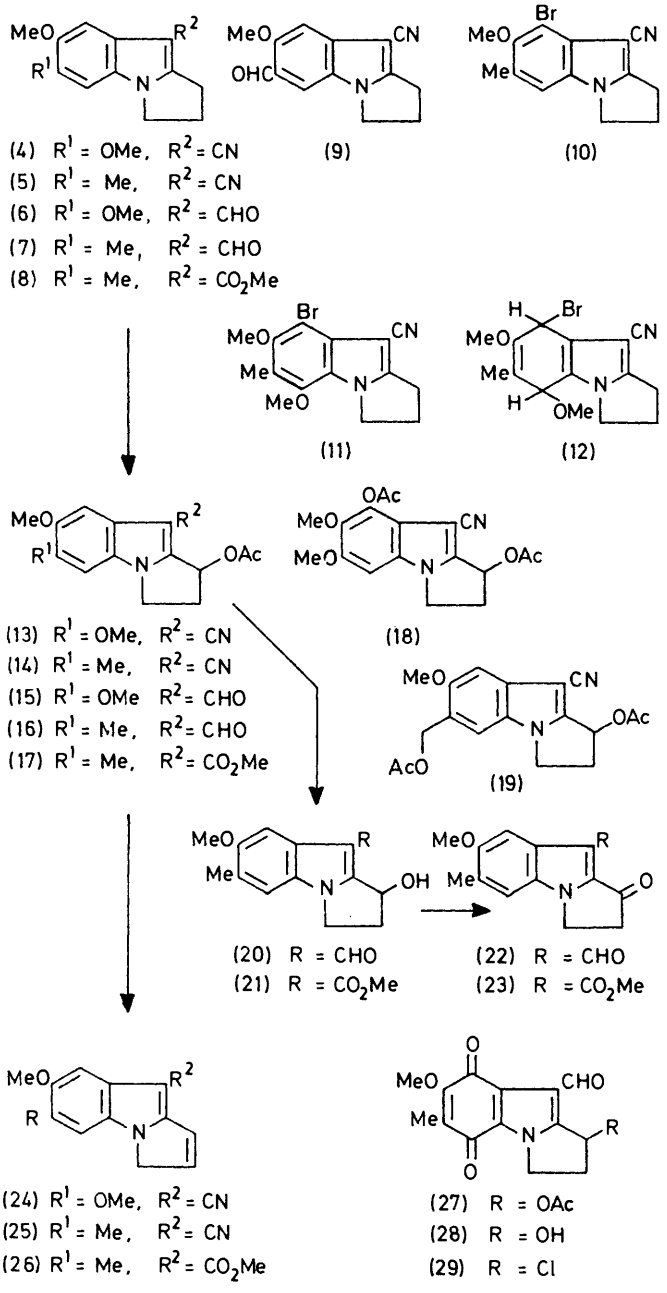
dihydro-7-methoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo-[1,2-*a*]indole-9-carbaldehyde (27), prepared from (16) according to Remers' method,[3] in acetic acid gave only unidentified material. Hydrolysis of (27) with



methanolic potassium hydroxide as in the case of (20) yielded no alcohol (28), whereas stirring (27) with aqueous methanolic sodium hydrogen carbonate at room temperature afforded the alcohol (28) in 95% yield. Stirring the alcohol (28) in dry dimethylformamide in the presence of methanesulphonyl chloride and lithium chloride at 75 °C furnished 1-chloro-2,3-dihydro-7-methoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carbaldehyde (29). Dehydration of (28) and dehydrochlorination of (29) under several sets of conditions gave unsatisfactory results. The nitrile (7) was converted into methyl 2,3-dihydro-7-methoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (8) in 65% yield by hydrolysis with potassium hydroxide in aqueous ethylene glycol, followed by esterification with diazomethane. Acetoxylation of (8) was carried out with 1 mol. equiv. of lead tetra-acetate in acetic acid at room temperature, and the acetate (17), obtained in 71% yield, was then hydrolysed to the alcohol (21) in 79% yield with aqueous methanolic sodium hydrogen carbonate. Oxidation of the alcohol (21) with manganese dioxide gave methyl 2,3-dihydro-7-methoxy-6-methyl-1-oxo-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (23) in 80% yield.

Heating the acetate (17) in acetic acid furnished methyl 7-methoxy-6-methyl-3*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (26), whose spectral data were consistent with those reported.[4] The olefinic compound (26) has been transformed into the *N*-methoxycarbonylazirinopyrrolo[1,2-*a*]indole (3) by Matsui and his co-workers.[4]

EXPERIMENTAL

M.p.s were taken with a Yanagimoto apparatus (MP-S2). I.r. spectra were measured with a Hitachi EPI-3 recording spectrophotometer, n.m.r. spectra with a JEOL JNM-PMX 60 spectrophotometer, and mass spectra with a Hitachi RMU-7 spectrometer.

6-*Formyl*-2,3-*dihydro*-7-*methoxy*-1H-*pyrrolo*[1,2-a]*indole*-9-*carbonitrile* (9).—A solution of the nitrile (5) (28 mg) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (62 mg) in methanol (5 ml) was stirred at room temperature for 2 h to give a precipitate which was filtered off. The filtrate was concentrated and chromatographed on alumina (Woelm, grade III). Elution with chloroform gave a solid which was recrystallised from chloroform to give the aldehyde (9) (21 mg, 71%) as *prisms*, m.p. 254—255° (Found: C, 70.05; H, 4.95; N, 11.65. $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.05; N, 11.65%), $\nu_{max.}$ ($CHCl_3$) 1 664 (C=O) and 2 210 cm^{-1} (CN); δ ($CDCl_3$) 2.45—3.50 (4 H, m, 1- and 2-H_2), 3.96 (3 H, s, OMe), 4.20 (2 H, t, *J* 6 Hz, 3-H_2), 7.02 (each 1 H, each s, 5- and 8-H respectively), and 10.42 (1 H, s, CHO); *m/e* 240 (M^+).

8-*Bromo*-2,3-*dihydro*-5,7-*dimethoxy*-6-*methyl*-1H-*pyrrolo*-[1,2-a]*indole*-9-*carbonitrile* (11) *and* 8-*Bromo*-2,3-*dihydro*-7-*methoxy*-6-*methyl*-1H-*pyrrolo*[1,2-a]*indole*-9-*carbonitrile* (10). —A solution of the nitrile (5) (0.45 g) and *N*-bromosuccinimide (0.36 g) in methanol (300 ml) was stirred at room temperature for 1 h, then evaporated. The residue was chromatographed on silica gel (15 g). Elution with benzene gave a solid, which was recrystallised from methanol to give (11) as *needles* (188 mg, 31%), m.p. 119—121° (Found: C, 53.55; H, 4.45; N, 8.15. $C_{15}H_{15}BrN_2O_2$ requires C, 53.75; H, 4.5; N, 8.35%), $\nu_{max.}$ ($CHCl_3$) 2 210 cm^{-1} (CN); δ ($CDCl_3$) 2.42 (3 H, s, ArMe), 2.30—3.30 (4 H, m, 1- and 2-H_2), 3.84 and 4.00 (each 3 H, each s, 2 × OMe), and 4.56 (2 H, t, *J* 6 Hz, 3-H_2); *m/e* 336/334 (M^+). Benzene–methanol (99 : 1 v/v) eluted a solid which was recrystallised from chloroform to give (10) (173 mg, 29%) as *needles*, m.p. 222—224° (Found: C, 54.85; H, 4.3; N, 9.15. $C_{14}H_{13}BrN_2O$ requires C, 55.1; H, 4.3; N, 9.15%), $\nu_{max.}$ ($CHCl_3$) 2 210 cm^{-1} (CN); δ ($CDCl_3$) 2.34 (3 H, s, ArMe), 2.50—3.30 (4 H, m, 1- and 2-H_2), 3.80 (3 H, s, OMe), 4.06

(2 H, t, *J* 6 Hz, 3-H_2), and 6.90 (1 H, s, 5-H); *m/e* 306/304 (M^+).

Methyl 2,3-Dihydro-7-methoxy-6-methyl-1H-pyrrolo[1,2-a]-indole-9-carboxylate (8).—A mixture of the nitrile (7) (2.26 g), potassium hydroxide (10 g), ethylene glycol (5 ml), and water (5 ml) was stirred under reflux for 48 h, then acidified with 10% hydrochloric acid and extracted with chloroform. The extract was evaporated, the residue was dissolved in methanol, and a solution of diazomethane in ether was added. The resulting mixture was set aside at room temperature for 5 h. Evaporation afforded a solid which was recrystallised from ether to give the *ester* (8) (1.68 g, 65%), m.p. 147—149° (Found: C, 69.5; H, 6.7; N, 5.1. $C_{15}H_{17}NO_3$ requires C, 69.5; H, 6.6; N, 5.4%), $\nu_{max.}$ ($CHCl_3$) 1 680 cm^{-1} (C=O); δ ($CDCl_3$) 2.34 (3 H, s, ArMe), 2.40—3.50 (4 H, m, 1- and 2-H_2), 3.86 and 3.90 (each 3 H, each s, 2 × OMe), 4.00 (2 H, t, *J* 7 Hz, 3-H_2), and 6.96 and 7.56 (each 1 H, each s, 5- and 8-H); *m/e* 259 (M^+).

1-Acetoxy-2,3-dihydro-6,7-dimethoxy-1H-pyrrolo[1,2-a]-indole-9-carbonitrile (13).—A solution of the nitrile (4) (0.24 g) and lead tetra-acetate (0.66 g) in acetic acid (30 mg) was stirred at room temperature under nitrogen for 5 h, then evaporated under reduced pressure at 40 °C. The residue was dissolved in water and extracted with benzene. The organic layer was washed with aqueous sodium hydrogen carbonate solution and water, dried (Na_2SO_4), and evaporated to give a brown solid which was recrystallised from ethanol to afford (13) (0.23 g, 76%) as *needles*, m.p. 192—193° (Found: C, 63.8; H, 5.45; N, 9.4. $C_{16}H_{16}N_2O_4$ requires C, 64.0; H, 5.35; N, 9.35%), $\nu_{max.}$ ($CHCl_3$) 2 210 (CN) and 1 730 cm^{-1} (C=O); δ ($CDCl_3$) 2.14 (3 H, s, Ac), 3.95 (6 H, s, 2 × OMe), 6.30 (1 H, dd, *J* 3 and 7 Hz, 1-H), 6.80 (1 H, s, 5-H), and 7.14 (1 H, s, 8-H); *m/e* 300 (M^+).

1-Acetoxy-2,3-dihydro-7-methoxy-6-methyl-1H-pyrrolo-[1,2-a]indole-9-carbonitrile (14).—A solution of the nitrile (5) (0.45 g) and lead tetra-acetate (1.32 g) in acetic acid (40 ml) was stirred at room temperature under nitrogen for 5 h. Work-up as above gave the *acetate* (14) (0.42 g, 74%), m.p. 133—134° (from ether) (Found: C, 67.6; H, 5.7; N, 9.85. $C_{16}H_{16}N_2O_3$ requires C, 67.6; H, 5.65; N, 9.85%), $\nu_{max.}$ ($CHCl_3$) 2 210 (CN) and 1 730 cm^{-1} (C=O); δ ($CDCl_3$) 2.10 (3 H, s, Ac), 2.30 (3 H, s, ArMe), 3.86 (3 H, s, OMe), 6.26 (1 H, dd, *J* 3 and 7 Hz, 1-H), and 7.02 and 7.06 (each 1 H, each s, 5- and 8-H, respectively); *m/e* 284 (M^+).

1-Acetoxy-2,3-dihydro-6,7-dimethoxy-1H-pyrrolo[1,2-a]-indole-9-carbaldehyde (15).—A solution of the aldehyde (6) (0.44 g) and lead tetra-acetate (1.18 g) in acetic acid (30 ml) was stirred at room temperature under nitrogen for 15 h. Work-up as above gave (15) (0.36 g, 65%) as *needles*, m.p. 182—183° (from ethanol) (Found: C, 62.85; H, 5.6; N, 5.0. $C_{16}H_{17}NO_5$ requires C, 63.35; H, 5.65; N, 4.6%), $\nu_{max.}$ ($CHCl_3$) 1 730 (C=O) and 1 640 cm^{-1} (CHO); δ ($CDCl_3$) 2.06 (3 H, s, Ac), 3.89 (3 H, s, OMe), 3.92 (3 H, s, OMe), 6.42 (1 H, dd, *J* 3 and 7 Hz, 1-H), 6.72 (1 H, s, 5-H), 7.75 (1 H, s, 8-H), and 9.96 (1 H, s, CHO); *m/e* 303 (M^+).

1-Acetoxy-2,3-dihydro-7-methoxy-6-methyl-1H-pyrrolo-[1,2-a]indole-9-carbaldehyde (16).—A solution of the aldehyde (7) (0.23 g) and lead tetra-acetate (0.66 g) in acetic acid (20 ml) was stirred at room temperature under nitrogen for 15 h. Work-up as above gave (16) (0.22 g, 74%) as needles, m.p. 169—170° (from ether–ethanol) (lit.,[3] 170—172°), $\nu_{max.}$ ($CHCl_3$) 1 730 (C=O) and 1 640 cm^{-1} (CHO); δ ($CDCl_3$) 2.10 (3 H, s, Ac), 2.34 (3 H, s, ArMe), 3.92 (3 H, s, OMe), 6.48 (1 H, dd, *J* 3 and 7 Hz, 1-H), 7.06 (1 H, s, 5-H), 7.72 (1 H, s, 8-H), and 9.96 (1 H, s, CHO); *m/e* 287 (M^+).

Methyl 1-Acetoxy-2,3-dihydro-7-methoxy-6-methyl-1H-pyrrolo[1,2-a]indole-9-carboxylate (17).—A solution of the ester (8) (0.7 g) and lead tetra-acetate (1.8 g) in acetic acid (60 ml) was stirred at room temperature for 15 h under nitrogen. Work-up as above gave (17) (0.61 g, 71%) as *prisms*, m.p. 136—138° (from ether–n-hexane) (Found: C, 64.15; H, 5.95; N, 4.35. $C_{17}H_{19}NO_5$ requires C, 64.35; H, 6.05; N, 4.4%), $\nu_{max.}$ ($CHCl_3$) 1 730 (C=O) and 1 680 cm^{-1} (C=O), δ ($CDCl_3$) 2.06 (3 H, s, Ac), 2.34 (3 H, s, ArMe), 3.84 and 3.92 (each 3 H, each s, 2 × OMe), 6.52 (1 H, dd, *J* 3 and 7 Hz, 1-H), 7.02 (1 H, s, 5-H), and 7.56 (1 H, s, 8-H); *m/e* 317 (M^+).

1,8-Diacetoxy-2,3-dihydro-6,7-dimethoxy-1H-pyrrolo-[1,2-a]indole-9-carbonitrile (18).—A solution of the nitrile (4) (0.48 g) and lead tetra-acetate (2.65 g) in acetic acid (20 ml) was stirred at room temperature under nitrogen for 48 h. The mixture was then heated at 100 °C for 4 h, and evaporated under reduced pressure, and the residue was dissolved in water and extracted with benzene. The extract was washed with aqueous sodium hydrogen carbonate solution and water, dried (Na_2SO_4), and evaporated to leave a syrup, which was chromatographed on alumina (Woelm, grade III). Elution with benzene gave a solid, recrystallisation of which from ether afforded (18) (76 mg, 11%) as *needles*, m.p. 163—164° (Found: C, 60.15; H, 5.25; N, 7.9. $C_{18}H_{18}N_2O_6$ requires C, 60.35; H, 5.05; N, 7.8%), $\nu_{max.}$ ($CHCl_3$) 2 210 (CN) and 1 730 cm^{-1} (C=O); δ ($CDCl_3$) 2.13 (3 H, s, Ac), 2.42 (3 H, s, Ac), 3.86 (3 H, s, OMe), 3.94 (3 H, s, OMe), 6.26 (1 H, dd, *J* 3 and 7 Hz, 1-H), and 7.02 (1 H, s, 5-H); *m/e* 358 (M^+).

1-Acetoxy-6-acetoxymethyl-2,3-dihydro-7-methoxy-1H-pyrrolo[1,2-a]indole-9-carbonitrile (19).—A solution of the nitrile (5) (0.45 g) and lead tetra-acetate (2.64 g) in acetic acid (20 ml) was stirred at 90 °C under nitrogen for 9 h, then evaporated. The residue was dissolved in water and extracted with benzene. The organic layer was washed with aqueous sodium hydrogen carbonate solution and water, dried (Na_2SO_4), and evaporated. The residual reddish syrup was chromatographed on silica gel. Elution with benzene gave a solid, recrystallisation of which from methanol afforded (19) (120 mg, 18%) as brownish *needles*, m.p. 158—160° (Found: C, 63.15; H, 5.45; N, 8.0. $C_{18}H_{18}N_2O_5$ requires C, 63.15; H, 5.3; N, 8.2%), $\nu_{max.}$ ($CHCl_3$) 2 210 (CN) and 1 730 cm^{-1} (C=O); δ ($CDCl_3$) 2.10 (6 H, s, 2 × Ac), 3.86 (3 H, s, OMe), 5.20 (2 H, s, $ArCH_2O$), 6.24 (1 H, dd, *J* 3 and 7 Hz, 1-H), 7.02 and 7.26 (each 1 H, each s, 5- and 8-H, respectively); *m/e* 342 (M^+).

2,3-Dihydro-1-hydroxy-7-methoxy-6-methyl-1H-pyrrolo-[1,2-a]indole-9-carbaldehyde (20).—A solution of the aldehyde (16) (0.574 g) in methanolic potassium hydroxide (40 ml) was refluxed for 30 min, then evaporated, and the residue was extracted with benzene. The extract was washed with water, dried (Na_2SO_4), and evaporated to leave a solid, which afforded (20) (0.421 g, 86%) as *needles*, m.p. 154—155° (from ethanol) (Found: C, 68.2; H, 6.0; N, 5.7. $C_{14}H_{15}NO_3$ requires C, 68.55; H, 6.15; N, 5.7%), $\nu_{max.}$ ($CHCl_3$) 1 630 cm^{-1} (C=O); δ ($CDCl_3$) 2.22 (3 H, s, ArMe), 3.80 (3 H, s, OMe), 5.36 (1 H, t, *J* 6 Hz, 1-H), 6.66 (1 H, s, 5-H), 7.28 (1 H, s, 8-H), 9.76 (1 H, s, CHO); *m/e* 245 (M^+).

Methyl 2,3-Dihydro-1-hydroxy-7-methoxy-6-methyl-1H-pyrrolo[1,2-a]indole-9-carboxylate (21).—A mixture of the ester (17) (160 mg), saturated sodium hydrogen carbonate solution (12 ml), water (20 ml), and methanol (60 ml) was

stirred at room temperature for 24 h, and then concentrated under reduced pressure. The residue was extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated to leave a syrup, which was chromatographed on silica gel. Elution with benzene gave a solid, recrystallisation of which from ether afforded (21) (110 mg, 79%) as *prisms*, m.p. 121—123° (Found: C, 65.5; H, 6.2; N, 5.1. $C_{15}H_{17}NO_4$ requires C, 65.45; H, 6.2; N, 5.1%), $\nu_{max.}$ ($CHCl_3$) 1 660 cm^{-1} (C=O); δ ($CDCl_3$) 2.28 (3 H, s, ArMe), 3.86 and 3.92 (each 3 H, each s, 2 × OMe), 5.54 (1 H, t, *J* 6 Hz, 1-H), and 7.00 and 7.38 (each 1 H, s, 5- and 8-H); *m/e* 275 (M^+).

2,3-*Dihydro*-1-*hydroxy*-7-*methoxy*-6-*methyl*-5,8-*dioxo*-1H-*pyrrolo*[1,2-a]*indole*-9-*carbaldehyde* (28).—A mixture of the quinone (27) [3] (90 mg), saturated sodium hydrogen carbonate solution (6 ml), water (10 ml), and methanol (30 ml) was stirred at room temperature for 1 h, then concentrated under reduced pressure at 15 °C. The residue was extracted with chloroform and the organic layer was washed with water, dried (Na_2SO_4), and evaporated to leave a solid, recrystallisation of which from ethanol afforded (28) (74 mg, 95%) as orange *needles*, m.p. 179—181° (Found: C, 61.45; H, 5.05; N, 5.25. $C_{14}H_{13}NO_5$ requires C, 61.1; H, 4.75; N, 5.1%), $\nu_{max.}$ ($CHCl_3$) 1 660, 1 650, and 1 636 cm^{-1} (C=O); δ ($CDCl_3$) 1.96 (3 H, s, ArMe), 4.02 (3 H, s, OMe), 5.40 (1 H, t, *J* 6 Hz, 1-H), and 10.20 (1 H, s, CHO); *m/e* 275 (M^+).

2,3-*Dihydro*-7-*methoxy*-6-*methyl*-1-*oxo*-1H-*pyrrolo*[1,2-a]-*indole*-9-*carbaldehyde* (22).—To a solution of the aldehyde (20) (0.25 g) in methylene chloride (10 ml) was added activated manganese dioxide (2 g). The mixture was stirred at room temperature for 2 h, then filtered through Celite, and the Celite and inorganic material were washed with methylene chloride. The combined filtrate and washings were concentrated to leave a solid, which was recrystallised from chloroform to give (22) as pale yellow *needles* (0.18 g, 74%), m.p. 248—249° (Found: C, 68.7; H, 5.45; N, 5.85. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.4; N, 5.75%), $\nu_{max.}$ ($CHCl_3$) 1 710 (C=O) and 1 655 cm^{-1} (C=O); δ ($CDCl_3$) 2.34 (3 H, s, ArMe), 3.22 (2 H, t, *J* 6 Hz, 2-H_2), 3.92 (3 H, s, OMe), 4.22 (2 H, t, *J* 6 Hz, 3-H_2), 7.34 and 7.76 (each 1 H, each s, 5- and 8-H, respectively), and 10.34 (1 H, s, CHO); *m/e* 243 (M^+).

Methyl 2,3-*Dihydro*-7-*methoxy*-6-*methyl*-1-*oxo*-1H-*pyrrolo*-[1,2-a]*indole*-9-*carboxylate* (23).—A mixture of the ester (21) (20 mg), activated manganese dioxide (200 mg), and methylene chloride (3 ml) was stirred at room temperature under nitrogen for 7 h. Work-up as above gave (23) (16 mg, 80%) as pale yellow *prisms*, m.p. 213—215° (from methanol) (Found: C, 65.9; H, 5.8; N, 5.5. $C_{15}H_{15}NO_4$ requires C, 65.9; H, 5.55; N, 5.1%), $\nu_{max.}$ ($CHCl_3$) 1 720 (C=O) and 1 700 cm^{-1} (C=O); δ ($CDCl_3$) 2.30 (3 H, s, ArMe), 3.16 (2 H, t, *J* 6 Hz, 2-H_2), 3.86 and 3.92 (each 3 H, each s, 2 × OMe), 4.30 (2 H, t, *J* 6 Hz, 3-H_2), 7.10 and 7.54 (each 1 H, each s, 8- and 5-H); *m/e* 273 (M^+).

1-*Chloro*-2,3-*dihydro*-7-*methoxy*-6-*methyl*-5,8-*dioxo*-1H-*pyrrolo*[1,2-a]*indole*-9-*carbaldehyde* (29).—A mixture of the aldehyde (28) (10 mg), methanesulphonyl chloride (1 ml), and lithium chloride (1 g) in dry dimethylformamide (2 ml) was stirred at 75 °C under nitrogen for 45 min. The mixture was diluted with water, basified with solid sodium hydrogen carbonate, and extracted with chloroform. The organic layer was washed with water, dried (Na_2SO_4), and evaporated to leave an oil, which was chromatographed on silica gel. Elution with chloroform gave an orange solid, $\nu_{max.}$ ($CHCl_3$) 1 675, 1 660, and 1 640 cm^{-1} (C=O); δ ($CDCl_3$) 1.94 (3 H, s, ArMe), 4.00 (3 H, s, OMe), 4.96 (1 H, t, *J* 6 Hz, 1-H), and 10.34 (1 H, s, CHO); *m/e* 295 (M^+), which was unstable at room temperature.

6,7-*Dimethoxy*-3H-*pyrrolo*[1,2-a]*indole*-9-*carbonitrile* (24).—A solution of the nitrile (13) (60 mg) in acetic acid (5 ml) was heated at 90—100 °C for 6 h, then evaporated under reduced pressure to leave a solid, which was chromatographed on silica gel. Elution with chloroform eluate gave a solid, recrystallisation of which from methanol gave (13) (23 mg, 48%) as *needles*, m.p. 171—172° (Found: C, 69.6; H, 5.0; N, 11.65. $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.0; N, 11.65%), $\nu_{max.}$ ($CHCl_3$) 2 210 cm^{-1} (CN); δ ($CDCl_3$) 3.92 (6 H, s, 2 × OMe), 4.58br (2 H, s, 3-H_2), 6.48br (3 H, s, 1-, 2-, and 5-H), and 7.06 (1 H, s, 8-H); *m/e* 240 (M^+).

7-*Methoxy*-6-*methyl*-3H-*pyrrolo*[1,2-a]*indole*-9-*carbonitrile* (25).—A solution of the nitrile (14) (60 mg) in acetic acid (3 ml) was heated at 105—110 °C under a stream of nitrogen for 5 h, then evaporated under reduced pressure. The residue was chromatographed on silica gel. Benzene–chloroform (1 : 1 v/v) eluted a syrup which was purified by thick-layer chromatography on silica gel (chloroform). Recrystallisation from methanol gave *needles* (25 mg, 53%), m.p. 142—143° (Found: C, 74.95; H, 5.4; N, 12.75. $C_{14}H_{12}N_2O$ requires C, 75.0; H, 5.4; N, 12.5%), $\nu_{max.}$ ($CHCl_3$) 2 210 cm^{-1} (CN); δ ($CDCl_3$) 2.30 (3 H, s, ArMe), 3.84 (3 H, s, OMe), 4.54br (2 H, s, 3-H_2), and 6.70—7.00 (4 H, m, 2 × ArH and 2 × olefinic H); *m/e* 224 (M^+).

Methyl 7-*Methoxy*-6-*methyl*-3H-*pyrrolo*[1,2-a]*indole*-9-*carboxylate* (26).—A solution of the ester (17) (32 mg) in acetic acid (5 ml) was heated at 105—110 °C for 3 h, then evaporated under reduced pressure. The residual syrup was chromatographed on silica gel. Elution with benzene–chloroform (1 : 1 v/v) gave a syrup which was purified by thick-layer chromatography on silica gel (chloroform) to give a solid (6 mg, 23%). This was recrystallised from methanol to give prisms, m.p. 153—155° (lit.,[4] 151—155°), $\nu_{max.}$ ($CHCl_3$) 1 680 cm^{-1} (C=O); δ ($CDCl_3$) 2.26 (3 H, s, ArMe), 3.82 and 3.89 (each 3 H, each s, 2 × OMe), 4.45 (3 H, t, *J* 2 Hz, 3-H_2), 6.52 (1 H, d, *J* 6 Hz, 1-H), 6.88 (1 H, s, 5-H), 7.02 (1 H, m, 2-H), and 7.48 (1 H, s, 8-H); *m/e* 257 (M^+).

We thank Dr. M. Koizumi, Mr. K. Kawamura, Mrs. C. Koyanagi, Miss K. Mushiake, Mrs. R. Kobayashi, Miss R. Suenaga, Miss E. Nagaoka, and Miss M. Tanno for microanalyses and spectral measurements.

[6/1226 *Received*, 24*th June*, 1976]