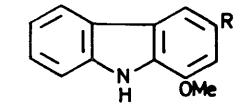
A New Route to 1-Oxygenated Carbazoles. Synthesis of the Carbazole Alkaloids Murrayafoline-A and Murrayaquinone-A[1]

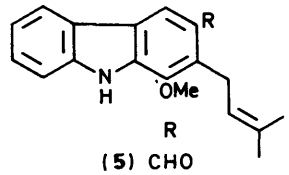
Tracey Martin and Christopher J. Moody*
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

1-Oxygenated carbazoles are prepared in 4 steps from indole-2-carboxylates by condensation with γ-butyrolactones to give the lactones (**12**), followed by hydrolysis with concomitant decarboxylation to the alcohols (**13**), and oxidation to the aldehydes (**14**). The aldehydes (**14**) cyclise to 1-methoxycarbazoles on treatment with boron trifluoride–methanol or with methanolic hydrogen chloride. The methoxycarbazoles (**15a**) and (**4**) were converted into the corresponding carbazolequinones (**18**) and (**7**) by demethylation, and oxidation. The carbazole alkaloids murrayafoline-A (**4**) and murrayaquinone-A (**7**) were prepared.

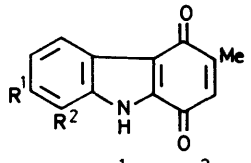
The plants of the genus *Murraya* (Rutaceae) are the major source of carbazole alkaloids, of which there are now about 50 known.[2] Several of these contain an oxygen substituent at the 1-position, and typical examples include the C_{13}-group alkaloids murrayanine (**1**),[2] mukoeic acid (**2**),[2] mukonine (**3**),[2] and murrayafoline-A (**4**),[3,4,5] and the C_{18}-alkaloids indizoline (**5**)[2] and clausenapin (**6**).[6] Recently the first naturally occurring carbazolequinones, murrayaquinone-A (**7**) and -B (**8**),[4] and pyrayaquinone-B (**9**),[7] have been isolated from *M. euchrestifolia* Hayata.



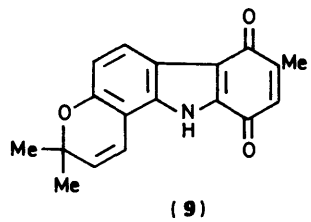
R
(**1**) CHO
(**2**) CO_2H
(**3**) CO_2Me
(**4**) Me



R
(**5**) CHO
(**6**) Me

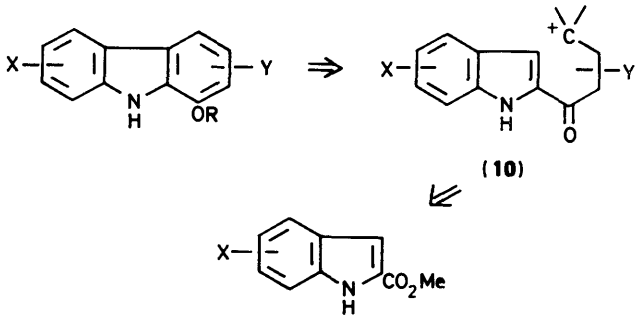


R^1 R^2
(**7**) H H
(**8**) OMe $CH_2CH{=}CMe_2$



(**9**)

Although many carbazole alkaloids have been synthesized by the classical Fischer–Borsche cyclisation of the appropriate cyclohexanone arylhydrazones,[2,8] the vigorous conditions required for the subsequent dehydrogenation step render the method inappropriate when sensitive substituents are present. We have developed a new synthesis of 1-oxygenated carbazoles based on the simple strategy shown in Scheme 1. This approach, which involves ring closure of a 2-substituted indole (**10**) bearing a 4-carbon chain, in which the terminal carbon is rendered electrophilic, to the indole-3-position, has surprisingly found little use in carbazole synthesis to date.[9] We now report full details of this work which has resulted in the synthesis of the alkaloids murrayafoline-A (**4**) and murrayaquinone-A (**7**), and in the following paper[10] we describe the synthesis of the slightly more complex alkaloid, murrayaquinone-B (**8**).



(**10**)

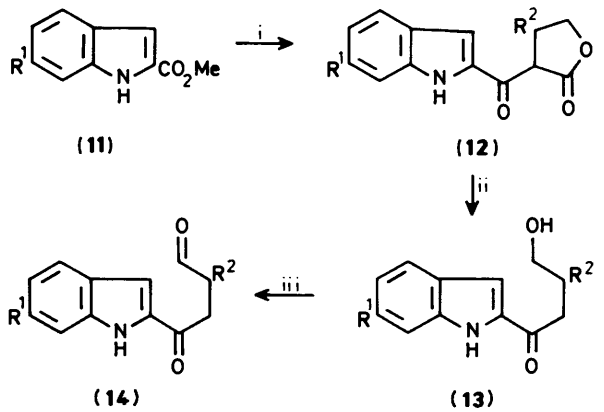
Scheme 1.

Results and Discussion

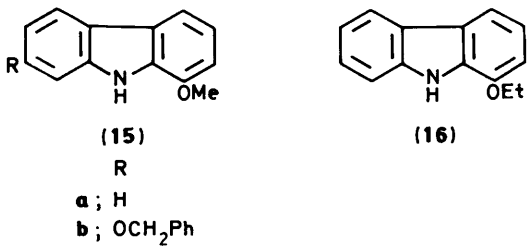
The starting materials for the preparation of the required substrates (**10**) for the cyclisation were the indole-2-carboxylates (**11**). Methyl indole-2-carboxylate (**11a**) was prepared by esterification of the commercially available acid, and the 6-benzyloxyindole (**11c**) was prepared from 4-benzyloxybenzaldehyde *via* an azidocinnamate.[11] The additional carbon atoms required for the third ring were added by condensation[12] of the indole ester (**11**) with γ-butyrolactone or 4-methylbutyrolactone in the presence of sodium methoxide to give the lactones (**12**). On heating in aqueous dioxane containing a trace amount of sodium hydroxide, the lactones (**12**) underwent hydrolysis and concomitant decarboxylation to give the alcohols (**13**), which were isolated by simple filtration from the cooled reaction mixture. Oxidation of the alcohols with pyridinium chlorochromate (PCC) gave the corresponding aldehydes (**14**) (Scheme 2).

Although the alcohols (**13**) could not be cyclised under Lewis acid conditions,[13] the aldehydes (**14**) cyclised smoothly to the corresponding 1-methoxycarbazoles simply on stirring in a boron trifluoride–methanol complex at room temperature. Thus the aldehyde (**14a**) gave 1-methoxycarbazole (**15a**) (59%), the aldehyde (**14c**) gave the carbazole (**15b**) (46%), and the aldehyde (**14b**) gave 1-methoxy-3-methylcarbazole (**4**) (58%) (murrayafoline-A). The sample of murrayafoline-A prepared by the above route was identical with material obtained from natural sources.

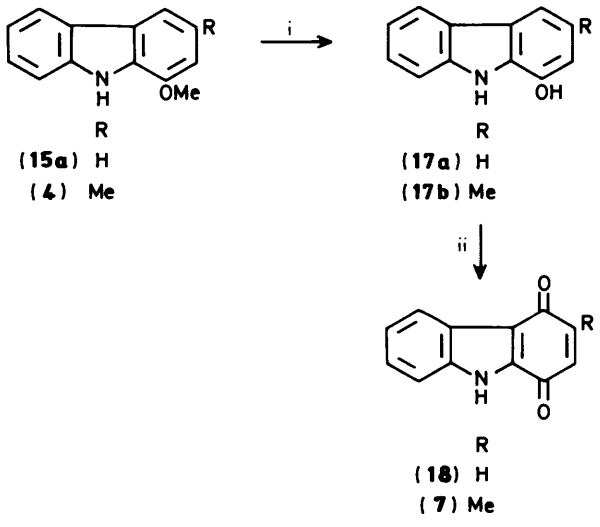
The cyclisation step could also be effected using hydrogen chloride in methanol or ethanol, and under these conditions the aldehyde (**14a**) gave the carbazoles (**15a**) (56%) and (**16**) (46%), respectively.



Scheme 2. (**a**, $R^1 = R^2 = H$; **b**, $R^1 = H$, $R^2 = Me$; **c**, $R^1 = OCH_2Ph$, $R^2 = H$) *Reagents*: i, 4-R^2-butyrolactone, NaOMe, dioxane; ii, H_2O, NaOH, dioxane; iii, PCC, NaOAc, CH_2Cl_2

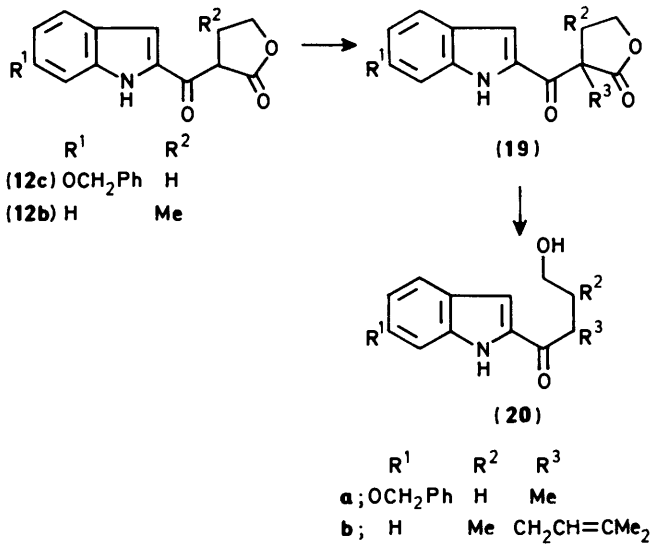


The 1-methoxycarbazoles (**15a**) and (**4**) were converted into the carbazolequinones (**18**)[14a] and (**7**)[14b] *via* the corresponding 1-hydroxy derivatives (**17**) (Scheme 3). Thus treatment of the carbazoles (**15a**) and (**4**) with boron tribromide in dichloromethane resulted in demethylation in high yield, and the resulting hydroxycarbazoles (**17**) were oxidised with Fremy's salt to the quinones. The spectral data for the quinone (**7**) (murrayaquinone-A) were comparable with those reported for the natural product.[4,5]



Scheme 3. *Reagents*: i, BBr_3, CH_2Cl_2, −78 °C; ii, $(KO_3S)_2NO^{\bullet}$, acetone–water

An attempt was also made to extend the new carbazole synthesis to the preparation of slightly more complex alkaloids such as clausenapin (**6**). It was envisaged that the additional 5-carbon substituent could be introduced either by use of the appropriate 2-substituted γ-butyrolactone in the condensation step, or by alkylation of the lactone (**12b**). A model study established that the first route was not viable, whereas the second proceeded easily. Thus the lactone (**12c**) was readily converted into the *C*-methyl derivative (**19a**) by treatment with sodium hydride in dimethylformamide (DMF) followed by iodomethane, the relative p*K* values of the indole NH (*ca.* 16) and the β-dicarbonyl group (*ca.* 11) ensuring that no *N*-alkylation occurred. Attempts to prepare such *C*-methylated lactones by the condensation of the indole-2-carboxylates with 2-methyl-γ-butyrolactone were unsuccessful. In a similar manner, the lactone (**12b**) was alkylated with 3,3-dimethylallyl bromide to give the lactone (**19b**), hydrolysis of which gave, after decarboxylation, the alcohol (**20b**) (Scheme 4). However,



Scheme 4.

attempts to oxidise the alcohol (**20b**) using PCC resulted in decomposition, and the aldehyde required for the cyclisation to clausenapin was not obtained. Similarly, the model alcohol (**20a**) was also unstable towards oxidation.

Experimental

U.v. spectra were recorded in the range 450—200 nm on a Pye Unicam SP800 instrument, calibrated against holmium glass (360.8 nm). I.r. spectra were recorded in the range 4 000—600 cm^{-1} on a Perkin-Elmer 298 spectrophotometer, and were calibrated against polystyrene. ^1H N.m.r. spectra were recorded at 90 MHz on Perkin-Elmer R32, and at 250 MHz on Bruker WM250 instruments using tetramethylsilane as internal standard. Mass spectra were obtained on a VG Micromass 7070B instrument operating at 70 eV and at the source temperature indicated. Column chromatography was carried out on Merck Kieselgel 60H under hand pump pressure. Light petroleum refers to the fraction boiling in the range 40—60 °C unless otherwise stated. All solvents were dried by standard procedures, and ether refers to diethyl ether.

Methyl Indole-2-carboxylate (**11a**).—This compound was prepared in 98% yield by esterification of the commercially available acid using methanol and concentrated sulphuric acid and had m.p. 148—152 °C (lit.,[15] 150–151 °C).

Methyl 6-Benzyloxyindole-2-carboxylate (**11c**).—Sodium (2.15 g, 0.093 mol) was added to dry methanol (50 ml) under nitrogen and the solution cooled to −15 °C. A solution of 4-benzyloxybenzaldehyde[16] (5.00 g, 0.024 mol) and methyl azidoacetate (10.85 g, 0.094 mol) in dry methanol (80 ml) was added over 45 min the temperature being maintained at −15 °C. The reaction mixture was stirred for 3 h at this temperature and then allowed to warm up slowly to room temperature over 3 h. The flask contents were poured into saturated aqueous ammonium chloride (200 ml) and extracted with ether (300 ml). The organic extracts were washed with water (2 × 100 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give *methyl 2-azido-3-(4-benzyloxyphenyl)-propenoate* (5.77 g, 78%) as a lemon-yellow solid, m.p. 93.5—95.5 °C (purified by chromatography) (Found: C, 65.9; H, 4.7; N, 13.5. $C_{17}H_{15}N_3O_3$ requires C, 66.0; H, 4.85; N, 13.6%); $\nu_{max.}$(Nujol) 2 120, 1 700, 1 600, 1 270, 1 240, and 1 170 cm^{-1}; δ(90 MHz; $CDCl_3$) 3.84 (3 H, s, CO_2Me), 5.07 (2 H, s, CH_2Ph), 6.82 (1 H, s, 3-H), 6.91 (2 H, d, *J* 8 Hz, ArH), 7.32 (5 H, s, Ph), and 7.70 (2 H, d, *J* 8 Hz, ArH); *m/z* (90 °C) 309 (M^+, 1%), 281 (60), 190 (23), 158 (8), 130 (6), and 91 (100).

A vigorously stirred solution of the above azide (4.00 g, 0.013 mol) in dry xylene (400 ml) was plunged into a Woods metal bath at 210 °C and refluxed under nitrogen for 2 h. The xylene was evaporated under reduced pressure to give the *title compound* (**11c**) (3.53 g, 97%) as a lemon-yellow solid, m.p. 139.5—140 °C (from hexane–chloroform) (Found: C, 72.5; H, 5.35; N, 5.2. $C_{17}H_{15}NO_3$ requires C, 72.6; H, 5.3; N, 5.0%); $\nu_{max.}$(Nujol) 3 310 and 1 690 cm^{-1}; δ(90 MHz; $CDCl_3$) 3.88 (3 H, s, CO_2Me), 5.06 (2 H, s, CH_2Ph), 6.78—7.18 (3 H, m, ArH), 7.34 (5 H, m, Ph), 7.49 (1 H, d, *J* 9 Hz, 4-H), and 8.85 (1 H, br s, NH); *m/z* (130 °C) 281 (M^+, 44%), 250 (3), 190 (46), 158 (17), 130 (11), and 91 (100).

4,5-Dihydro-3-indol-2-ylcarbonylfuran-2-one (**12a**).—A mixture of methyl indole-2-carboxylate (**11a**) (1.00 g, 5.71 mmol), 4,5-dihydrofuran-2-one (1.97 g, 22.86 mmol), and sodium methoxide (2.97 g, 55.00 mmol) in dry dioxane (25 ml) was heated at 110 °C for 45 h under nitrogen. Ice–water (25 ml) was added and the mixture was then cooled and acidified to pH 4—6. The mixture was extracted with chloroform (250 ml) all the extracts were washed with water (500 ml), dried (Na_2SO_4), and evaporated under reduced pressure. The crude product was chromatographed on silica (25 g) eluting with light petroleum and ether–ethyl acetate to give (i) methyl indole-2-carboxylate (**11a**) (0.11 g, 11%), and (ii) the title compound (**12a**) (0.90 g, 69%) as a pale lemon-yellow solid, m.p. 172—173 °C (lit.,[12] m.p. 170—173 °C); $\nu_{max.}$(Nujol) 3 320, 1 750, 1 650, 1 630, and 1 615 cm^{-1}; δ[250 MHz; $(CD_3)_2SO$] 2.60 (2 H, m, 4-H), 4.42 (2 H, m, 5-H), 4.87 (1 H, t, *J* 6 Hz, 3-H), 7.12 (1 H, t, *J* 6 Hz, 5-ArH or 6-ArH), 7.33 (1 H, t, *J* 6 Hz, 6-ArH or 5-ArH), 7.48 (1 H, d, *J* 6 Hz, 7-ArH), 7.54 (1 H, d, *J* 2 Hz, 3-ArH), 7.75 (1 H, d, *J* 6 Hz, 4-ArH), and 10.97 (1 H, br s, NH); *m/z* (160 °C) 229 (M^+, 60%), 198 (8), 185 (7), 144 (100), 117 (23), and 89 (39).

4,5-Dihydro-3-indol-2-ylcarbonyl-4-methylfuran-2-one (**12b**).—A mixture of methyl indole-2-carboxylate (**11a**) (0.24 g, 1.37 mmol), 4,5-dihydro-4-methylfuran-2-one (0.56 g, 5.60 mmol), and sodium methoxide (0.60 g, 11.11 mmol) in dry dioxane (6 ml) was heated at 110 °C for 45 h under nitrogen. Work-up as above and chromatography gave the *title compound* (**12b**) (0.24 g, 72%) as a pale lemon-yellow solid, m.p. 157—158 °C (from hexane–chloroform) (Found: C, 69.0; H, 5.4; N, 5.75. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.35; N, 5.8%); $\nu_{max.}$(Nujol) 3 300, 1 775, 1 640, and 1 620 cm^{-1}; δ(250 MHz; $CDCl_3$) 1.28 (3 H, d, *J* 6 Hz, Me), 3.25 (1 H, m, 4-H), 4.00 (1 H, dd, *J* 8, 6 Hz, 5-H), 4.03 (1 H, d, *J* 6 Hz, 3-H), 4.63 (1 H, dd, *J* 8, 6 Hz, 5-H), 7.18 (1 H, m, ArH), 7.34—7.47 (3 H, m, ArH), 7.74 (1 H, d, *J* 8 Hz, 4-ArH), and 9.15 (1 H, br s, NH); *m/z* (120 °C) 243 (M^+, 82%), 228 (7), 212 (8), 185 (12), 170 (10), 144 (100), 127 (10), and 117 (20).

4,5-Dihydro-3-(6-benzyloxyindol-2-ylcarbonyl)furan-2-one (**12c**).—A mixture of methyl 6-benzyloxyindole-2-carboxylate (**11c**) (1.00 g, 3.56 mmol), 4,5-dihydrofuran-2-one (1.22 g, 14.19 mmol), and sodium methoxide (1.54 g, 28.52 mmol) in dry dioxane (17 ml) was heated at 110 °C for 45 h under nitrogen. Work-up as above and chromatography gave (i) methyl 6-benzyloxyindole-2-carboxylate (**11c**) (0.19 g, 19%), and (ii) the *title compound* (**12c**) (0.60 g, 50%) as a pale lemon-yellow solid, m.p. 194—195 °C (Found: C, 71.5; H, 5.0; N, 4.1. $C_{20}H_{17}NO_4$ requires C, 71.6; H, 5.1; N, 4.2%); $\nu_{max.}$(Nujol) 3 380, 1 760, 1 740, 1 660, and 1 625 cm^{-1}; δ[250 MHz; $(CD_3)_2SO$] 2.55 (2 H, m, 4-H), 4.30—4.50 (2 H, m, 5-H), 4.78 (1 H, t, *J* 6 Hz, 3-H), 5.14 (2 H, s, CH_2Ph), 6.85 (1 H, d, *J* 6 Hz, 5-ArH), 6.96 (1 H, s, 7-ArH), 7.29—7.53 (6 H, m, Ph, 3-ArH), 7.63 (1 H, d, *J* 8 Hz, 4-ArH), and 11.75 (1 H, s, NH); *m/z* (160 °C) 335 (M^+, 25%), 244 (36), and 91 (100).

4-Hydroxy-1-indol-2-ylbutan-1-one (**13a**).—The indole (**12a**) (0.63 g, 2.74 mmol), dioxane (10 ml), and water (10 ml) were heated together at 110 °C in the presence of a few drops of dilute aqueous sodium hydroxide for 17 h. The mixture was evaporated under reduced pressure to precipitate a solid which was filtered off and dried to give the title compound (**13a**) (0.52 g, 94%) as a beige crystalline solid, m.p. 130.5—132.5 °C (lit.,[12] m.p. 130—133 °C); $\nu_{max.}$(Nujol) 3 400br (OH), 3 320 (NH), 1 650, and 1 620 cm^{-1}; δ[250 MHz; $(CD_3)_2SO$] 1.62 (1 H, br s, OH), 2.06 (2 H, m, 3-H), 3.12 (2 H, t, *J* 6 Hz, 4-H), 3.76 (2 H, t, *J* 4 Hz, 2-H), 7.16 (1 H, m, ArH), 7.26 (1 H, m, ArH), 7.30—7.47 (2 H, m, ArH), 7.72 (1 H, d, *J* 6 Hz, 4-ArH), and 9.12 (1 H, br s, NH); *m/z* (140 °C) 203 (M^+, 31%), 185 (8), 159 (78), 144 (89), 116 (22), and 89 (100).

4-Hydroxy-1-indol-2-yl-3-methylbutan-1-one (**13b**).—The indole (**12b**) (90.5 mg, 0.37 mmol), dioxane (1.4 ml), and water (1.4 ml) were heated together at 110 °C in the presence of a few drops of dilute aqueous sodium hydroxide for 18 h. The mixture was evaporated under reduced pressure, followed by ice-cooling to precipitate a solid, which was filtered off and dried to give the *title compound* (**13b**) (59 mg, 73%) as a beige crystalline solid, m.p. 109.5—110.5 °C (from hexane–chloroform) (Found: C, 71.7; H, 6.9; N, 6.3. $C_{13}H_{15}NO_2$ requires C, 71.9; H, 6.9; N, 6.45%); $\nu_{max.}$(Nujol) 3 320br (NH, OH), 1 650, and 1 620 cm^{-1}; δ(250 MHz; $CDCl_3$) 1.07 (3 H, d, *J* 6 Hz, Me), 2.00 (1 H, br s, OH), 2.40 (1 H, m, 3-H), 2.88 (1 H, dd, *J* 14, 6 Hz, 4-H), 3.11 (1 H, dd, *J* 14, 6 Hz, 4-H), 3.60 (2 H, m, 2-H), 7.16 (1 H, m, ArH), 7.26 (1 H, m, ArH), 7.31—7.48 (2 H, m, ArH), 7.72 (1 H, d, *J* 7 Hz, 4-ArH), and 9.13 (1 H, br s, NH); *m/z* (160 °C) 217 (M^+, 37%), 199 (17), 184 (20), 159 (100), 144 (79), 130 (8), 117 (24), and 89 (54).

4-Hydroxy-1-(6-benzyloxyindol-2-yl)butan-1-one (**13c**).—The indole (**12c**) (0.23 g, 0.70 mmol), dioxane (3.2 ml), and water (3.2 ml) were heated together at 110 °C in the presence of a few drops of dilute aqueous sodium hydroxide for 18 h. The mixture was cooled to precipitate a solid which was filtered off and dried to give the *title compound* (**13c**) (0.21 g, 98%) as a fluffy lemon-yellow crystalline solid, m.p. 155.5—156.5 °C (from hexane–chloroform) (Found: C, 73.7; H, 6.0; N, 4.5. $C_{19}H_{19}NO_3$ requires C, 73.8; H, 6.15; N, 4.5%); $\nu_{max.}$(Nujol) 3 380br (OH), 3 310 (NH), 1 640, and 1 620 cm^{-1}; δ(250 MHz; $CDCl_3$) 2.03 (3 H, m, 3-H, OH), 3.07 (2 H, t, *J* 6 Hz, 4-H), 3.75 (2 H, br s, 2-H), 5.12 (2 H, s, CH_2Ph), 6.89 (2 H, m, 5-ArH and 3-ArH or 7-ArH), 7.19 (1 H, s, 7-ArH or 3-ArH), 7.29—7.51 (5 H, m, Ph), 7.58 (1 H, d, *J* 8 Hz, 4-ArH), and 9.05 (1 H, br s, NH); *m/z*

(140 °C) 309 (M^+, 26%), 291 (16), 218 (6), 200 (92), 158 (6), 130 (6), and 91 (100).

1-*Indol*-2-*ylbutane*-1,4-*dione* (**14a**).—A solution of the alcohol (**13a**) (30.0 mg, 0.148 mmol) in dry dichloromethane (1 ml) was added to PCC (49.3 mg, 0.229 mmol) in dry dichloromethane (1.5 ml) under nitrogen. The mixture was stirred at room temperature for 2 h. Dry ether (1 ml) was added and the liquid decanted off; this procedure was repeated three times. The ethereal product was filtered through a Florisil pad and the filtrate was evaporated under reduced pressure to yield the *title compound* (**14a**) (20.9 mg, 70%) as a beige solid, m.p. 133—135 °C (from hexane–chloroform) (Found: C, 71.4; H, 5.4; N, 6.95. $C_{12}H_{11}NO_2$ requires C, 71.6; H, 5.5; N, 7.0%); $\nu_{max.}$(Nujol) 3 320, 2 730, 1 720, 1 655, and 1 620 cm^{-1}; δ(90 MHz; $CDCl_3$) 2.93 (2 H, t, *J* 6 Hz, 3-H), 3.31 (2 H, t, *J* 6 Hz, 2-H), 6.94—7.44 (4 H, m, ArH), 7.65 (1 H, d, *J* 8 Hz, 4-ArH), 9.03 (1 H, br s, NH), and 9.79 (1 H, s, CHO); *m/z* (140 °C) 201 (M^+, 66%), 173 (41), 159 (11), 144 (100), 130 (11), 117 (32), and 89 (56).

1-*Indol*-2-*yl*-3-*methylbutane*-1,4-*dione* (**14b**).—A solution of the alcohol (**13b**) (65 mg, 0.30 mmol) in dry dichloromethane (2 ml) was added to PCC (96 mg, 0.45 mmol) and anhydrous sodium acetate (7.2 mg, 0.09 mmol) in dry dichloromethane (4 ml) under nitrogen. The mixture was stirred at room temperature for 2.5 h. Work-up as above gave the *title compound* (**14b**) (53.4 mg, 83%) as a lemon-yellow solid, m.p. 116—118 °C (from hexane–chloroform) (Found: C, 72.5; H, 6.1; N, 6.4. $C_{13}H_{13}NO_2$ requires C, 72.6; H, 6.05; N, 6.5%); $\nu_{max.}$(Nujol) 3 330, 1 725, 1 650, and 1 620 cm^{-1}; δ(250 MHz; $CDCl_3$) 1.27 (3 H, d, *J* 7 Hz, Me), 3.02 (1 H, dd, *J* 16, 5 Hz, 2-H), 3.14 (1 H, m, 3-H), 3.46 (1 H, dd, *J* 16, 5 Hz, 2-H), 7.17 (1 H, m, ArH), 7.31—7.48 (3 H, m, ArH), 7.72 (1 H, d, *J* 7 Hz, with additional fine coupling, 4-ArH), 9.07 (1 H, br s, NH), and 9.80 (1 H, s, CHO); *m/z* (160 °C) 215 (M^+, 48%), 199 (6), 187 (27), 172 (28), 159 (26), 144 (100), 130 (8), 117 (49), and 89 (87).

1-(6-*Benzyloxyindol*-2-*yl*)*butane*-1,4-*dione* (**14c**).—A solution of the alcohol (**13c**) (150 mg, 0.485 mmol) in dry dichloromethane (4 ml) was added to PCC (155 mg, 0.14 mmol) and anhydrous sodium acetate (11.6 mg, 0.14 mmol) in dry dichloromethane (7 ml) under nitrogen. The mixture was stirred at room temperature for 2.5 h. Work-up as above gave the *title compound* (**14c**) (91.3 mg, 61%) as a yellow solid, m.p. 154—155 °C (purified by chromatography) (Found: M^+, 307.1206. $C_{19}H_{17}NO_3$ requires *M*, 307.1208); $\nu_{max.}$(Nujol) 3 320, 1 720, 1 640, and 1 620 cm^{-1}; δ(250 MHz; $CDCl_3$) 2.93 (2 H, t, *J* 6 Hz, 3-H), 3.28 (2 H, t, *J* 6 Hz, 2-H), 5.13 (2 H, s, CH_2Ph), 6.84—7.00 (2 H, m, 5-ArH and 7-ArH or 3-ArH), 7.21 (1 H, m, 3-ArH or 7-ArH), 7.30—7.52 (5 H, m, Ph), 7.60 (1 H, m, 4-ArH), 8.97 (1 H, br s, NH), and 9.90 (1 H, s, CHO); *m/z* (140 °C) 307 (M^+, 41%), 216 (51), 198 (14), 187 (5), and 91 (100).

1-*Methoxy*-9H-*carbazole* (**15a**).—(a) Boron trifluoride–methanol complex (14% w/v; 1 ml, 2.06 mmol) was added to a solution of the aldehyde (**14a**) (30 mg, 0.15 mmol) in dry methanol (0.75 ml) under nitrogen and the mixture stirred at room temperature for 17 h. The dark brown solution was poured into water (8 ml) and extracted with ether (25 ml). The organic extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure and the crude product chromatographed on silica (1 g) eluting with light petroleum–ether to give the title compound (**15a**) (17.3 mg, 59%) as a colourless solid, m.p. 70—72 °C (lit.,[17] m.p. 69—70 °C) (Found: C, 79.1; H, 5.6; N, 7.0. Calc. for $C_{13}H_{11}NO$: C, 79.2; H, 5.6; N, 7.1%); $\lambda_{max.}$(EtOH) 219 (log ε 4.48), 237 (4.61), 246 (4.48), 254sh (4.22), 277sh (3.79), 287 (4.02), 311sh (3.40), 324 (3.54), and 337 nm (3.51); $\nu_{max.}$(Nujol) 3 420 and 1 580 cm^{-1}; δ(250 MHz; $CDCl_3$) 4.02 (3 H, s, OMe), 6.90 (1 H, d, *J* 7 Hz, 2-H), 7.16 (1 H, t, *J* 7 Hz, 3-H), 7.24 (1 H, m, 6-H), 7.42 (2 H, m, 7- and 8-H), 7.69 (1 H, d, *J* 7 Hz, 4-H), 8.06 (1 H, d, *J* 7 Hz, 5-H), and 8.27 (1 H, br s, NH); *m/z* (130 °C) 197 (M^+, 100%), 182 (73), 166 (8), 154 (44), 139 (8), and 127 (9).

(b) A solution of the aldehyde (**14a**) (31 mg, 0.154 mmol) in dry methanol (1 ml) under nitrogen was treated with dry methanol saturated with dry hydrogen chloride (1 ml) and stirred at room temperature for 16 h. The methanol was evaporated under reduced pressure and the residue chromatographed on silica (1 g), eluting with light petroleum–dichloromethane to give the title compound (**15a**) as a colourless solid (16.9 mg, 56%).

1-*Ethoxy*-9H-*carbazole* (**16**).—Dry ethanol saturated with dry hydrogen chloride (1 ml) was added to a solution of the aldehyde (**14a**) (27.9 mg, 0.139 mmol) in dry ethanol (1 ml) under nitrogen and the resultant brown solution was stirred at room temperature for 17 h. The ethanol was evaporated under reduced pressure and the crude product chromatographed on silica (2 g), eluting with light petroleum (b.p. 60—80 °C)–dichloromethane, to give the title compound (**16**) (13.4 mg, 46%) as a colourless solid, m.p. 93.5—94.5 °C (lit.,[17] m.p. 95 °C) (Found: C, 79.7; H, 6.3; N, 6.7. Calc. for $C_{14}H_{13}NO$: C, 79.6; H, 6.2; N, 6.6%); $\lambda_{max.}$(EtOH) 224 (log ε 4.40), 242 (4.44), 250sh (4.42), 258sh (4.22), 280sh (3.84), 289 (4.05), 312sh (3.44), 324 (3.57), and 337 nm (3.54); $\nu_{max.}$(Nujol) 3 400 and 1 585 cm^{-1}; δ(250 MHz; $CDCl_3$) 1.53 (3 H, t, *J* 8 Hz, Me), 4.25 (2 H, q, *J* 8 Hz, CH_2), 6.88 (1 H, d, *J* 8 Hz, 2-H), 7.14 (1 H, t, *J* 8 Hz, 3-H), 7.20 (1 H, m, 6-H), 7.36—7.50 (2 H, m, 7- and 8-H), 7.67 (1 H, d, *J* 8 Hz, 4-H), 8.06 (1 H, d, *J* 8 Hz, 5-H), and 8.30 (1 H, br s, NH); *m/z* (170 °C) 211 (M^+, 100%), 182 (53), 166 (4), 154 (39), and 127 (11).

1-*Methoxy*-3-*methyl*-9H-*carbazole* (*Murrayafoline-A*) (**4**).—Boron trifluoride–methanol complex (14% w/v; 1.7 ml, 3.5 mmol) was added to a solution of the aldehyde (**14b**) (55 mg, 0.26 mmol) in dry methanol (1.3 ml) under nitrogen and the reaction mixture stirred at room temperature for 17 h. The dark brown solution was poured into water (12 ml) and extracted with ether (50 ml). The organic extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to give a brown oil. The crude product was chromatographed on silica (1 g) eluting with light petroleum–ether to yield the title compound (**4**) (31.3 mg, 58%) as a colourless oil; $\lambda_{max.}$(EtOH) 221 (log ε 4.62), 233sh (4.65), 239 (4.74), 249 (4.58), 252sh (4.30), 280sh (3.95), 290 (4.18), 316sh (3.57), 329 (3.71), and 343 nm (3.63); $\nu_{max.}$(Nujol) 3 430br, 1 590, 1 310, and 1 230 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.52 (3 H, s, Me), 3.97 (3 H, s, OMe), 6.72 (1 H, s, 2-H), 7.19 (1 H, m, 6-H), 7.38 (2 H, m, 7- and 8-H), 7.47 (1 H, s, 4-H), 8.00 (1 H, d, *J* 8 Hz, 5-H), and 8.15 (1 H, br s, NH); pre-irradiation of the signal at 2.52 caused enhancements at 6.72 and 7.47; pre-irradiation at 3.97 caused an enhancement at 6.72; pre-irradiation at 6.72 caused enhancements at 2.52 and 3.97; pre-irradiation at 7.47 caused enhancements at 2.52 and 8.00; and pre-irradiation at 8.15 caused enhancements at 2.52 and 7.38; *m/z* (110 °C) 211 (M^+, 100%), 196 (56), 180 (6), and 168 (25); picrate m.p. 186—186.5 °C (from benzene) and mixed m.p. with authentic sample 186.5—187 °C (lit.,[5] m.p. 188—190 °C) (Found: C, 54.6; H, 3.6; N, 12.7. $C_{20}H_{16}N_4O_8$ requires C, 54.55; H, 3.6; N, 12.7%).

7-*Benzyloxy*-1-*methoxy*-9H-*carbazole* (**15b**).—Boron trifluoride–methanol complex (14% w/v; 1 ml, 2.06 mmol) was added to a solution of the aldehyde (**14c**) (44 mg, 0.14 mmol) in dry methanol (1 ml) under nitrogen and the mixture stirred at room temperature for 17 h. The dark mauve solution was poured into water (8 ml) and extracted with ether (25 ml). The

organic extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give a mauve residue. The crude product was chromatographed on silica (1 g), eluting with light petroleum–dichloromethane, to yield the *title compound* (**15b**) (19.7 mg, 46%) as a colourless solid, m.p. 139.5—140.5 °C (Found: C, 79.0; H, 5.8; N, 4.5. $C_{20}H_{17}NO_2$ requires C, 79.2; H, 5.6; N, 4.6%); $\lambda_{max.}$(EtOH) 238 (log ε 4.55), 249sh (4.40), 296 (3.97), 316sh (3.61), and 329sh nm (3.43); $\nu_{max.}$(Nujol) 3 400, 1 630, 1 615, 1 580, and 1 270 cm^{-1}; δ(250 MHz; $CDCl_3$) 4.00 (3 H, s, OMe), 5.16 (2 H, s, CH_2Ph), 6.84 (1 H, d, *J* 8 Hz, with additional fine coupling, 2-H), 6.92 (1 H, dd, *J* 8, 2 Hz, 6-H), 6.99 (1 H, d, *J* 2 Hz, 8-H), 7.13 (1 H, t, *J* 8 Hz, 3-H), 7.29—7.52 (5 H, m, Ph), 7.58 (1 H, d, *J* 8 Hz, 4-H), 7.92 (1 H, d, *J* 8 Hz, 5-H), and 8.16 (1 H, br s, NH); *m/z* (150 °C) 303 (M^+, 50%) 212 (100), 184 (33), 169 (5), 141 (13), and 91 (53).

1,4-*Dihydrocarbazole*-1,4-*dione* (**18**).—A solution of 1-methoxy-9*H*-carbazole (**15a**) (17 mg, 0.086 mmol) in dry dichloromethane (0.5 ml) was kept at −78 °C under nitrogen during the dropwise addition of boron tribromide in dichloromethane (1M; 0.2 ml, 0.2 mmol). The mixture was stirred for 16 h and then poured into ice–water (5 ml) and extracted with ether (20 ml). The ethereal extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to yield 1-hydroxy-9*H*-carbazole (**17a**) (13.6 mg, 86%) as a beige solid, m.p. 163—165 °C (lit.,[17] m.p. 162 °C); $\lambda_{max.}$(EtOH) 219 (log ε 4.51), 239 (4.60), 246sh (4.47), 278sh (3.81), 288 (4.03), 313sh (3.44), 326 (3.59), and 340 nm (3.56); $\nu_{max.}$(Nujol) 3 440 (NH), 3 250br (OH), and 1 585 cm^{-1}; δ(250 MHz; $CDCl_3$) 5.16 (1 H, br s, OH), 6.82 (1 H, d, *J* 8 Hz, 2-H), 7.08 (1 H, t, *J* 8 Hz, 3-H), 7.23 (1 H, m, 6-H), 7.43 (2 H, m, 7- and 8-H), 7.69 (1 H, d, *J* 8 Hz, 4-H), 8.06 (1 H, d, *J* 8 Hz, 5-H), and 8.26 (1 H, br s, NH); *m/z* (150 °C) 183 (M^+, 100%), 164 (5), 154 (28), and 127 (7).

A solution of Fremy's salt (105 mg, 0.392 mmol) and potassium dihydrogen orthophosphate (6 mg, 0.044 mmol) in water (6 ml) was added to a solution of the above 1-hydroxycarbazole (**17a**) (25 mg, 0.137 mmol) in acetone (6 ml) at room temperature. The reaction mixture was stirred at room temperature for 30 min and then evaporated under reduced pressure. The resulting precipitate was filtered off, washed well with water, and dried to give the title compound (**18**) (23 mg, 85%) as a bright red solid, m.p. > 300 °C (purified by chromatography) (lit.,[18] m.p. 220 °C, lit.,[14a] 136 °C)* (Found: M^+, 197.0480. $C_{12}H_7NO_2$ requires *M*, 197.0477); $\lambda_{max.}$(EtOH) 221 (log ε 4.44), 247sh (4.24), 254 (4.29), 266sh (4.10), 278sh (3.55), and 401 nm (3.55); $\nu_{max.}$(KBr) 3 200br, 1 665, 1 635, and 1 620; $\nu_{max.}$(Nujol) 3 270br, 1 665, 1 640, and 1 620 cm^{-1}; δ[250 MHz; $(CD_3)_2CO$] 6.73 (2 H, s, 2- and 3-H), 7.28—7.47 (2 H, m, ArH), 7.64 (1 H, m, ArH), 8.13 (1 H, m, ArH), and 11.76 (1 H, br s, NH); *m/z* (180 °C) 197 (M^+, 100%), 169 (35), 143 (30), and 115 (31).

1,4-*Dihydro*-3-*methylcarbazole*-1,4-*dione* (*Murrayaquinone-A*) (7).—A solution of 1-methoxy-3-methyl-9*H*-carbazole (**4**) (13.5 mg, 0.064 mmol) in dry dichloromethane (0.4 ml) was cooled to −78 °C under nitrogen and kept at this temperature during the dropwise addition of boron tribromide in dichloromethane (1M; 0.14 ml, 0.14 mmol). The reaction mixture was stirred for 18 h and the resultant milky brown solution poured into ice–water (4 ml) and extracted with ether (20 ml). The ethereal extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to yield 1-hydroxy-3-methyl-9*H*-carbazole (**17b**) as a beige solid in quantitative yield, m.p. 153—156 °C (lit.,[19] m.p. 158 °C); $\lambda_{max.}$(EtOH) 220 (log ε 4.60), 240 (4.70), 249sh (4.55), 280sh (3.96), 290 (4.18), 320sh (3.60), 331 (3.71), and 344 nm (3.64); $\nu_{max.}$(Nujol) 3 400br (NH, OH) and 1 590 cm^{-1}; δ(250 MHz; $CDCl_3$) 2.46 (3 H, s, Me), 5.04 (1 H, br s, OH), 6.64 (1 H, m, 2-H), 7.20 (1 H, m, 6-H), 7.40 (2 H, m, 7- and 8-H), 7.47 (1 H, s, 4-H), 8.00 (1 H, d, *J* 8 Hz, with additional fine coupling, 5-H), and 8.11 (1 H, br s, NH); *m/z* (150 °C) 197 (M^+, 100%), 180 (8), and 168 (11).

A solution of Fremy's salt (35 mg, 0.13 mmol) and potassium dihydrogen orthophosphate (2 mg, 0.015 mmol) in water (2 ml) was added to a solution of 1-hydroxy-3-methyl-9*H*-carbazole (**17b**) (9 mg, 0.046 mmol) in acetone (2 ml) at room temperature. The reaction mixture was stirred at room temperature for 30 min and then evaporated under reduced pressure. The brown, solid precipitate was filtered off and the orange filtrate extracted with ether. The ethereal extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give the title compound (**7**) (3.9 mg, 40%) as an orange solid, m.p. 241 °C (decomp.) (purified by chromatography) (lit.,[4,5] m.p. 246—247 °C) (Found: M^+, 211.0630. $C_{13}H_9NO_2$ requires *M*, 211.0633); $\lambda_{max.}$(EtOH) 221 (log ε 4.38), 254 (4.20), 265sh (4.09), 277sh (3.82), and 391 nm (3.46); $\nu_{max.}$(KBr) 3 220br, 1 665, 1 640, and 1 605; $\nu_{max.}$(Nujol) 3 240br, 1 665, 1 640, and 1 605 cm^{-1}; δ[250 MHz; $(CD_3)_2CO$] 2.11 (3 H, d, *J* 1.5 Hz, Me), 6.56 (1 H, q, *J* 1.5 Hz, 2-H), 7.28—7.46 (2 H, m, ArH), 7.63 (1 H, m, ArH), 8.15 (1 H, m, ArH), and 11.69 (1 H, br s, NH); *m/z* (225 °C) 211 (M^+, 100%), 183 (33), 168 (3), 154 (20), 143 (31), 127 (5), and 115 (28).

3-(6-*Benzyloxyindol*-2-*ylcarbonyl*)-4,5-*dihydro*-3-*methylfuran*-2-*one* (**19a**).—A solution of the indole (**12c**) (73 mg, 0.218 mmol) in dry DMF (0.7 ml) was added in one portion to a stirred suspension of sodium hydride (5.2 mg, 0.217 mmol) in dry DMF (2.2 ml) at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 30 min and then iodomethane (16.3 μl, 0.26 mmol) was added. The solution was allowed to warm to room temperature over 1 h and then stirred for a further 2 h at room temperature. The lemon-yellow solution was poured into water (7 ml) and the resultant precipitate filtered off. The remaining filtrate was extracted with ethyl acetate (10 ml), the extracts were washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The combined crude products were chromatographed on silica (2 g) eluting with light petroleum and ethyl acetate–methanol to give the *title compound* (**19a**) (43.4 mg, 57%) as a pale lemon-yellow crystalline solid, m.p. 236.5—237.5 °C [from light petroleum (b.p. 60—80 °C)–ether] (Found: C, 72.25; H, 5.5; N, 4.0. $C_{21}H_{19}NO_4$ requires C, 72.2; H, 5.4; N, 4.0%); $\nu_{max.}$(Nujol) 3 330, 1 780, 1 625, and 1 600 cm^{-1}; δ[250 MHz; $(CD_3)_2SO$] 1.58 (3 H, s, Me), 2.36 (1 H, m, 4-H), 2.99 (1 H, m, 4-H), 4.41 (2 H, m, 5-H), 5.12 (2 H, s, CH_2Ph), 6.82 (1 H, dd, *J* 7, 1 Hz, 5-ArH), 6.94 (1 H, m, 3-ArH or 7-ArH), 7.24 (1 H, m, 7-ArH or 3-ArH), 7.28—7.50 (5 H, m, Ph), 7.60 (1 H, d, *J* 7 Hz, 4-ArH), and 11.60 (1 H, s, NH); *m/z* (220 °C) 349 (M^+, 54%), 258 (40), and 91 (100).

4,5-*Dihydro*-3-*indol*-2-*ylcarbonyl*-4-*methyl*-3-(3-*methylbut*-2-*enyl*)*furan*-2-*one* (**19b**).—A solution of the indole (**12b**) (50 mg, 0.206 mmol) in dry DMF (0.75 ml) was added in one portion to a stirred suspension of sodium hydride (5 mg, 0.206 mmol) in dry DMF (2 ml) at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 30 min and then 3,3-dimethylallyl bromide (37 mg, 0.248 mmol) was added dropwise. The solution was allowed to warm to room temperature over 1 h and then stirred for a further 2 h at this temperature. The lemon-yellow solution was poured into water (7 ml) and extracted with ether (40 ml). The ethereal extracts were washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was chromatographed on silica (2 g), eluting with light petroleum–ether, to give the *title compound* (**19b**) (45.5 mg,

* Despite the widely differing m.p., the spectral data suggests that compound (**18**) is the same as that prepared by other authors.[14a]

71%) as a colourless crystalline solid, m.p. 116.5—118.5 °C (from hexane–chloroform) (Found: C, 73.1; H, 6.8; N, 4.5. $C_{19}H_{21}NO_3$ requires C, 73.3; H, 6.75; N, 4.5%); $\nu_{max.}$(Nujol) 3 280, 1 765, 1 655, and 1 620 cm^{-1}; δ(250 MHz; $CDCl_3$) 0.97 (3 H, d, *J* 6 Hz, CH*Me*), 1.71 (3 H, s, Me), 1.76 (3 H, s, Me), 2.77 (2 H, m, 4-H and C*H*$_2$CH=), 3.02 (1 H, m, C*H*$_2$CH=), 4.00 (1 H, t, *J* 8 Hz, 5-H), 4.49 (1 H, t, *J* 8 Hz, 5-H), 5.13 (1 H, m, CH$_2$C*H*=), 7.15 (1 H, m, ArH), 7.30—7.41 (3 H, m, ArH), 7.71 (1 H, d, *J* 8 Hz, with additional fine coupling, ArH), and 9.22 (1 H, br s, NH); *m/z* (170 °C) 311 (M^+, 50%), 296 (4), 283 (5), 268 (5), 252 (10), 243 (12), 228 (12), 224 (6), 212 (7), 198 (7), 184 (6), 167 (100), 144 (59), 130 (8), and 117 (53).

1-(6-*Benzyloxyindol*-2-*yl*)-4-*hydroxy*-2-*methylbutan*-1-*one* (**20a**).—The indole (**19a**) (17 mg, 0.049 mmol), water (0.25 ml), and dioxane (0.25 ml) were refluxed together in the presence of a few drops of dilute aqueous sodium hydroxide under nitrogen for 20 h. The solution was cooled to room temperature, saturated brine added, and the mixture extracted with ethyl acetate (20 ml). The extracts were washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was chromatographed on silica (1 g), eluting with light petroleum (b.p. 60—80 °C)–ethyl acetate, to give the *title compound* (**20a**) (9.7 mg, 61%) as a beige solid, m.p. 115—117 °C (Found: C, 74.1; H, 6.5; N, 4.25. $C_{20}H_{21}NO_3$ requires C, 74.3; H, 6.5; N, 4.3%); $\nu_{max.}$(Nujol) 3 410br, 3 300br, and 1 620 cm^{-1}; δ [250 MHz; $(CD_3)_2SO$] 1.12 (3 H, d, *J* 6 Hz, Me), 1.53 (1 H, m, 3-H), 1.89 (1 H, m, 3-H), 3.40 (3 H, m, 4-H and OH), 4.51 (1 H, m, 2-H), 5.12 (2 H, s, C*H*$_2$Ph), 6.80 (1 H, dd, *J* 7, 1 Hz, 5-ArH), 6.95 (1 H, s, 3-ArH or 7-ArH), 7.29 (1 H, s, 7-ArH or 3-ArH), 7.31—7.51 (5 H, m, Ph), 7.58 (1 H, d, *J* 7 Hz, 4-ArH), and 11.50 (1 H, br s, NH); *m/z* (150 °C) 323 (M^+, 12%), 305 (22), 214 (100), and 91 (78).

4-*Hydroxy*-1-*indol*-2-*yl*-3-*methyl*-2-(3-*methylbut*-2-*enyl*)-*butan*-1-*one* (**20b**).—The indole (**19b**) (46.3 mg, 0.15 mmol), water (0.9 ml), and dioxane (0.9 ml) were refluxed together in the presence of a few drops of dilute aqueous sodium hydroxide under nitrogen for 18 h. The solution was cooled to room temperature, saturated brine added, and the mixture extracted with ether (40 ml). The ethereal extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The crude product was chromatographed on silica (2 g), eluting with light petroleum–ether, to give the *title compound* (**20b**) (21.8 mg, 51%) as a colourless oil (Found: M^+, 285.1732. $C_{18}H_{23}NO_2$ requires *M*, 285.1729); $\nu_{max.}$(Nujol) 3 400br, 3 320br, 1 640, and 1 620 cm^{-1}; δ(250 MHz; $CDCl_3$) 1.02 (3 H, t, *J* 6 Hz, CH*Me*), 1.59 (3 H, s, Me), 1.62 (3 H, s, Me), 1.65 (1 H, br s, OH), 2.16 (1 H, m, 3-H), 2.37 (1 H, m, C*H*$_2$CH=), 2.55 (1 H, m, C*H*$_2$CH=), 3.50 (1 H, m, 2-H), 3.63 (2 H, m, 4-H), 5.07 (1 H, m, CH$_2$C*H*=), 7.16 (1 H, t, *J* 8 Hz, ArH), 7.27 (1 H, d, *J* 2 Hz, ArH), 7.31—7.47 (2 H, m, ArH), 7.73 (1 H, d, *J* 8 Hz, 4-ArH), and 9.20 (1 H, br s, NH); *m/z* (150 °C) 285 (M^+, 66%), 267 (50), 252 (30), 226 (100), 210 (16), 199 (23), 184 (48), 170 (17), 159 (31), 144 (96), 130 (21), and 117 (34).

Acknowledgements

We thank the S.E.R.C. for a studentship (to T. M.), and Professor H. Furukawa for an authentic sample of murrayafoline-A picrate.

References

1 Preliminary communication, T. Martin and C. J. Moody, *Tetrahedron Lett.*, 1985, **26**, 5841.
2 D. P. Chakraborty, *Fortschr. Chem. Org. Naturst.*, 1977, **34**, 299.
3 H. Furukawa, T.-S. Wu, and T. Ohta, *Chem. Pharm. Bull.*, 1983, **31**, 4202.
4 T.-S. Wu, T. Ohta, H. Furukawa, and C.-S. Kuoh, *Heterocycles*, 1983, **20**, 1267.
5 H. Furukawa, T.-S. Wu, T. Ohta, and C.-S. Kuoh, *Chem. Pharm. Bull.*, 1985, **33**, 4132.
6 P. Bhattacharyya and B. K. Chowdhury, *Chem. Ind. (London)*, 1984, 301.
7 H. Furukawa, M. Yogo, C. Ito, T.-S. Wu, and C.-S. Kuoh, *Chem. Pharm. Bull.*, 1985, **33**, 1320.
8 D. Sowmithran and K. J. R. Prasad, *Heterocycles*, 1986, **24**, 711.
9 J. A. Joule, *Adv. Heterocycl. Chem.*, 1984, **35**, 83.
10 T. Martin and C. J. Moody, *J. Chem. Soc., Perkin Trans. 1*, 1987, following paper.
11 *cf.* A. R. MacKenzie, C. J. Moody, and C. W. Rees, *Tetrahedron*, 1986, **42**, 3259; R. E. Bolton, C. J. Moody, C. W. Rees, and G. Tojo, *J. Chem. Soc., Chem. Commun.*, 1985, 1775.
12 M. Sato, H. Tagawa, A. Kosasayama, F. Uchimaru, H. Kojima, T. Yamasaki, and T. Sakurai, *Chem. Pharm. Bull.*, 1978, **26**, 3296.
13 *cf.* A. H. Jackson, B. Naidoo, and P. Smith, *Tetrahedron*, 1968, **24**, 6119.
14 (*a*) D. W. M. Benzies and R. A. Jones, *J. Chem. Soc., Chem. Commun.*, 1986, 1019; (*b*) see also K. Ramesh and R. S. Kapil, *Chem. Ind. (London)*, 1986, 614.
15 D. Knittel, *Synthesis*, 1985, 186.
16 E. Worner, *Chem. Ber.*, 1896, **29**, 139.
17 C. S. Barnes, K. H. Pausacker, and C. I. Schubert, *J. Chem. Soc.*, 1949, 1381.
18 H.-J. Teuber and G. Staiger, *Chem. Ber.*, 1954, **87**, 1251.
19 D. P. Chakraborty and B. K. Chowdhury, *J. Org. Chem.*, 1968, **33**, 1265.

Received 9th February 1987; *Paper* 7/223