Further Observations on and Novel Products from Acid-catalysed Indole–Pyrrole Condensations: Formation of Pyrrolo[2,3-*b*]carbazoles

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The clay-catalysed reaction between indole and ethyl 5-acetoxymethyl-4-acetyl-3-methylpyrrole-2-carboxylate **1a** has been shown to give 2-ethoxycarbonyl-3,4-dimethylpyrrolo[3,2-*b*]carbazole **3a** as the major product, accompanied by 3.9% of the isomeric pyrrolo[2,3-*b*]carbazole **4a**. The minor product was rationalised by the correspondingly small amount of indole-2-pyrrolylmethyl substituted product observed when an alternative pyrrole was used. The proportion of pyrrolo[2,3-*b*]-carbazole **4** formed was shown to increase with the presence of strongly electron-donating groups in the indole. In the case of 5-methylindole, which gave 6.4% of the [2,3-*b*] isomer, when the reaction was run at a lower temperature, the intermediate 3-substituted pyrrolylmethylindole **7c** could be isolated. Cyclisation of this, under the original reaction conditions gave *only* the pyrrolo[3,2-*b*]-carbazole **3h**. There was no equilibration between the isomeric pyrrolocarbazoles under the reaction conditions.

The electrophilic substitution of the pyrrolo[3,2-*b*]carbazole **3a** was examined. The pyrrolylmethyl and dimethylallyl cations, pyridine hydrobromide perbromide and Vilsmeier formylation all gave predominant, prior attack at the 10-position of the pyrrolo[3,2-*b*]carbazole. For the 10-pyrrolylmethylpyrrolo[3,2-*b*]carbazole **6a** bromination gave the 8-bromo and 6,8-dibromo derivatives.

In a recent publication,[1] we described the clay-catalysed condensation between pyrroles of type **1** with the indoles **2a–d** to give the pyrrolo[3,2-*b*]carbazoles **3a–d**. These compounds, like the structurally related ellipticines, have been demonstrated to have anti-tumour activity.[2]

For the original indoles **2a–d** we isolated only the tetracyclic pyrrolo[3,2-*b*]carbazoles **3**—and none of the isomeric [2,3-*b*] systems, **4**. In earlier work,[3] however, we showed that the acid-catalysed reaction between indole and the pyrrole **1c**, gave, apart from the main 3-pyrrolylmethyl substituted product, 5% of the mono-2-pyrrolylmethyl indole **5**.

It would be expected that analogues of **5** derived from acylpyrroles of type **1** (R^3 = Ac), would rapidly cyclise at the indolyl 3-position to give the alternative pyrrolo[2,3-*b*]carbazole systems **4** (see Scheme 1). We therefore re-examined the indole–pyrrole **1a** reaction in detail. In the event, two new minor products were isolated by chromatography apart from the pyrrolocarbazole **3a**. The least-polar was a pale yellow solid, M^+ 306, clearly isomeric with the deeper yellow tetracycle **3a**. In the ^1H NMR spectrum all of the expected signals were present—but the chemical-shift difference between the aromatic 3 and 4 methyls (δ 3.17 and 2.95) was greater than for the isomer **3a** (δ 2.91 and 2.90) and the 10-H singlet was at much higher field (δ 7.18; δ 7.85 in **3a**). These two features were found to be characteristic differences between the [3,2-*b*] and [2,3-*b*] isomers. Further confirmation of the structure **4a** of the by-product as the pyrrolo[2,3-*b*]carbazole (3.9%) was obtained by the NOE enhancements shown. As expected, isomer **4a** showed in its UV spectrum shorter wavelength bands above 300 nm than **3a**.

The more polar of the two by-products gave a strong molecular ion at *m/z* 513. The ^1H NMR spectrum showed all the signals characteristic of the pyrrolo[3,2-*b*]carbazole **3a**, but with the absence of the 10-H singlet. In addition signals due to a pyrrolylmethyl substituent were obvious. The orientation of the pyrrolocarbazole nucleus and the position of substitution of the pyrrolylmethyl unit were confirmed by the NOE enhancements shown in structure **6a**.

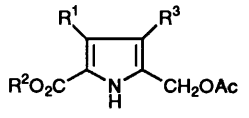
The presence of the pyrrolylmethyl group at the 10 position implied that the latter was the most reactive site in the pyrrolo[3,2-*b*]carbazole towards electrophilic substitution and this was confirmed by the additional experiments described below. The use of K10 clay is not essential for the pyrrole–indole condensations and, in fact, toluene-*p*-sulfonic acid gave an enhanced yield of the pyrrolocarbazole **6a**.

Earlier work[4–6] on indoles has shown that 4- or 6-methoxy groups can increase the amount of electrophilic substitution at the 2-position. We therefore thought that 4-hydroxyindole would give an enhanced degree of 2-substitution by the pyrrolylmethyl group and hence a greater proportion of the pyrrolo[2,3-*b*]carbazole **4b** when compared with indole itself.

In the event this proved to be so. Treatment of 4-hydroxyindole with K10 clay and the pyrrole **1a** gave, as expected, a number of impure products including 3-, 5- and 7-pyrrolylmethyl substituted indoles. From the product mixture, however, crystallisation and chromatography of the mother liquors afforded the two pure pyrrolocarbazoles **3e** (10.6%) and **4b** (4.3%). The spectral properties of these isomers enabled an unambiguous structure assignment to be made.

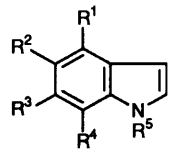
It is known[7] that *N*-methylation of indoles (and pyrroles) increases the rate of electrophilic substitution at the indole-3 (and pyrrole-5) positions. We therefore next investigated the pyrrole condensation with 4-methoxy-1-methylindole **2f**.[8] The main product (46%) from **2f** and pyrrole **1a** was the pyrrolo[3,2-*b*]carbazole **3f** with no detectable amounts of the [2,3-*b*] isomer. It would appear that the *N*-methyl group in the indole **2f** restores the 3-position as the predominant site of electrophilic substutition. It is likely that, when predominant initial substitution at the indolyl 3-position occurs (as for indole itself, and for the indole **2f**), a spirocyclic intermediate **7** is formed, as in the cyclisation of tryptamides[9] followed by a highly regioselective migration of the C(Me)OH-pyrrolyl bridge leading to a predominance of the [3,2-*b*] isomer (see Scheme 2). A minor product (4.6%) from the reaction of the indole **2f** was the 10-substituted pyrrolocarbazole **6b**.

5-Hydroxyindole underwent reaction with the pyrrole **1a** more slowly than with 4-hydroxyindole. The total yields of the two isomeric pyrrolocarbazoles obtained (**3g**, 5.7% and **4c** 1.1%)

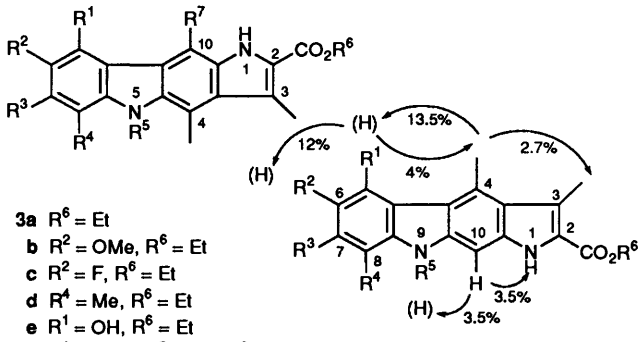


1a R^1 = Me, R^2 = Et, R^3 = Ac
b R^1 = Me, R^2 = CH_2Ph, R^3 = Ac
c R^1 = Me, R^2 = CH_2Ph, R^3 = $CH_2CH_2CO_2Me$

R^n = H unless stated otherwise



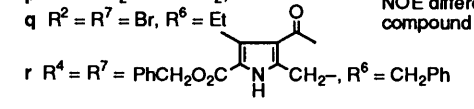
2a all R = H
b R^2 = OMe
c R^2 = F
d R^4 = Me
e R^1 = OH
f R^1 = OMe, R^5 = Me
g R^2 = OH
h R^2 = Me
i R^2 = R^3 = OMe
j R^2 = R^3 = OCH_2O
k R^1 = F
l R^3 = F
m R^2 = Cl
n R^2 = Br



3a R^6 = Et
b R^2 = OMe, R^6 = Et
c R^2 = F, R^6 = Et
d R^4 = Me, R^6 = Et
e R^1 = OH, R^6 = Et
f R^1 = OMe, R^5 = Me, R^6 = Et
g R^2 = OH, R^6 = Et
h R^2 = Me, R^6 = Et
i R^2 = R^3 = OMe, R^6 = Et
j R^2 = R^3 = OCH_2O, R^6 = Et
k R^1 = F, R^6 = Et
l R^3 = F, R^6 = Et
m R^2 = Cl, R^6 = Et
n R^2 = Br, R^6 = Et
o R^6 = CH_2Ph
p R^7 = $Me_2C{=}CHCH_2$, R^6 = Et
q R^2 = R^7 = Br, R^6 = Et

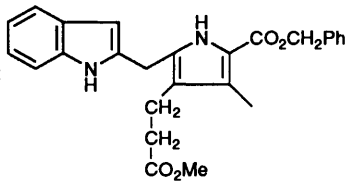
4a R^6 = Et
b R^1 = OH, R^6 = Et
c R^2 = OH, R^6 = Et
d R^2 = Me, R^6 = Et
e R^2 = R^3 = OMe, R^6 = Et
f R^2 = R^3 = OCH_2O, R^6 = Et
g R^3 = F, R^6 = Et
h R^2 = Me, R^6 = et
i R^2 = Br, R^6 = Et

NOE differences shown for compound **4a**



r R^4 = R^7 = $PhCH_2O_2C$, CH_2–, R^6 = CH_2Ph

s R^7 = CHO, R^6 = Et
t R^7 = CHO, R^2 = Me, R^6 = Et
u R^4 = $Me_2C{=}CHCH_2$, R^6 = Et
v R^7 = Br, R^6 = Et



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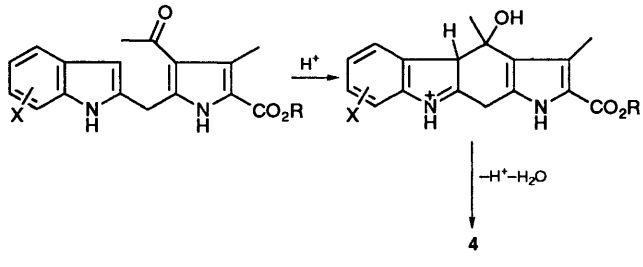
were less. It proved difficult to purify the products in the presence of large amounts of starting materials. The [3,2-*b*] isomer **3g** first co-crystallised with the pyrrole—but treatment of this mixture with additional 5-hydroxyindole and clay,



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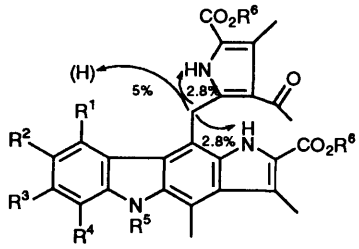
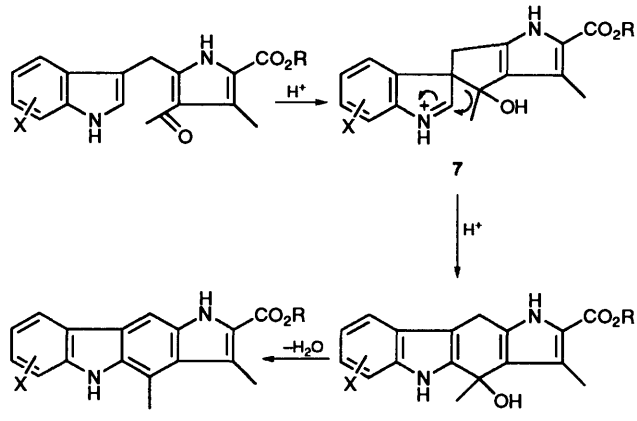
Scheme 1



6a R^6 = Et
b R^1 = OMe, R^5 = Me, R^6 = Et
c R^2 = OH, R^6 = Et
d R^2 = R^3 = OMe, R^6 = Et
e R^2-R^3 = OCH_2O, R^6 = Et
f R^3 = F, R^6 = Et
g R^6 = CH_2Ph
h R^2 = Me, R^6 = Et
i R^2 = Br, R^6 = Et
j R^2 = R^4 = Br, R^6 = Et

followed by chromatography, afforded a pure sample of **3g**. Its isomer **4c** could not be separated on crystallisation from *ca.* 12% of **3g**. It was clear that the isomer **3g** was tenaciously adsorbed by the clay and the yields quoted do not necessarily represent the amounts or proportions actually formed.



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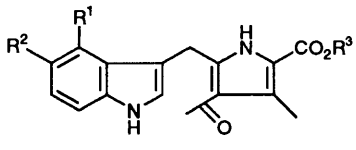
Scheme 2

Small amounts of the 10-substituted compound **6c** were also isolated as well as, significantly, the 3-monosubstituted intermediate **8a**, the major product (11.5%). The structure of the latter was evident from the molecular weight (M^+, 340, 100%) and the presence of the indole 2 H (δ 7.10, d, J 2.5 Hz) and the methylene bridge (δ 4.31, s) in the ^{1}H NMR spectrum.



8a R^2 = OH, R^3 = Et
b R^1 = F, R^3 = Et
c R^2 = Me, R^3 = Et
d R^3 = Et
e R^2 = Cl, R^3 = Et
f R^2 = Br, R^3 = Et

It appeared that electron-donating groups in the indole were linked with the formation of the [2,3-*b*]pyrrolocarbazole isomer, and this proved to be the case with 5-methylindole—which gave the isomers **3h** and **4d** in the ratio 5 : 1, respectively. The 10-pyrrolylmethyl derivative **6h** was also isolated (12.9%).

Where two strongly electron-donating groups were present, this effect was larger. Thus, 5,6-dimethoxyindole gave, as well as the 10-substituted product **6d**, both isomers **3i** and **4e** in the

ratio 8.1:4.8. In fact, in the case of 5,6-methylenedioxyindole, the major product was the [2,3-*b*] isomer **4f** (9.2%) with substantial amounts of the isomer **3j** (7.4%) and the 10-substituted product **6e**.

By contrast with the effect of the electron-donating groups in the indole, a series of halogenated indoles (**2k–n**) were also condensed with pyrroles **1a**—but they gave predominantly the [3,2-*b*]pyrrolocarbazoles with little or none of the [2,3-*b*] isomers. Thus, 6-fluoroindole gave the [2,3-*b*] isomer **4g** (3.1%) along with the 10-pyrrolylmethyl derivative **6f**. These results paralleled those with 5-chloro- and 5-bromo-indoles. It is noteworthy that both 4-fluoro- and 5-fluoro-indole [1] gave none of the [2,3-*b*] isomer. In the former case the [3,2-*b*] isomer **3k** (from 4-fluoroindole) was accompanied by the 3-monosubstituted derivative **8b**.

It can be seen from the above examples (*a*) that 10-pyrrolylmethyl substituted pyrrolo[3,2-*b*]carbazoles often accompany the pyrrolo[2,3-*b*]carbazole as reaction products and (*b*) there seems little doubt that the primary site of electrophilic substitution in the [3,2-*b*] isomer is at C-10. In fact, when the pyrrolo[3,2-*b*]carbazole **3o** was treated with toluene-*p*-sulfonic acid and 1 equiv. of the pyrrole **1b**, the major product (27.8%) was the 10-pyrrolylmethyl derivative **6g**. A second product was also isolated. This high melting point compound had M^+ 906 and analysed for $C_{56}H_{50}N_4O_8$. In the ^1H NMR spectrum all the signals expected of a 10-pyrrolylmethylpyrrolo[3,2-*b*]carbazole were seen, but, only two doublets and a triplet could be seen for the ring A aromatic protons. The 9 H doublet signal was at characteristically lowfield (δ 7.70) and was shown by double resonance to be coupled to a triplet at δ 6.90 which, in turn, was coupled to a doublet at δ 6.83. The 6-position was, therefore, substituted by the second pyrrolylmethyl group and this led to the 6,10-disubstituted pyrrolocarbazole structure **3r**. Similar results were obtained by treatment of the pyrrolocarbazole **3a** with the pyrrole **1a** but using clay.

In the light of the evident ease of substitution of the [3,2-*b*] system of **3a** by the pyrrolylmethyl group, we examined some additional electrophiles.

Formylation of **3a** under Vilsmeier conditions gave the 10-formyl derivative **3s** in high yield; the methyl analogue **3h** gave the aldehyde **3t** in 54% yield. Similarly treatment of **3a** with 2-methylbut-3-en-2-ol [10] and clay gave the 10-(2-methylbut-2-enyl) analogue **3p** with unchanged starting material and a very minor by-product (0.6%) shown by ^1H NMR spectroscopy to be the 6-substituted product **3u**. Bromination of **3a** with 1 equiv. of pyridinium hydrobromide perbromide in dichloromethane gave the 10-bromo compound **3v** as the major product, but significant quantities of the 8-bromo **3n** and 8,10 dibromo derivative **3q** were also formed. When 2 equiv. of the brominating agent were used only the 8,10-dibromo compound **3q** was isolated (68%). The relative selectivity of the bromination was illustrated by treatment of the 10-pyrrolylmethylpyrrolocarbazole **6a** with 1 equiv. of the perbromide. The main product (42%) was the 8-bromo compound **6i**, but the 6,8-dibromo analogue **6j** (16.5%) was a minor but significant product.

The circumstantial evidence that exists suggests that when the initial step in the indole–pyrrole condensation is formation of a 2-substituted indole, *e.g.* **5**, cyclisation takes place very rapidly at the indole-3 position to give only the pyrrolo-[2,3-*b*]carbazole. In keeping with this, no 2-monosubstituted intermediates have been isolated, except in the case of **5** in which cyclisation on the indole is precluded by the absence of the pyrrole-3-carbonyl group. By contrast, we have been able to isolate the 3-substituted intermediates of the pyrrolo[3,2-*b*]-carbazoles. In these cases, if the mechanism shown in Scheme 2 is correct, treatment of the 3-substituted intermediate with clay should give only the pyrrolo[3,2-*b*]carbazoles **3**—even in cases where the reaction from pyrrole and indole gives both the [3,2-*b*] and [2,3-*b*] isomers. Such a case is that of 5-methylindole. We isolated both [3,2-*b*] (31.5%) and [2,3-*b*] (6.42%) isomers when the parent pyrrole **1a** and the indole **2h** with clay were the starting materials. By using a lower temperature for the reaction, we were able to isolate useful quantities (*ca.* 12%) of the 3-substituted intermediate **8c**. Treatment of the latter with clay under the conditions of the normal reaction and virtually quantitative recovery (92.5% weight) of the reaction components showed that no detectable amount of the [2,3-*b*] product **4h** was present.

Whilst this experiment proves that no [2,3-*b*] isomer **4h** is formed from the 3-substituted indole **8c** it does not rule out direct cyclisation at the 2-position of **8c** as a pathway to the [3,2-*b*] isomer. We attempted to trap a spirocyclic intermediate from the 3-substituted intermediate **8d** using trifluoroacetic acid anhydride,[9] and acetic anhydride, but this was unsuccessful.

Finally, the unlikely possibility of equilibration of the [3,2-*b*] and [2,3-*b*] systems was ruled out. Treatment of either of the pyrrolocarbazoles **3h** and **4h** with clay under the original (pyrrole–indole) reaction conditions gave none of the alternative isomer.

Experimental

IR spectra were recorded on a Perkin-Elmer 1600 series FTIR; UV spectra were measured in ethanol on a Perkin-Elmer Lambda 2 UV–VIS spectrophotometer; and ^1H NMR spectra were obtained on a Bruker WM 360-NMR spectrophotometer at 360 MHz. *J* Values are given in Hz. EI mass spectra were run on a Varian CH5D instrument. Flash column chromatography was carried out with Fisons, Matrex silica 60, 35–70 μm. Light petroleum was of boiling range 40–60 °C.

Synthesis of the Pyrrolo[3,2-b]*carbazoles* **3a**, **3e–n**, *Pyrrolo*-[2,3-b]*carbazoles* **4a–i**, *and the* 10-*Pyrrolylmethylpyrrolo*[3,2-b]*carbazoles* **6a–i**: *General Procedure*.—A solution of each indole **2a**, **e–k** (2.0 mmol) and the 5-acetoxymethyl-4-acetylpyrrole **1a** (2.0 mmol) in 1,2-dichloroethane (20 cm^3) was heated under reflux and stirred with Montmorillonite clay (2 g) for 4–7 h. The reaction was followed to completion by TLC. After the clay had been filtered off and washed well with 1,2-dichloroethane, evaporation of the combined filtrates under reduced pressure gave a yellow solid or an oil. Flash chromatography of this on silica, eluting with ethyl acetate in dichloromethane, gave the corresponding pyrrolo[3,2-*b*]- and pyrrolo[2,3-*b*]-carbazoles and 10-pyrrolylmethylpyrrolo-[3,2-*b*]carbazole.

Ethyl 3,4-*Dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3a** *and Ethyl* 3,4-*Dimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4a**.—These compounds were obtained from indole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Chromatographic separation yielded the [3,2-*b*] isomer **3a** as a yellow solid (0.400 g, 65.4%), m.p. 209.5–211 °C (lit.,[1] 209.5–211 °C); δ_H([$^2H_6$]-DMSO) 11.22 (1 H, s, 1-NH), 10.7 (1 H, s, 5-NH), 8.06 (1 H, d, *J* 7, 9-H), 7.85 (1 H, s, 10-H), 7.40 (1 H, d, *J* 7, 6-H), 7.35 (1 H, t, *J* 7, 7-H), 7.08 (1 H, t, *J* 7, 8-H), 4.35 (2 H, q, OCH_2CH_3), 2.91 (3 H, s, CH_3), 2.90 (3 H, s, CH_3) and 1.35 (3 H, t, OCH_2CH_3); λ_{max}(EtOH)/nm (log ε_{max}/dm^3 mol^{-1} cm^{-1}) 410sh (3.69), 392.8 (3.74), 340.7 (4.67), 325sh (4.48), 310sh (4.23) and 268.8 (4.34); the [2,3-b]*isomer* **4a** was a pale yellow solid (0.024 g, 3.9%), m.p. 276–278 °C (Found: C, 74.45; H, 5.7; N, 9.0. $C_{19}H_{18}N_2O_2$ requires C, 74.49; H, 5.92; N, 9.15%); δ_H([$^2H_6$]-DMSO) 11.10 (1 H, s, 1-NH), 10.91 (1 H, s, 9-NH), 8.17 (1 H, d, *J* 7.5, 5-H), 7.37 (1 H, d, *J* 7, 8-H), 7.32 (1 H, dt, *J* 1.5 and 7, 7-H), 7.18 (1 H, s, 10-H), 7.11 (1 H, dt, *J* 1.5 and 7, 6-H), 4.37 (2 H, q, OCH_2CH_3),

3.17 (3 H, s, 4-CH_3), 2.95 (3 H, s, 3-CH_3) and 1.39 (3 H, t, OCH_2CH_3); saturation of the 10-H at δ 7.18 enhanced singlets due to 1-NH at δ 11.10 (3.5%) and 9-NH at δ 10.91 (3.5%), and saturation of the 4-CH_3 at δ 3.17 enhanced the singlet due to 3-CH_3 at δ 2.95 (2.7%) and 5-H doublet at δ 8.17 (13.5%); *m/z* (%) 306 (80, M^+) 260 (100), 232 (48) and 102 (10); λ_{max}(EtOH)/nm (log ε_{max}/dm^3 mol^{-1} cm^{-1}) 380sh (4.04), 349 (4.21), 305.3 (4.95) and 260.2 (5.09); and the 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6a** as a yellow solid (0.034 g, 6.6%), m.p. 243–245 °C (decomp.) (Found: C, 69.9; H, 6.1; N, 8.1. $C_{30}H_{31}N_3O_5$ requires C, 70.16; H, 6.08; N, 8.18%); δ_H([$^2H_6$]-DMSO) 10.85 (1 H, s, 5-NH), 10.15 (1 H, s, pyr-NH), 10.11 (1 H, s, 1-NH), 7.88 (1 H, d, *J* 7.5, 9-H), 7.46 (1 H, d, *J* 7.5, 6-H), 7.36 (1 H, t, *J* 7.5, 7-H), 7.03 (1 H, t, *J* 7.5, 8-H), 5.15 (2 H, s, 10-CH_2), 4.27 (2 H, q, 2-OCH_2CH_3), 4.11 (2 H, q, 5'-OCH_2CH_3), 2.95 (3 H, s, 4-CH_3), 2.90 (3 H, s, 3-CH_3), 2.55 (3 H, s, 4'-CH_3), 2.51 (3 H, s, $COCH_3$), 1.34 (3 H, t, 2-OCH_2CH_3) and 1.13 (3 H, t, 5'-OCH_2CH_3); saturation of the 10-CH_2 at δ 5.15 enhanced the doublet due to 9-H at δ 7.88 (5%) and the singlets due to pyr-NH at δ 10.15 (2.8%) and 1-NH at δ 10.11 (2.8%); *m/z* (%) 513 (88, M^+), 487 (65), 439 (29), 322 (29) and 260 (28); λ_{max}(EtOH)/nm (log ε_{max}/dm^3 mol^{-1} cm^{-1}) 414sh (3.90), 398 (3.91), 339.6 (4.72) 323.5sh (4.51), 308.9sh (4.36) and 270.9 (4.62).

Ethyl 9-*hydroxy*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3e** *and ethyl* 5-*hydroxy*-3,4-*dimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4b**. These compounds were obtained from 4-hydroxyindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. The [2,3-b] *isomer* **4b**, after recrystallisation from ethyl acetate, gave pale green crystals (0.028 g, 4.3%), m.p. 251–254 °C (decomp.); δ_H([$^2H_6$]-DMSO) 10.95 (1 H, s, 1-NH), 10.85 (1 H, s, 9-NH), 9.89 (1 H, s, OH), 7.08 (1 H, t, *J* 7.5, 7-H), 7.07 (1 H, s, 10-H), 6.77 (1 H, d, *J* 7.5, 8-H), 6.52 (1 H, d, *J* 7.5, 6-H), 4.32 (2 H, q, OCH_2CH_3), 3.44 (3 H, s, 4-CH_3), 2.92 (3 H, s, 3-CH_3) and 1.37 (3 H, t, OCH_2CH_3); *m/z* (%) 322 (65, M^+), 276 (100), 248 (88), 219 (15), 205 (10), 191 (10) and 178 (5) (Found: M^+, 322.1317. $C_{19}H_{18}N_2O_3$ requires *M*, 322.1317). Further elution gave the [3,2-b] *isomer* **3e** after recrystallisation from ethyl acetate–light petroleum as green crystals (0.0686 g, 10.6%), m.p. 260–262 °C (decomp.); δ_H([$^2H_6$]-DMSO) 11.13 (1 H, s, 1-NH), 10.56 (1 H, s, 5-NH), 10.00 (1 H, s, OH), 8.02 (1 H, s, 10-H), 7.12 (1 H, t, *J* 7.5, 7-H), 6.83 (1 H, d, *J* 7.5, 6-H), 6.48 (1 H, d, *J* 7.5, 8-H), 4.39 (2 H, q, OCH_2CH_3), 2.87 (3 H, s, 4-CH_3), 2.85 (3 H, s, 3-CH_3) and 1.38 (3 H, t, OCH_2CH_3); *m/z* (%) 322 (61, M^+), 276 (100), 248 (20), 219 (5) and 138 (11) (Found: M^+ 322.1305. $C_{19}H_{18}N_2O_3$ requires *M*, 322.1317). Next to be eluted was 4-hydroxy-5-pyrrolylmethylindole (0.033 g, 4.85%) as an impure, light yellow solid, δ_H($CDCl_3$) 9.00 (1 H, br, s, pyr-NH), 8.92 (1 H, s, OH), 8.11 (1 H, br, s, 1-NH), 7.08 (1 H, t, *J* 2.5, 2-H), 7.03 (1 H, d, *J* 7.5, 7-H), 6.91 (1 H, d, *J* 7.5, 6-H), 6.63 (1 H, dt, *J* 2.5 and 2, 3-H), 4.29 (2 H, q, OCH_2CH_3), 4.22 (2 H, s, 5-CH_2), 2.58 (3 H, s, 4'-CH_3), 2.55 (3 H, s, $COCH_3$) and 1.33 (3 H, t, OCH_2CH_3); *m/z* (%) 340 (41, M^+), 298 (20), 251 (13), 225 (28), 145 (100) and 133 (7) (Found: M^+, 340.1423. $C_{19}H_{20}N_2O_4$ requires *M*, 340.1423); similarly obtained was 4-hydroxy-7-pyrrolylmethylindole (0.032 g, 4.70%); δ_H($CDCl_3$) 10.40 (1 H, s, pyr-NH), 8.91 (1 H, br, d, ind-NH), 7.13 (1 H, t, *J* 2.5, 2-H), 6.94 (1 H, d, *J* 7, 6-H), 6.55 (1 H, t, *J* 2.5, 3-H), 6.46 (1 H, d, *J* 7, 5-H), 5.55 (1 H, br, s, OH), 4.29 (2 H, s, 7-CH_2), 4.26 (2 H, q, OCH_2CH_3), 2.61 (3 H, s, 4'-CH_3) 2.55 (3 H, s, $COCH_3$) and 1.30 (3 H, t, OCH_2CH_3); *m/z* (%) 340 (30, M^+), 294 (10), 267 (100), 224 (70) and 125 (25); and the 4-hydroxy-3-pyrrolylmethylindole (0.0318 g, 4.68%); δ_H($CDCl_3$) 10.17 (1 H, s, pyr-NH), 8.08 (1 H, s, NH), 7.15 (1 H, d, *J* 2, 2-H), 6.98 (1 H, t, *J* 7, 6-H), 6.95 (1 H, dd, *J* 7 and 1.5, 7-H), 6.52 (1 H, br, s, OH), 6.45 (1 H, dd, *J* 7 and 1.5, 5-H), 4.52 (2 H, s, 3-CH_2), 4.26 (2 H, q, OCH_2CH_3), 2.55 (3 H, s, 4'-CH_3), 2.50 (3 H, s, $COCH_3$) and 1.32 (3 H, t, OCH_2CH_3); *m/z* (%) 340 (100, M^+), 298 (20), 294 (30), 276 (36), 266 (20), 252 (88), 225 (80) and 145 (53).

Ethyl 9-*methoxy*-3,4,5-*trimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3f**. This compound, obtained from 4-methoxy-1-methylindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**, was a yellow solid (0.322 g, 46%), m.p. 263–266 °C (Found: C, 71.8; H, 6.3; N, 7.9. $C_{21}H_{22}N_2O_3$ requires C, 71.98; H, 6.33; N, 8.00%); δ_H($CDCl_3$) 8.60 (1 H, br, s, NH), 8.15 (1 H, s, 10-H), 7.40 (1 H, t, *J* 8, 7-H), 6.95 (1 H, d, *J* 8, 6-H), 6.66 (1 H, d, *J* 8, 8-H), 4.43 (2 H, q, OCH_2CH_3), 4.10 (3 H, s, OCH_3), 4.04 (3 H, s, NCH_3), 3.19 (3 H, s, 4-CH_3), 2.98 (3 H, s, 3-CH_3) and 1.46 (3 H, t, OCH_2CH_3); saturation of the N-CH_3 protons at δ 4.04 enhanced the signals due to 6-H at δ 6.95 (9.7%) and 4-CH_3 at δ 3.19 (3.2%), and saturation of the 8-H proton at δ 6.66 enhanced the signals due to OCH_3 at δ 4.10 (2.4%) and 7-H at δ 7.40 (7.3%); *m/z* (%) 350 (74, M^+), 304 (100), 276 (17), 233 (10) and 152 (10). The 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6b** was a yellow solid (0.026 g, 4.59%), m.p. 268–270 °C (Found: C, 69.1; H, 6.4; N, 7.8. $C_{32}H_{35}N_3O_6$ requires C, 68.92; H, 6.33; N, 7.54%); δ_H($CDCl_3$) 10.97 (1 H, br, s, pyr-NH), 9.65 (1 H, br, s, 1-NH), 7.45 (1 H, t, *J* 8, 7-H), 7.04 (1 H, d, *J* 8, 6-H), 6.73 (1 H, d, *J* 8, 8-H), 5.27 (2 H, s, 10-CH_2), 4.42 (2 H, q, 2-OCH_2CH_3), 4.14 (2 H, q, 5'-OCH_2CH_3), 4.03 (3 H, s, N-CH_3), 4.00 (3 H, s, OCH_3), 3.14 (3 H, s, 4-CH_3), 2.93 (3 H, s, 3-CH_3), 2.66 (3 H, s, 4'-CH_3), 2.60 (3 H, s, $COCH_3$), 1.48 (3 H, t, 2-OCH_2CH_3) and 1.15 (3 H, t, 5'-OCH_2CH_3); *m/z* (%) 557 (100, M^+), 511 (22), 450 (16), 304 (13), 256 (14) and 233 (21).

Ethyl 8-*hydroxy*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3g** *and ethyl* 6-*hydroxy*-3,4-*dimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4c**. These compounds were obtained from 5-hydroxyindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. The chromatographic separation yielded starting 5-hydroxyindole (0.100 g, 37.6%) and the pyrrole **1a** (0.117 g, 21.91%); the third fraction was a solid mixture of the [2,3-*b*]- and [3,2-*b*]-isomer and the starting pyrrole **1a** (0.231g). Fraction 4 gave the 3-*pyrrolylmethylindole* **8a** (0.078 g, 11.5%), m.p. 99–102 °C (Found: C, 66.9; H, 6.2; N, 8.0. $C_{19}H_{20}N_2O_4$ requires C, 67.04; H, 5.92; N, 8.23%); δ_H($CDCl_3$) 8.84 (1 H, s, pyr-NH), 8.14 (1 H, s, ind-NH), 7.20 (1 H, d, *J* 8, 7-H), 7.10 (1 H, d, *J* 2.5, 2-H), 6.81 (1 H, d, *J* 1.5, 4-H), 6.79 (1 H, dd, *J* 8 and 1.5, 6-H), 5.60 (1 H, br, s, OH), 4.31 (2 H, s, 3-CH_2), 4.21 (2 H, q, OCH_2CH_3), 2.58 (3 H, s, 4'-CH_3), 2.48 (3 H, s, $COCH_3$) and 1.27 (3 H, t, OCH_2CH_3); *m/z* (%) 340 (100, M^+), 325 (44), 293 (21), 279 (35), 266 (35), 251 (31), 223 (25) and 196 (5). Fraction 5 gave the 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6c** as a yellow solid (0.015 g, 1.4%), δ_H([$^2H_6$]-DMSO) 10.48 (1 H, s, 5-NH), 10.13 (1 H, s, pyr-NH), 9.85 (1 H, s, 1-NH), 8.84 (1 H, s, OH), 7.28 (1 H, d, *J* 8, 6-H), 7.25 (1 H, s, 9-H), 6.93 (1 H, d, *J* 8, 7-H), 5.11 (2 H, s, 10-CH_2), 4.33 (2 H, q, 2-OCH_2CH_3), 4.10 (2 H, q, 5'-OCH_2CH_3), 2.93 (3 H, s, 4-CH_3), 2.90 (3 H, s, 3-CH_3), 2.56 (3 H, s, 4'-CH_3), 2.53 (3 H, s, $COCH_3$), 1.35 (3 H, t, 2-OCH_2CH_3) and 1.13 (3 H, t, 5'-OCH_2CH_3); *m/z* (%) 529 (18, M^+), 483 (25), 422 (17), 322 (28), 290 (25), 276 (100), 248 (53) and 234 (20) (Found: M^+, 529.2220. $C_{30}H_{31}N_3O_6$ requires *M*, 529.2211).

Recrystallisation of the third fraction from ethyl acetate–light petroleum gave a mixture (9:1) of the [2,3-*b*] isomer **4c** and the [3,2-*b*]-isomer **3g**, respectively (1.11 and 0.12%). The [2,3-*b*] isomer **4c** showed δ_H([$^2H_6$]-DMSO) 11.00 (1 H, s, 1-NH), 10.52 (1 H, s, 9-NH), 8.80 (1 H, s, OH), 7.59 (1 H, s, 5-H), 7.16 (1 H, d, *J* 7.8, 8-H), 7.11 (1 H, s, 10-H), 6.80 (1 H, s, *J* 7.8, 7-H), 4.35 (2 H, q, OCH_2CH_3), 3.13 (3 H, s, 4-CH_3), 2.92 (3 H, s, 3-CH_3) and 1.38 (3 H, t, OCH_2CH_3). Removal of the solvent and crystallisation of the residue from the remaining filtrate from methanol gave a 1:1 ratio mixture of the [3,2-*b*] isomer **3g** and the pyrrole **1a** (0.067 g) which was further treated with 5-hydroxyindole (0.016 g, 0.12 mmol) and montmorillonite clay (40 mg) in 1,2-dichloroethane (5 cm^3) for 7 h. After the clay had been filtered off and washed well with 1,2-dichloroethane, evaporation of the combined filtrates gave a yellow solid. Crystallisation from

methanol yielded the [3,2-*b*] *isomer* **3g** as yellow crystals (0.037 g, 5.69%), m.p. 250 °C (decomp.); δ_H([$^2H_6$]-DMSO) 11.11 (1 H, s, 1-NH), 10.21 (1 H, s, 5-NH), 8.83 (1 H, s, OH), 7.73 (1 H, s, 10-H), 7.37 (1 H, d, *J* 2.5, 9-H), 7.21 (1 H, d, *J* 8, 6-H), 6.87 (1 H, dd, *J* 8 and 2.5, 7-H), 4.36 (2 H, q, OCH_2CH_3), 2.87 (3 H, s, 4-CH_3), 2.84 (3 H, s, 3-CH_3) and 1.38 (3 H, t, OCH_2CH_3); *m*/*z* (%) 322 (69, M^+), 276 (100), 248 (24), 220 (3) and 138 (5) (Found: M^+, 322.1322. $C_{19}H_{18}N_2O_3$ requires *M*, 322.1317).

Ethyl 3,4,8-*trimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3h** *and ethyl* 3,4,6-*trimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4d**. These compounds were obtained from 5-methylindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Chromatographic separation yielded the [3,2-*b*] *isomer* **3h** as a yellow solid (0.201 g, 31.5%), m.p. 215–216.5 °C (Found: C, 74.8; H, 6.3; N, 9.0. $C_{20}H_{20}N_2O_2$ requires C, 74.97; H, 6.29; N, 8.74%); δ_H([$^2H_6$]-DMSO) 11.19 (1 H, s, 1-NH), 10.47 (1 H, s, 5-NH), 7.86 (1 H, s, 9-H), 7.82 (1 H, s, 10-H), 7.29 (1 H, d, *J* 8, 6-H), 7.18 (1 H, dd, *J* 8 and 2, 5-H), 4.37 (2 H, q, OCH_2CH_3), 2.91 (3 H, s, 4-CH_3), 2.89 (3 H, s, 3-CH_3), 2.46 (3 H, s, 8-CH_3) and 1.39 (3 H, t, OCH_2CH_3); *m*/*z* (%) 320 (64, M^+), 274 (100), 246 (24), 137 (14) and 123 (10) (Found: M^+, 320.1514. $C_{20}H_{20}N_2O_2$ requires *M*, 320.1524); the [2,3-*b*] *isomer* **4d** as a pale yellow solid (0.041 g, 6.42%), m.p. 288–290 °C (Found: C, 75.2; 6.5; N, 8.6. $C_{20}H_{20}N_2O_2$ requires C, 74.97; H, 6.29; N, 8.74%); δ_H([$^2H_6$]-DMSO) 11.05 (1 H, s, 1-NH), 10.76 (1 H, s, 9-NH), 7.98 (1 H, s, 5-H), 7.25 (1 H, d, *J* 8, 8-H), 7.15 (1 H, d, *J* 8, 7-H), 7.13 (1 H, s, 10-H), 4.36 (2 H, q, OCH_2CH_3), 3.17 (3 H, s, 4-CH_3), 2.93 (3 H, s, 3-CH_3), 2.49 (3 H, s, 6-CH_3) and 1.39 (3 H, t, OCH_2CH_3); *m*/*z* (%) 320 (80, M^+), 274 (100), 246 (42), 149 (13) and 127 (15) (Found: M^+, 320.1528. $C_{20}H_{20}N_2O_2$ requires *M*, 320.1524). The 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6h** was a yellow solid (0.068 g, 12.9%), m.p. 245–248 °C; δ_H([$^2H_6$]-DMSO) 10.68 (1 H, s, 5-NH), 10.41 (1 H, s, pyr-NH), 9.99 (1 H, s, 1-NH), 7.72 (1 H, s, 9-H), 7.35 (1 H, d, *J* 7.5, 6-H), 7.19 (1 H, d, *J* 7.5, 7-H), 5.16 (2 H, s, 10-CH_2), 4.31 (2 H, q, 2-OCH_2CH_3), 4.12 (2 H, q, 5′-OCH_2CH_3), 2.93 (3 H, s, 4-CH_3), 2.89 (3 H, s, 3-CH_3), 2.57 (3 H, s, 4′-CH_3), 2.48 (3 H, s, $COCH_3$), 2.38 (3 H, s, 8-CH_3), 1.32 (3 H, t, 2-OCH_2CH_3) and 1.18 (3 H, t, 5′-OCH_2CH_3); *m*/*z* (%) 527 (100, M^+), 481 (97), 435 (23), 420 (43), 218 (34), 202 (36) and 130 (18) (Found: M^+, 527.2420. $C_{31}H_{33}N_3O_5$ requires *M*, 527.2420).

Ethyl 7,8-*dimethoxy*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3i** *and ethyl* 6,7-*dimethoxy*-3,4-*dimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4e**. These compounds were obtained from 5,6-dimethoxyindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Crystallisation of the crude oil from dichloromethane gave the [2,3-b] *isomer* **4e** as pale yellow crystals (0.035 g, 4.78%), m.p. 265–268 °C (Found: C, 68.2; H, 5.91; N, 7.38. $C_{21}H_{22}N_2O_4$ requires C, 68.83; H, 6.05; N, 7.65%); δ_H([$^2H_6$]-DMSO) 11.00 (1 H, s, 1-NH), 10.65 (1 H, s, 9-NH), 7.68 (1 H, s, 5-H), 7.14 (1 H, s, 8-H), 6.97 (1 H, s, 10-H), 4.37 (2 H, q, OCH_2CH_3), 3.87 (3 H, s, OCH_3), 3.85 (3 H, s, OCH_3), 3.15 (3 H, s, 4-CH_3), 2.93 (3 H, s, 3-CH_3) and 1.38 (3 H, t, OCH_2CH_3); *m*/*z* (%) 366 (97, M^+), 320 (100), 305 (21), 277 (21), 249 (14), 183 (14) and 160 (29). Crystallisation of the remaining filtrate from dichloromethane–light petroleum gave the 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6d** as yellow crystals (0.019 g, 3.31%), m.p. 270–273 °C (decomp.); δ_H([$^2H_6$]-DMSO) 10.59 (1 H, s, 5-NH), 10.30 (1 H, s, pyr-NH), 10.12 (1 H, s, 1-NH), 7.23 (1 H, s, 9-H), 6.98 (1 H, s, 6-H), 5.16 (2 H, s, 10-CH_2), 4.34 (2 H, q, 2-OCH_2CH_3), 4.08 (2 H, q, 5′-OCH_2CH_3), 3.85 (3 H, s, OCH_3), 3.62 (3 H, s, OCH_3), 2.91 (6 H, s, 4-CH_3 and 3-CH_3), 2.54 (3 H, s, 4′-CH_3), 2.48 (3 H, s, $COCH_3$), 1.34 (3 H, t, 2-OCH_2CH_3) and 1.15 (3 H, t, 5′-OCH_2CH_3); *m*/*z* (%) 573 (80, M^+), 527 (100), 466 (60), 366 (28), 320 (20), 240 (23) and 148 (16) (Found: M^+ 573.2475. $C_{32}H_{35}N_3O_7$ requires M^+, 573.2475). Chromatographic separation of the remaining filtrate yielded the [3,2-b] *isomer* **3i** as a yellow solid (0.0595 g, 8.1%), m.p. 237–240 °C (decomp.) (Found: C, 68.9; H, 6.1; N, 7.5. $C_{20}H_{22}N_2O_4$ requires C, 68.83; H, 6.05; N, 7.65%); δ_H([$^2H_6$]-DMSO) 11.15 (1 H, s, 1-NH), 10.36 (1 H, s, 5-NH), 7.73 (1 H, s, 10-H), 7.62 (1 H, s, 9-H), 6.95 (1 H, s, 6-H), 4.37 (2 H, q, OCH_2CH_3), 3.87 (6 H, s, 2 × OCH_3), 2.90 (3 H, s, 4-CH_3), 2.87 (3 H, s, 3-CH_3) and 1.39 (3 H, t, OCH_2CH_3); *m*/*z* (%) 366 (100), 320 (99), 305 (11), 277 (19), 249 (8), 183 (11) and 160 (29); and the starting pyrrole **1a** (0.1687 g, 31.59%).

Ethyl 7,8-*methylenedioxy*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3i** *and ethyl* 6,7-*methylenedioxy*-3,4-*dimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4f**. These compounds were obtained from 5,6-methylenedioxyindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Chromatographic separation yielded the [3,2-*b*] *isomer* **3j** as a yellow solid (0.052 g, 7.43%), m.p. 263–265 °C (Found: C, 68.45; H, 4.95; N, 7.8. $C_{20}H_{18}N_2O_4$ requires C, 68.56; H, 5.18; N, 8.00%); δ_H([$^2H_6$]-DMSO) 11.13 (1 H, s, 1-NH), 10.49 (1 H, s, 5-NH), 7.72 (1 H, s, 10-H), 7.62 (1 H, s, 9-H), 6.95 (1 H, s, 6-H), 6.04 (2 H, s, OCH_2O), 4.37 (2 H, q, OCH_2CH_3), 2.89 (3 H, s, 4-CH_3), 2.87 (3 H, s, 3-CH_3) and 1.39 (3 H, t, OCH_2CH_3); *m*/*z* (%) 350 (84, M^+), 304 (100), 276 (44), 152 (22) and 138 (14). The [2,3-b] *isomer* **4f** was a pale yellow solid (0.0647 g, 7.43%), m.p. 270–270.5 °C (Found: C, 68.4; H, 5.1; N, 8.3. $C_{20}H_{18}N_2O_4$ requires C, 68.56; H, 5.18; N, 8.00%); δ_H([$^2H_6$]-DMSO) 11.00 (1 H, s, 1-NH), 10.78 (1 H, s, 9-NH), 7.66 (1 H, s, 5-H), 7.13 (1 H, s, 8-H), 6.98 (1 H, s, 10-H), 6.04 (2 H, s, OCH_2O), 4.36 (2 H, q, OCH_2CH_3), 3.10 (3 H, s, 4-CH_3) 2.91 (3 H, s, 3-CH_3) and 1.38 (3 H, t, OCH_2CH_3); *m*/*z* (%) 350 (93, M^+), 304 (100), 276 (35) and 152 (30). The 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6e** was a yellow solid (0.050 g, 8.92%), m.p. 239–242 °C (decomp.); δ_H([$^2H_6$]-DMSO) 10.73 (1 H, s, 5-NH), 10.08 (2 H, s, 1-NH and pyr-NH), 7.33 (1 H, s, 9-H), 6.99 (1 H, s, 6-H), 6.02 (2 H, s, OCH_2O), 5.08 (2 H, s, 10-CH_2), 4.32 (2 H, q, 2-OCH_2CH_3), 4.12 (2 H, q, 5′-OCH_2CH_3), 2.92 (3 H, s, 4-CH_3), 2.90 (3 H, s, 3-CH_3), 2.58 (3 H, s, 4′-CH_3), 2.54 (3 H, concealed by DMSO, $COCH_3$), 1.35 (3 H, t, 2-OCH_2CH_3) and 1.17 (3 H, t, 5′-OCH_2CH_3); *m*/*z* (%) 557 (95, M^+), 511 (100), 465 (22), 450 (60), 350 (23), 304 (33) and 276 (28) (Found: M^+, 557.2160. $C_{31}H_{31}N_3O_7$ requires *M*, 557.2161).

Ethyl 9-*fluoro*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3k** *and* 3-(3′-*acetyl*-5′-*ethoxycarbonyl*-4′-*methylpyrrol*-2′-*ylmethyl*)-4-*fluoroindole* **8b**. These compounds were obtained from 4-fluoroindole and the 5-acetoxymethylpyrrole **1a**. The *pyrrolo*[3,2-b]*carbazole* **3k** was a yellow solid (0.156 g, 24.0%), m.p. 233–235.5 °C (Found: C, 70.5; H, 5.4; N, 8.5. $C_{19}H_{17}FN_2O_2$ requires C, 70.36; H, 5.28; N, 8.64%); δ_H([$^2H_6$]-DMSO) 11.28 (1 H, s, 1-NH), 11.00 (1 H, s, 5-NH), 7.91 (1 H, s, 10-H), 7.36 (1 H, dt, *J* 5 and 7, 7-H), 7.24 (1 H, d, *J* 7, 6-H), 6.86 (1 H, dd, *J* 10 and 7, 8-H), 4.39 (2 H, q, OCH_2CH_3), 2.93 (3 H, s, 4-CH_3), 2.91 (3 H, s, 3-CH_3) and 1.40 (3 H, t, OCH_2CH_3); *m*/*z* (%) 324 (58, M^+), 278 (100), 250 (22), 222 (9) and 139 (9). The 3-*pyrrolylmethylindole* **8b** was an off-white solid (0.214 g, 31.3%), m.p. 179–182 °C (Found: C, 66.7; H, 5.79; N, 7.96. $C_{19}H_{19}FN_2O_3$ requires C, 66.65; H, 5.59; N, 8.18%); δ_H([$^2H_6$]-DMSO) 11.90 (1 H, s, pyr-NH), 11.10 (1 H, s, ind-NH), 7.19 (1 H, d, *J* 7, 7-H), 7.04 (1 H, dt, *J* 5 and 7, 6-H), 6.75 (1 H, dd, *J* 11 and 7, 5-H), 6.59 (1 H, br s, 2 H), 4.47 (2 H, s, CH_2), 4.27 (2 H, q, OCH_2CH_3), 2.55 (3 H, s, 4′-CH_3), 2.32 (3 H, s, $COCH_3$) and 1.32 (3 H, t, OCH_2CH_3); *m*/*z* (%) 342 (100, M^+), 327 (34), 295 (15), 281 (36), 268 (27), 253 (23) and 225 (17).

Ethyl 7-*fluoro*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3l** *and ethyl* 7-*fluoro*-3,4-*dimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4g**. These compounds were obtained from 6-fluoroindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. The [3,2-b] *isomer* **3l** was a yellow solid (0.305 g, 47.1%), m.p. 231–234 °C (Found: C, 70.45; H, 5.5; N, 8.7. $C_{19}H_{17}FN_2O_2$ requires C, 70.37; H, 5.25; N, 8.64%); δ_H([$^2H_6$]-DMSO) 11.27 (1 H, s, 1-NH), 10.82 (1 H, s, 5-NH), 8.90 (1 H, dd, *J* 9 and 6, 9-H), 7.85 (1

H, s, 10-H), 7.12 (1 H, dd, *J* 10 and 2, 6-H), 6.89 (1 H, dt, *J* 2 and 9, 8-H), 4.37 (2 H, q, OCH_2CH_3), 2.89 (6 H, s, 4-CH_3 and 3-CH_3) and 1.39 (3 H, t, OCH_2CH_3); *m/z* (%) 324 (60, M^+), 278 (100), 250 (34), 222 (10) and 139 (7) (Found: M^+, 324.1267. $C_{19}H_{17}FN_2O_2$ requires *M*, 324.1274). The [2,3-b] *isomer* **4g** was a pale yellow solid (0.020 g, 3.08%), m.p. 262–265 °C (decomp.); $\delta_H([^2H_6]$-DMSO) 11.14 (1 H, s, 1-NH), 11.06 (1 H, s, 9-NH), 8.12 (1 H, dd, *J* 9 and 6, 5-H), 7.19 (1 H, s, 10-H), 7.15 (1 H, dd, *J* 10 and 2, 8-H), 6.92 (1 H, dt, *J* 2 and 9, 6-H), 4.36 (2 H, q, OCH_2CH_3), 3.13 (3 H, s, 4-CH_3), 2.93 (3 H, s, 3-CH_3) and 1.39 (3 H, t, OCH_2CH_3); saturation of the 10-H proton at δ 7.19 enhanced the signals due to 1-NH at δ 11.14 (2.2%) and 9-NH at δ 11.06 (2.2%); *m/z* (%) 324 (72, M^+), 278 (100), 250 (39), 222 (9) and 139 (6) (Found: M^+, 324.1280. $C_{19}H_{17}FN_2O_2$ requires *M*, 324.1274). The 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6f** was a yellow solid, m.p. 283–285 °C (0.0156 g, 2.9%); $\delta_H([^2H_6]$-DMSO) 11.04 (1 H, s, 5-NH), 10.31 (1 H, s, pyr-NH), 10.12 (1 H, s, 1-NH), 7.86 (1 H, dd, *J* 9 and 6, 9-H), 7.17 (1 H, dd, *J* 10 and 2, 6-H), 6.85 (1 H, dt, *J* 2 and 9, 8-H), 5.13 (2 H, s, 10-CH_2), 4.19 (2 H, q, 2-OCH_2CH_3), 4.11 (2 H, q, 5'-OCH_2CH_3), 2.93 (3 H, s, 4-CH_3), 2.90 (3 H, s, 3-CH_3), 2.56 (3 H, s, 4'-CH_3), 2.51 (3 H, concealed by DMSO, $COCH_3$), 1.34 (3 H, t, 2-OCH_2CH_3) and 1.16 (3 H, t, 5'-OCH_2CH_3); *m/z* (%) 532 (7, M^+H), 486 (12), 325 (90), 210 (100) and 196 (40) (Found: MH^+ 532.225. $C_{30}H_{30}FN_3O_5$ requires *M*H, 532.2249).

Ethyl 8-*chloro*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3m** *and* 3-(3'-*acetyl*-5-*ethoxycarbonyl*-4'-*methylpyrrol*-2'-*ylmethyl*)-5-*chloroindole* **8e**. These compounds were obtained from 5-chloroindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. The pyrrolo[3,2-b]*carbazole* **3m** was a yellow solid (0.112 g, 16.4%, m.p. 218–220 °C (Found: C, 66.8; H, 4.85; N, 8.3. $C_{19}H_{17}ClN_2O_2$ requires C, 66.96; H, 5.03; N, 8.22%); $\delta_H([^2H_6]$-DMSO) 11.33 (1 H, s, 1-NH), 10.84 (1 H, s, 5-NH), 8.19 (1 H, s, 9-H), 7.93 (1 H, s, 10-H), 7.41 (1 H, d, *J* 7, 6-H), 7.36 (1 H, dd, *J* 7 and 2, 7-H), 4.38 (2 H, q, OCH_2CH_3), 2.90 (6 H, s, 4-CH_3 and 3-CH_3) and 1.39 (3 H, t, OCH_2CH_3); *m/z* (%) 342 (20, $M^+[^{37}Cl]$), 340 (60, $M^+[^{35}Cl]$), 296 (34), 294 (100), 266 (19), 265 (11), 231 (10), 230 (14) and 229 (10). The 3-*pyrrolylmethylindole* **8e** was an off-white solid (0.251 g, 35.1%), m.p. 218–220 °C (Found: C, 63.8; H, 5.2; N, 7.7. $C_{19}H_{19}ClN_2O_3$ requires C, 63.60; H, 5.34; N, 7.81%); $\delta_H([^2H_6]$-DMSO) 12.07 (1 H, s, pyr-NH), 11.03 (1 H, s, ind-NH), 7.68 (1 H, d, *J* 2, 4-H), 7.35 (1 H, d, *J* 8, 7-H), 7.06 (1 H, dd, *J* 8 and 2, 6-H), 7.05 (1 H, br, s, 2-H), 4.30 (2 H, s, 3-CH_2), 4.28 (2 H, q, OCH_2CH_3), 2.53 (3 H, concealed by DMSO, 4'-CH_3), 2.34 (3 H, s, $COCH_3$) and 1.33 (3 H, t, OCH_2CH_3); *m/z* (%) 360 (34, $M^+[^{37}Cl]$), 358 (100, $M^+[^{35}Cl]$), 345 (15), 343 (51), 313 (13), 311 (18), 297 (36), 286 (12), 284 (36), 271 (8), 269 (24), 243 (8), 241 (17), 207 (13), 205 (9) and 151 (27).

Ethyl 8-*bromo*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3n**, *ethyl* 6-*bromo*-3,4-*dimethylpyrrolo*[2,3-b]*carbazole*-2-*carboxylate* **4i** *and* 3-(3'-*acetyl*-5-*ethoxycarbonyl*-4'-*methylpyrrol*-2'-*ylmethyl*)-5-*bromoindole* **8f**. These compounds were obtained from 5-bromoindole and the 5-acetoxymethyl-4-acetylpyrrole **1a**. The [3,2-b] *isomer* **3n** was a yellow solid (0.088 g, 11.4%), m.p. 228–231 °C (decomp.) (Found: C, 59.2; H, 4.35; N, 7.5. $C_{19}H_{17}BrN_2O_2$ requires C, 59.23; H, 4.45; N, 7.27%); $\delta_H([^2H_6]$-DMSO) 11.34 (1 H, s, 1-NH), 10.85 (1 H, s, 5-NH), 8.33 (1 H, d, *J* 2, 9-H), 7.93 (1 H, s, 10-H), 7.48 (1 H, dd, *J* 8 and 2, 7-H), 7.36 (1 H, d, *J* 8, 6-H), 4.37 (2 H, q, OCH_2CH_3) 2.91 (6 H, s, 4-CH_3 and 3-CH_2) and 1.39 (3 H, t, OCH_2CH_3); *m/z* (%) 386 (69, $M^+[^{81}Br]$), 384 (70, $M^+[^{79}Br]$), 340 (94), 338 (100), 312 (14), 310 (13), 231 (15), 229 (21) and 204 (11). The [2,3-b] *isomer* **4i** was a pale yellow solid (0.0182 g, 2.36%), m.p. 280–281 °C (decomp.) (Found: C, 59.4; H, 4.7; N, 7.3. $C_{19}H_{17}BrN_2O_2$ requires C, 59.23; H, 4.45; N, 7.27%); $\delta_H([^2H_6]$-DMSO) 11.16 (1 H, s, 1-NH), 11.11 (1 H, s, 9-NH), 8.25 (1 H, s, 5-H), 7.48 (1 H, dd, *J* 8 and 1.5, 7-H), 7.34 (1 H, d, *J* 8, 8-H), 7.22 (1 H, s, 10-H), 4.37 (2 H, q, OCH_2CH_3), 3.15 (3 H, s, 4-CH_3), 2.95 (3 H, s, 3-CH_3) and 1.40 (3 H, t, OCH_2CH_3); *m/z* (%) 386 (98, $M^+[^{81}Br]$), 384 (98, $M^+[^{79}Br]$), 340 (91), 338 (100), 312 (37), 310 (44), 312 (20), 229 (35) and 204 (16). The 3-*pyrrolylmethylindole* **8f** was an off-white solid (0.406 g, 50.3%), m.p. 222–225 °C (Found: C, 56.3; H, 4.7; N, 6.8. $C_{19}H_{19}BrN_2O_3$ requires C, 56.58; H, 4.75; N, 6.95%); $\delta_H([^2H_6]$-DMSO) 12.05 (1 H, s, pyr-NH), 11.05 (1 H, s, ind-NH), 7.82 (1 H, s, 4-H), 7.30 (1 H, d, *J* 7.5, 6-H), 7.16 (1 H, d, *J* 7.5, 7-H), 7.02 (1 H, d, *J* 1.5, 2-H), 4.29 (2 H, s, 3-CH_2), 4.27 (2 H, q, OCH_2CH_3), 2.52 (3 H, concealed by DMSO, 4'-CH_3), 2.33 (3 H, s, $COCH_3$) and 1.33 (3 H, t, OCH_2CH_3); *m/z* (%) 404 (100, $M^+[^{81}Br]$), 402 (98, $M^+[^{79}Br]$), 389 (38), 387 (43), 358 (15), 356 (14), 330 (31), 328 (30), 315 (20), 313 (22), 287 (12), 285 (10), 234 (17), 206 (47), 194 (33) and 178 (31).

Synthesis of 3-(3'-*Acetyl*-5'-*ethoxycarbonyl*-4'-*methylpyrrol*-2'-*ylmethyl*)-5-*methylindole* **8c**.—A solution of 5-methylindole (0.196 g, 1.5 mmol) and the 5-acetoxymethyl-4-acetylpyrrole **1a** (0.400 g, 1.5 mmol) in dichloromethane (15 cm^3) was gently heated at reflux and stirred with Montmorillonite clay (1.5 g) for 7 h. After the clay had been filtered off and washed well with dichloromethane, evaporation of the combined filtrates gave an oil. This was submitted to column chromatography on silica eluting with (0–20%) ethyl acetate in dichloromethane to give (*a*) 5-methylindole (0.075 g, 38.1%), (*b*) the pyrrolo[3,2-*b*]carbazole **3h** (0.037 g, 7.65%) and (*c*) the pyrrolo[2,3-*b*]carbazole **4d** (0.009 g, 1.89%) which were identical in all respects with the pyrrolo[3,2-*b*]carbazole **3h** and the pyrrolo[2,3-*b*]carbazole **4d** from previous experiment respectively. Further elution gave the 3-pyrrolylmethylindole **8c** (0.061 g, 12.1%), m.p. 192–195 °C (Found: C, 70.8; H, 6.6; N, 8.4. $C_{20}H_{22}N_2O_3$ requires C, 70.98; H, 6.55; N, 8.28%); $\delta_H([^2H_6]$-DMSO 11.95 (1 H, s, pyr-NH), 10.67 (1 H, s, ind-NH), 7.35 (1 H, br, s, 4-H), 7.21 (1 H, d, *J* 8, 7-H), 6.90 (1 H, d, *J* 8, 6-H), 6.79 (1 H, br, s, 2-H), 4.29 (2 H, s, 3-CH_2), 4.27 (2 H, q, OCH_2CH_3), 2.52 (3 H, concealed by DMSO, 5-CH_3), 2.39 (3 H, s, 4'-CH_3), 2.32 (3 H, s, $COCH_3$) and 1.32 (3 H, t, OCH_2CH_3); *m/z* (%) 338 (100, M^+), 323 (56), 277 (44), 264 (33), 249 (26), 221 (25), 194 (13), 145 (24) and 131 (38); and the starting pyrrole **1a** (0.152 g, 38%).

Cyclisation of the 3-*Pyrrolylmethylindole* **8c**.—A solution of the 3-pyrrolylmethylindole **8c** (0.034 g, 0.1 mmol) in 1,2-dichloroethane (5 cm^3) was heated at gentle reflux and stirred with Montmorillonite clay (0.1 g) for 1.5 h. TLC showed that only one product had formed and the reaction was complete. After the clay had been filtered off and washed well with 1,2-dichloroethane, evaporation of the combined filtrates gave a yellow solid (0.029 g, 92.5%) which was identical in all respects with the pyrrolo[3,2-*b*]carbazole **3h** of the previous experiment. There was no detectable pyrrolo[2,3-*b*]carbazole **4d**.

Reaction of Indole and the 5-*Acetoxymethyl*-4-*acetylpyrrole* **1a** *with Toluene*-p-*sulfonic Acid*.—Toluene-*p*-sulfonic acid (30 mg) was added to a solution of indole (0.117 g, 1.0 mmol) and the 5-acetoxymethyl-4-acetylpyrrole **1a** (0.267 g, 1.0 mmol) in 1,2-dichloroethane (10 cm^3) and the reaction mixture was heated under reflux for 7 h. After cooling, the mixture was evaporated under reduced pressure and the remaining crude oil was submitted to column chromatography eluting with (5.35%) ethyl acetate in light petroleum. This gave the pyrrolo[3,2-*b*]carbazole **3a** as a yellow solid (0.043 g, 14.1%), m.p. 209.5–211 °C (lit.,[1] 209.5–211 °C) and the 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6a** as a yellow solid (0.074 g, 28.8%), m.p. 243–245 °C (decomp.) which was identical in all respects with the 10-pyrrolylmethylpyrrolo[3,2-*b*]carbazole **6a** of the previous experiment.

Reaction of the Pyrrolo[3,2-b]*carbazole* **3a** *and the* 5-*Acetoxymethyl*-4-*acetylpyrrole* **1a**.—A solution of the pyr-

rolo[3,2-*b*]carbazole **3a** (0.076 g, 0.25 mmol) and the pyrrole **1a** (0.069 g, 0.25 mmol) in 1,2-dichloroethane (5 cm^3) was heated under reflux and stirred with Montmorillonite clay (250 mg) for 7 h. After the clay had been filtered off and washed well with 1,2-dichloroethane, evaporation of the combined filtrates gave a yellow solid which was chromatographed, eluting with (0–10%) ethyl acetate in dichloromethane. This gave starting pyrrolo[3,2-*b*]carbazole **3a** (0.029 g, 37.5%) and the 10-pyrrolylmethylpyrrolo[3,2-*b*]carbazole **6a** (0.038 g, 29.9%) which was identical in all respects to the 10-pyrrolylmethylpyrrolo[3,2-*b*]carbazole **6a** of the earlier experiment.

Reaction of the Pyrrolo[3,2-b]*carbazole* **3o** *and the 5-Acetoxymethyl-4-acetylpyrrole* **1b**.—Toluene-*p*-sulfonic acid (10 mg) was added to a solution of the pyrrolo[3,2-*b*]carbazole **3o** (0.074 g, 0.2 mmol) and the pyrrole **1b** (0.066 g, 0.2 mmol) in 1,2-dichloroethane (5 cm^3) and the reaction mixture was heated under reflux for 7 h. Evaporation of the mixture under reduced pressure gave a yellow solid which was chromatographed eluting with (0.15%) ethyl acetate in dichloromethane. This gave the starting pyrrolo[3,2-*b*]carbazole **3o** (0.014 g, 19.2%); the 10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6g** as a yellow solid (0.035 g, 27.8%), m.p. 233–236 °C (Found: C, 75.5; H, 5.43; N, 6.42. $C_{40}H_{35}N_3O_5$ requires C, 75.33; H, 5.53; N, 6.59%); $\delta_H([^2H_6]$-DMSO) 10.89 (1 H, s, 5-NH), 10.50 (1 H, s, pyr-NH), 9.98 (1 H, s, 1-NH), 7.83 (1 H, d, *J* 8, 9-H), 7.47–7.11 (12 H, m, 2 × ArH, 6-H and 7-H), 6.99 (1 H, t, *J* 7.5, 8-H), 5.39 (2 H, s, 2-OCH_2Ph), 5.19 (2 H, s, 10-CH_2) 5.10 (2 H, s, 5'-OCH_2Ph), 2.96 (3 H, s, 4-CH_3), 2.91 (3 H, s, 3-CH_3) and 2.52 (6 H, s, 4'-CH_3 and $COCH_3$); *m/z* (%) 637 (25, M^+), 529 (18), 108 (63), 91 (100) and 77 (36); and the 6,10-*dipyrrolylmethylpyrrolo*[3,2-b]*carbazole* **3r** (0.012 g, 12.8%), m.p. 254–256 °C (Found: C, 73.9; H, 5.72; N, 6.33. $C_{56}H_{50}N_4O_8$ requires C, 74.15; H, 5.56; N, 6.18%); $\delta_H([^2H_6]$-DMSO) 12.24 (1 H, s, 6-pyr-NH), 10.49 (2 H, s, 5-NH and 10-pyr-NH), 10.00 (1 H, s, 1-NH), 7.70 (1 H, d, *J* 7.5, 9-H), 7.49 (15 H, m, 3 × ArH), 6.90 (1 H, t, *J* 7.5, 8-H), 6.89 (1 H, d, *J* 7.5, 7-H), 5.38 (2 H, s, 2-OCH_2Ph), 5.32 (2 H, s, 10-pyr-OCH_2Ph), 5.16 (2 H, s, 10-CH_2), 5.10 (2 H, s, 6-pyr-OCH_2Ph), 4.62 (2 H, s, 6-CH_2), 3.03 (3 H, s, 4-CH_3), 2.92 (3 H, s, 3-CH_3), 2.58 (3 H, s, 6-pyr-CH_3), 2.50 (6 H, s, 10-pyr-CH_3 and $COCH_3$) and 2.32 (3 H, s, 6-pyr-$COCH_3$); saturation of the 10-CH_2 at δ 5.16 enhanced the signals due to 9-H doublet at δ 7.70 (23.7%), 1-NH at δ 10.00 (3.9%) and 10-pyr-NH at δ 10.49 (11.8%); and saturation of the 6-CH_2 at δ 4.62 enhanced the signals due to 7-H doublet at δ 6.89 (8.3%), 6-pyr-NH at δ 12.24 (9.9%) and 5-NH at δ 10.49 (11.6%); *m/z* (FAB) M, 906.

Vilsmeier Formylation of the Pyrrolo[3,2-b]*carbazoles* **3a** *and* **3h**: *General Procedure*.—The pyrrolo[3,2-*b*]carbazole (0.3 mmol) was added to the solution of *N*-methylformanilide (0.037 cm^3, 0.3 mmol) and phosphorus oxychloride (0.041 cm^3, 0.45 mmol) in trichloroethylene (1 cm^3), and the mixture was gently heated under reflux for 30 min. After cooling, aqueous sodium acetate (0.13 g in water 1.5 cm^3) was added to the mixture which was then heated further for 10 min. The reaction mixture was extracted with chloroform (3 × 10 cm^3) and the combined extracts were washed with hydrochloric acid (0.1 mol dm^{-3}; 3 × 10 cm^3) and water (3 × 10 cm^3) and then evaporated under reduced pressure to give a yellow solid. This was submitted to column chromatography eluting with (0–10%) ethyl acetate in dichloromethane to give the 10-formylpyrrolo[3,2-*b*]carbazole.

Ethyl 10-*formyl*-3,4-*dimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3s** was obtained from the pyrrolo[3,2-*b*]carbazole **3a** as a yellow solid (0.0646 g, 64.5%), m.p. 292 °C (decomp.); $\delta_H([^2H_6]$-DMSO) 11.38 (1 H, s, 1-NH), 11.21 (1 H, s, CHO), 10.82 (1 H, s, 5-NH), 8.52 (1 H, d, *J* 7.5, 9-H) 7.85 (1 H, d, *J* 7.5, 6-H), 7.52 (1 H, t, *J* 7.5, 8-H), 7.19 (1 H, t, *J* 7.5, 7-H), 4.12 (2 H, q, OCH_2CH$_3$), 3.02 (3 H, s, 4-CH_3), 2.89 (3 H, s, 3-CH_3) and 1.42 (3 H, t, OCH$_2$CH_3); *m/z* (%) 334 (100, M^+), 288 (49), 260 (65), 231 (20) and 204 (12) (Found: M^+ 334.1325. $C_{20}H_{18}N_2O_3$ requires *M*, 334.1317); ν_{max}(Nujol)/cm^{-1} 3449, 3275, 1687 and 1639.

Ethyl 10-*formyl*-3,4,8-*trimethylpyrrolo*[3,2-b]*carbazole*-2-*carboxylate* **3t** was obtained from the pyrrolo[3,2-*b*]carbazole **3h** as a deep yellow solid (0.056 g, 54.0%), m.p. 293–294 °C; $\delta_H([^2H_6]$-DMSO) 11.24 (1 H, s, 1-NH), 11.17 (1 H, s, CHO), 10.77 (1 H, s, 5-NH), 8.29 (1 H, s, 9-H), 7.45 (1 H, d, *J* 8, 6-H), 7.33 (1 H, d, *J* 8, 7-H), 4.40 (2 H, q, OCH_2CH$_3$), 2.99 (3 H, s, 4-CH_3), 2.88 (3 H, s, 3-CH_3), 2.50 (3 H, s, 8-CH_3) and 1.42 (3 H, t, OCH$_2$CH_3); *m/z* (%) 348 (100, M^+), 302 (52), 274 (54) and 245 (15) (Found: M^+ 348.1465. $C_{21}H_{20}N_2O_3$ requires *M*, 348.1474); ν_{max}(Nujol)/cm^{-1} 3446, 3236, 1716 and 1642.

Reaction of the Pyrrolo[3,2-b]*carbazole* **3a** *and* 2-*Methylbut*-3-*en*-2-*ol*.—A solution of the pyrrolo[3,2-*b*]carbazole **3a** (0.165 g, 0.54 mmol) and 2-methylbut-3-ene-2-ol (0.093 g, 1.08 mmol), in 1,2-dichloroethane (20 cm^3) was heated under reflux and stirred with Montmorillonite clay (0.5 g) for 15 h. The clay was filtered off and washed well with 1,2-dichloroethane and evaporation of the combined filtrates gave a brown oil. This was submitted to column chromatography eluting with (50–0%) light petroleum in dichloromethane to give the 10-(2-*methylbut*-2-*enyl*)*pyrrolo*[3,2-b]*carbazole* **3p** as a yellow solid (0.047 g, 23.3%), m.p. 168–171 °C (Found: C, 77.1; H, 7.18; N, 7.59. $C_{24}H_{26}N_2O_2$ requires C, 76.97; H, 7.00; N, 7.48%); $\delta_H([^2H_6]$-DMSO) 10.71 (1 H, s, 1-NH), 10.62 (1 H, s, 5-NH), 8.00 (1 H, d, *J* 7.5, 9-H), 7.43 (1 H, d, *J* 7.5, 6-H), 7.35 (1 H, t, *J* 7.5, 8-H), 7.08 (1 H, t, *J* 7.5, 7-H), 5.18 (1 H, br, t, *J* 6, CH_2CH=), 4.39 (2 H, q, OCH_2CH$_3$), 4.23 (2 H, br, d, *J* 6, CH_2CH=), 2.90 (3 H, s, 4-CH_3), 2.89 (3 H, s, 3-CH_3), 1.95 (3 H, s, =CCH_3), 1.65 (3 H, s, =CCH_3) and 1.39 (3 H, t, OCH$_2$CH_3); *m/z* (%) 374 (100, M^+), 328 (40), 313 (22), 300 (9), 299 (15), 285 (17), 284 (10) and 273 (24). Also obtained was the 6-(2-methylbut-2-enyl)pyrrolo[3,2-*b*]carbazole **3u** as a yellow solid (0.0012 g, 0.6%); $\delta_H([^2H_6]$-DMSO) 11.22 (1 H, s, 1-NH), 10.11 (1 H, s, 5-NH), 7.91 (1 H, d, *J* 7.5, 9-H), 7.85 (1 H, s, 10-H), 7.14 (1 H, d, *J* 7.5, 7-H), 7.03 (1 H, t, *J* 7.5, 8-H), 5.52 (1 H, br, t, *J* 6, CH_2CH=), 4.37 (2 H, q, OCH_2CH$_3$), 3.69 (2 H, d, *J* 6, CH_2CH=), 2.98 (3 H, s, 4-CH_3), 2.91 (3 H, s, 3-CH_3), 1.80 (3 H, s, =CCH_3), 1.79 (3 H, s, =CCH_3) and 1.40 (3 H, t, OCH$_2$CH_3); *m/z* (%) 374 (100, M^+), 328 (93), 273 (14), 245 (18) and 243 (10); and the starting pyrrolo[3,2-*b*]carbazole **3a** (0.063 g, 38%).

Reaction of the Pyrrolo[3,2-b]*carbazole* **3a** *with Pyridine Hydrobromide Perbromide*.—Pyridine hydrobromide perbromide (0.092 g, 0.3 mmol) was added to a solution of the pyrrolo[3,2-*b*]carbazole **3a** (0.096 g, 0.3 mmol) in dichloromethane (10 cm^3), and the mixture was stirred and gently heated under reflux for 30 min. Evaporation of the mixture under reduced pressure gave a yellow oil which was submitted to column chromatography eluting with (5–0%) light petroleum in dichloromethane. This gave the 10-*bromopyrrolo*[3,2-b]*carbazole* **3y** as a yellow solid (0.034 g, 29.9%), m.p. 248–251 °C (decomp.) (Found: C, 59.1; H, 4.6; N, 7.1. $C_{19}H_{17}BrN_2O_2$ requires C, 59.23; H, 4.45; N, 7.27%); $\delta_H([^2H_6]$-DMSO) 11.03 (1 H, s, 1-NH), 10.48 (1 H, s, 5-NH), 8.64 (1 H, d, *J* 7, 9-H), 7.50 (1 H, d, *J* 7, 6-H), 7.47 (1 H, dt, *J* 7 and 2, 8-H), 7.18 (1 H, dt, *J* 7 and 2, 7-H), 4.38 (2 H, q, OCH_2CH$_3$), 2.92 (3 H, s, 4-CH_3), 2.89 (3 H, s, 3-CH_3) and 1.40 (3 H, t, OCH$_2$CH_3); *m/z* (%) 386 (66, M^+ [^{81}Br]), 384 (65, M^+ [^{79}Br]), 340 (100), 339 (30), 338 (97), 312 (13), 311 (10), 310 (13), 231 (24), 230 (31) and 229 (29); the 8-bromopyrrolo[3,2-b]carbazole **3n** as a yellow solid (0.0076 g, 6.6%) which was identical in all respects with the pyrrolo-[3,2-*b*]carbazole **3n** in the previous experiment; the 8,10-

dibromopyrrolo[3,2-*b*]carbazole **3q** as a greenish yellow solid (0.0122 g, 8.76%) which was identical with the pyrrolo[3,2-*b*]carbazole **3q** of the next experiment; and the starting pyrrolo[3,2-*b*]carbazole **3a** (0.0247 g, 20.9%).

Synthesis of the 8,10-*Dibromopyrrolo*[3,2-b]*carbazole* **3q**.—Pyridine hydrobromide perbromide (0.064 g, 0.2 mmol) was added to a solution of the pyrrolo[3,2-*b*]carbazole **3a** (0.0306 g, 0.1 mmol) in dichloromethane (6 cm^3) and the mixture was stirred and gently heated under reflux for 30 min. After cooling of the mixture, the product crystallised and was filtered off to give the 8,10-*dibromopyrrolo*[3,2-b]*carbazole* **3q** as greenish yellow crystals (0.032 g, 68.8%), m.p. 276–278 °C (Found: C, 49.0; H, 3.2; N, 5.8. $C_{19}H_{16}BrN_2O_2$ requires C, 49.16; H, 3.47; N, 6.04%); δ_H([$^2H_6$]-DMSO) 11.24 (1 H, s, 1-NH), 10.62 (1 H, s, 5-NH), 8.75 (1 H, d, *J* 2, 9-H), 7.60 (1 H, dd, *J* 8 and 2, 7-H), 7.47 (1 H, d, *J* 8, 6-H), 4.39 (2 H, q, OCH_2CH_3), 2.91 (3 H, s, 4-CH_3), 2.88 (3 H, s, 3-CH_3) and 1.39 (3 H, t, OCH_2CH_3); *m*/*z* (%) 466 (41, M^+ [^{81}Br]), 464 (79), 462 (41, M^+ [^{79}Br]), 420 (55), 418 (100), 416 (57), 392 (8), 390 (14), 389 (11), 340 (15) and 338 (16).

Reaction of the 10-*Pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6a** *with Pyridine Hydrobromide Perbromide*.—Pyridine hydrobromide perbromide (0.0228 g, 0.07 mmol) was added to a solution of the pyrrolo[3,2-*b*]carbazole **6a** (0.035 g, 0.068 mmol) in dichloromethane (5 cm^3), and the mixture was stirred and gently heated under reflux for 30 min. After cooling of the mixture, the solution was washed with water (10 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give an oil. This was submitted to column chromatography eluting with (0–10%) ethyl acetate in dichloromethane to give the 6,8-*dibromo*-10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6j** as a yellow solid (0.0075 g, 16.5%), m.p. 250–253 °C (decomp.); δ_H($CDCl_3$) 10.50 (1 H, s, 5-NH), 8.98 (1 H, s, 1-NH), 8.72 (1 H, s, 1-NH), 8.63 (1 H, s, 9-H), 7.52 (1 H, s, 7-H), 4.47 (2 H, q, 2-OCH_2CH_3), 4.42 (2 H, s, 10-CH_2), 4.29 (2 H, q, 5′-OCH_2CH_3), 2.92 (3 H, s, 4-CH_3), 2.87 (3 H, s, 3-CH_3), 2.68 (3 H, s, 4′-CH_3), 2.59 (3 H, s, $COCH_3$), 1.48 (3 H, t, 2-OCH_2CH_3) and 1.34 (3 H, t, 5′-OCH_2CH_3); *m*/*z* (%) 671 (7, M^+ [^{81}Br]), 625 (8), 579 (12), 195 (40), 134 (30) and 108 (100) (Found: M^+ [^{79}Br], 669.047. $C_{30}H_{29}Br_2N_3O_5$ requires M [^{79}Br] 669.047); and the 8-*bromo*-10-*pyrrolylmethylpyrrolo*[3,2-b]*carbazole* **6i** as a yellow solid (0.017 g, 41.8%), m.p. 240 °C (decomp.) (Found: C, 60.8; H, 5.11; N, 7.13. $C_{30}H_{30}BrN_3O_5$ requires C, 60.81; H, 5.10; N, 7.09%); δ_H([$^2H_6$]-DMSO) 11.03 (1 H, s, 5-NH), 10.63 (1 H, s, pyr-NH), 10.22 (1 H, s, 1-NH), 7.94 (1 H, s, 9-H), 7.48 (1 H, d, *J* 7.5, 7-H), 7.40 (1 H, d, *J* 7.5, 6-H), 5.13 (2 H, s, 10-CH_2), 4.33 (2 H, q, 2-OCH_2CH_3), 4.14 (2 H, q, 5′-OCH_2CH_3), 2.95 (3 H, s, 4-CH_3), 2.91 (3 H, s, 3-CH_3), 2.58 (3 H, s, 4′-CH_3), 2.48 (3 H, s, $COCH_3$), 1.36 (3 H, t, 2-OCH_2CH_3) and 1.18 (3 H, t, 5′-OCH_2CH_3); *m*/*z* (%) 593 (49, M^+ [^{81}Br]), 591 (48, M^+ [^{79}Br], 513 (43), 202 (16), 181 (8), 134 (10), 82 (50), 81 (51) and 79 (100).

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References

1 L. Chunchatprasert, K. R. N. Rao and P. V. R. Shannon, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1779.
2 Patent application no. WO 93/01512.
3 L. Chunchatprasert, A. H. Jackson, K. R. N. Rao and P. V. R. Shannon, *J. Chem. Res.*, 1992, (*S*), 258.
4 R. Iyer, A. H. Jackson, B. Naidoo and P. V. R. Shannon, *Chem. Commun.*, 1972, 461.
5 A. H. Jackson, R. Iyer, B. Naidoo and P. V. R. Shannon, *J. Chem. Soc., Perkin Trans. 2*, 1973, 872.
6 J. S. L. Ibaceta-Lizana, R. Iyer, A. H. Jackson and P. V. R. Shannon, *J. Chem. Soc., Perkin Trans. 2*, 1978, 733.
7 A. C. Tinker, Ph.D. Thesis, Cardiff, 1976.
8 A. H. Jackson, P. R. Jenkins and P. V. R. Shannon, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1698.
9 K. M. Biswas, A. H. Jackson, M. M. Kobaisy and P. V. R. Shannon, *J. Chem. Soc., Perkin Trans. 1*, 1992, 461.
10 E. Collins and P. V. R. Shannon, *J. Chem. Soc., Perkin Trans. 1*, 1973, 419.

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