Anti-tumour heterocycles. Part XIV.[1] A new route to pyrrolo-[3,2-*f*]indoles and the novel pyrrolo[3,2-*f*; 4,5-*f'*]diindole system

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Vilsmeier formylation of the dipyrrolylmethane 14a gave the 8-formylpyrrolo[3,2-*f*]indole 15. Alternatively, condensation of the pyrrole 1a with a variety of 2,3-unsubstituted pyrroles 16a–e in the presence of Montmorillonite K-10 clay gave, in general, the corresponding pyrrolo[3,2-*f*]indoles 19 and 21a–d. These pyrroloindoles were unambiguously structurally indentified by ^{1}H NMR spectra and NOE experiments. Amongst the by-products of the reaction were the corresponding pyrrolo[2,3-*f*]indoles, uncyclised 2-monosubstituted intermediate pyrroles and the 2,3-disubstituted derivatives. Similar results were obtained by replacing the ethyl ester 1a by the benzyl ester 1b.

The pyrrole 1a, with K-10 clay and the tetrahydroindole 24 gave only a very low yield of the spirocyclopentylpyrrolo[1,2-*f*]indole 25, but with the *N*-benzyl-4-oxotetrahydroindole 27b gave both the tetrahydropyrrolo[2,3-*b*]carbazole 28 and its [3,2-*b*] isomer 29 and other products.

The pyrrole 1a condensed with *N*-methoxycarbonylpyrrole 32 to give the pyrrolo[3,2-*f*]indole 33, its isomer 34, the monosubstituted intermediate 35 and the two products 36 and 37 resulting from disubstitution. Both of these (36 and 37) were cyclised with toluene-*p*-sulfonic acid to the novel pentacyclic pyrrolo[3,2-*f*; 4,5-*f'*]diindole 38.

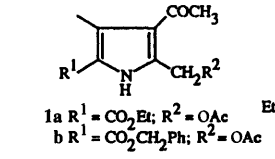
Regiospecific hydrolysis and decarboxylation of the *N*-methoxycarbonylpyrroloindole 33 gave the 2,3-unsubstituted pyrrolo[3,2-*f*]indole 21k, which on Vilsmeier formylation gave the 8-formyl derivative 39b.

Earlier[2] we showed that the pyrrole **1a**[3] could be condensed with indole in the presence of K-10 clay, to give predominantly the pyrrolo[3,2-*b*]carbazole **2** *via* an indolyl-3-monosubstituted intermediate **3**. Subsequently,[4] the reaction was shown to be a more general route to both pyrrolo-[3,2-*b*]- and -[2,3-*b*]-carbazoles **2** and **4** respectively.

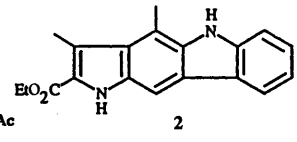
The novel anti-tumour properties[5] of the tetracyclic compounds **2** and **4** led us to seek a viable route to the simpler analogues, the pyrrolo-[2,3-*f*]- and -[3,2-*f*]-indoles **5** and **6** respectively. By analogy with our earlier work, acyl dipyrrolylmethanes of type **7** would be putative intermediates, and these should cyclise to the required systems **6**, either by direct intramolecular substitution at the vacant pyrrolyl-3 position or possibly *via* a spirocyclic intermediate of type **8** (Scheme 1). Acyl intermediates such as **7** could be prepared by 3-acylation of readily available 2,2-dipyrrolylmethanes, but this route to pyrrolo[3,2-*f*]indoles **6** has not been reported. As a simpler alternative, condensation of pyrrole **1a** (or its analogues) with 2,3-unsubstituted pyrroles **9** should afford the dipyrrolylmethanes **7** directly and hence the required pyrroloindoles **6**. An additional possibility exists of initial attack by the pyrrolylmethyl cation from **1a** at the pyrrolyl-4 position of **9** to give intermediates **10**, leading to the isomeric pyrroloindoles of type **5**.

Dutch workers have shown[6] that pyrromethenium cations, *e.g.* **11**, can be prepared by treatment of dimethyl bis(3-pyrrolyl)methanes with triethylorthoformate and acid. The only other known routes to the pyrrolo[3,2-*f*]indole nucleus are cyclisation of hydrazones[7,8] *e.g.* **12**, from which the pyrrolo[3,2-*f*]indole is the minor product (the angular isomer predominating) or cyclisation of dinitro bis-enamines,[9] *e.g.* **13**.

Initially we formylated the dipyrrolylmethane **14a**[10] under Vilsmeier conditions (1 equiv.) to give approximately equimolar amounts of starting material and the 8-formylpyrrolo[3,2-*f*]-indole **15** whose structure was confirmed by NOE effects. The 4-H singlet appeared at δ 8.45 and the NH and CHO singlets,



1a R^1 = CO_2Et; R^2 = OAc
b R^1 = CO_2CH_2Ph; R^2 = OAc



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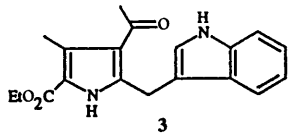

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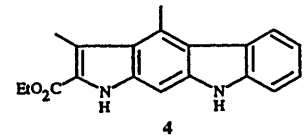

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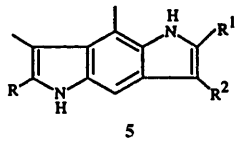

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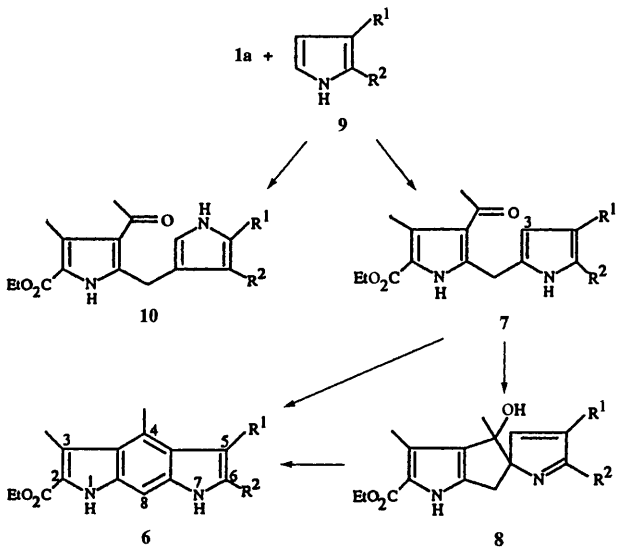
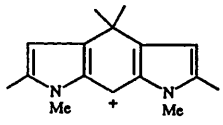
were, as expected, at abnormally low field (δ 11.25 and 10.84, respectively). The high reactivity of the 8-position in the nucleus of **15**, illustrated by its apparently spontaneous reactivity, was borne out by further results described below.

In the first attempt to simplify this synthesis, condensation of the pyrrole **1a** with the benzyl ester **16a** in the presence of K-10 clay gave a mixture of the 2-monosubstituted and 2,3-disubstituted pyrroles **17** (25%) and **18a** (28%), respectively. We also, however, isolated the pyrrolo[3,2-*f*]indole **19** (5.5%) and its [2,3-*f*] isomer **20** (3.7%). The structures and orientations of the product **17** and of the isomers **19** and **20** were established by NOE effects and in the ^{1}H NMR spectra there was a distinct difference in the chemical shift of the 8-H signal (δ 7.19 in the [3,2-*f*] **19** and δ 7.46 in the [2,3-*f*] isomer **20**) which proved to be general in this series. It was of interest that cyclisation of the pure 2-monosubstituted compound **17** with K-10 clay gave a 36% yield of the [3,2-*f*] isomer **19**.



Scheme 1



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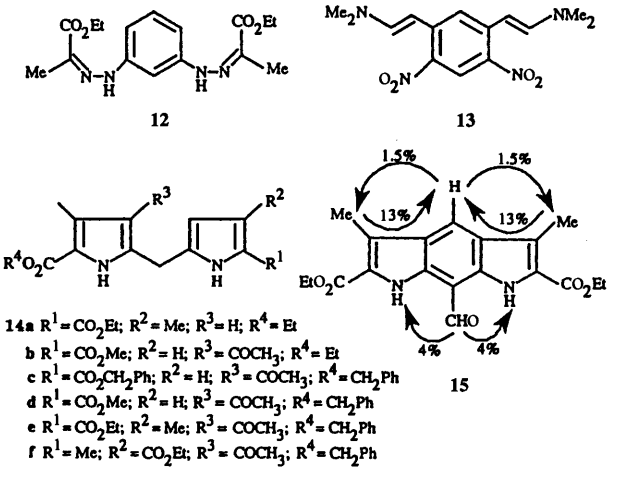


Similar products were obtained from the reaction of pyrrole **1a** and the methyl ester **16b**, which gave the pyrroloindoles **21a** and **22a** and the mono- and di-substituted products **14b** and **18b** in broadly comparable yields to those from the benzyl ester.

Surprisingly, introducing an alkyl group into the substrate pyrrole appeared to reduce the reactivity of the nucleus towards the pyrrolylmethyl cation. Thus, the alkyl pyrroles **16c**, **16d** and **16e** gave only low yields of the cyclised products **21b** and **22b**, **21c** and **22c**, and **21d** and **21e** respectively (the last having been decarboxylated *in situ*) and no detectable amounts of the uncyclised 2-monosubstitution products. In the case of **16c**, however, the major product (M^+, 549) showed symmetry in its ^1H NMR spectrum and an extra set of pyrrolylmethyl signals in place of the expected 8-H singlet at δ 7.47. It was therefore deduced to be the 8-substituted pyrrolo[3,2-*f*]indole **23**, in keeping with the high reactivity at that position in the tricyclic product. 2-Ethylpyrrole gave the 2-ethylpyrrolo[3,2-*f*]indole **21f** as the sole isolable product (10.5%).

Attempts to apply the condensation with pyrrole **1a** to 4,5,6,7-tetrahydroindole **24** gave none of the expected tetrahydropyrrolocarbazoles. We isolated instead only a very low yield (3%) of a crystalline product whose spectra were consistent with structure **25**. The molecular ion (M^+, 326.1630, 77%) confirmed that the product, after condensation and cyclisation, had gained an oxygen atom. In the ^1H NMR spectrum, apart from the expected signals from the ethyl and methyl groups and only *one* NH group, there were two vinyl proton signals at δ 7.10 and 6.36. Furthermore, the CH_2 multiplets in the starting material **24** had moved to higher field. The formation of **25** may be explained by the mechanism proposed in Scheme 2, as hydroperoxidation of tetrahydrocarbazoles and ring-contraction of the resultant hydroxy products is well known.[11] The alternative structure **26**, derivable *via* a similar route, can be ruled out by NOE experiments.

4-Oxo-4,5,6,7-tetrahydroindole **27a** proved to be completely unreactive towards the pyrrole **1a** in the presence of K-10 clay, even under forcing conditions, but the *N*-benzyl derivative **27b** gave four products separable by chromatography. The major one was the 5-oxotetrahydropyrrolo[2,3-*b*]carbazole **28** (16%), with substantially smaller amounts (3.3%) of its [3,2-*b*] isomer **29**. In addition, we isolated the 10-pyrrolylmethyl derivative **30** (6%) and the 2-monosubstituted product **31** (9.8%). Their structures followed unambiguously from the ^1H NMR spectra and NOE enhancements shown in Scheme 3. In accord with the nearby 5-C=O group, the 4-Me signal of the product **28** was deshielded to δ 3.28. It is noteworthy that the 4-oxotetrahydroindole **27b** behaves as a pyrrole towards the annulation reactions with pyrrole **1a** in that the major polycyclic isomer formed **28** is that with both nitrogens on the same side of the structure—presumably the result of initial predominant substitution at the 2-position of **27b**. The reverse is true of indole, which gave predominantly the pyrrolocarbazole **2**.

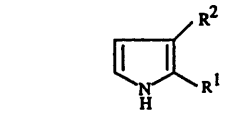
Condensation of the benzyl ester **1b** with the pyrroles **16a**, **16b**, **16c** and **16d** gave the pairs of isomers **21g** and **22d**, **21h** and **22e**, **21i** and **22f**, and **21j** and **22g**. In all these cases, the [3,2-*f*] isomer was formed in excess of the [2,3-*f*] isomer and the 2-monosubstituted intermediates **14c**, **14d**, **14e** and **14f** were isolated.

For the more reactive pyrroles **16a** and **16b**, the 2,3-bis(pyrrolylmethyl) substituted products **18c** and **18d** were formed as the major products.

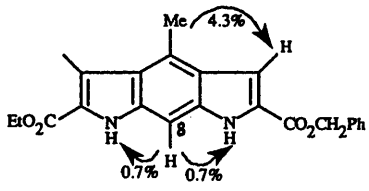
Having shown that the pyrrolyl unit **1a** could condense with a variety of 2-mono- and 2,3-di-substituted pyrrole substrates, we attempted to synthesise the 2,3-unsubstituted pyrrolo[3,2-*f*]-indole and [2,3-*f*] systems **21k** and **22h** respectively, since these should be precursors to a variety of new systems available *via* ring C. Attempted clay-catalysed condensation of the pyrrole **1a** with pyrrole gave no isolable products, but with *N*-methoxycarbonyl pyrrole **32** it gave, as the major product, the *N*-methoxycarbonylpyrrolo[3,2-*f*]indole **33** (24%) (Scheme 4). This isomer showed abnormal deshielding of the 8-H signal due to the proximity of the *N*-CO_2Me carbonyl group. The effect was absent in the isomer **34**, whose structure was confirmed by NOE experiments. The latter isomer was isolated in only 1% yield. The monosubstituted product **35** (6%) readily cyclised to the [3,2-*f*] isomer **33** with toluene-*p*-sulfonic acid. We also isolated the two products **36** (7.5%) and **37** (6%) resulting from condensation of the pyrrole **32** with *two* pyrrole **1a** units. The structure **36** (M^+, 521) followed from the ^1H NMR spectrum, which showed the retention of the 8-H signal at δ 8.01 and the disappearance of the 6-H doublet of **33**, together with an additional set of pyrrolylmethyl signals.

In the case of the tripyrrane **37** (M^+, 539) the ^1H NMR spectrum revealed a symmetrical substituted 2,5-dipyrrolylmethyl-*N*-carbomethoxypyrrole with a 2-proton singlet at δ 5.19 and a 4-proton singlet at δ 4.38.

Both **36** and **37** were converted to the pentacyclic pyrrolodiindole **38**, in each case in high yield, by treatment with toluene-*p*-sulfonic acid in refluxing ethanol. The ^1H NMR spectrum of the pyrrolodiindole **38** was fully in accord with its symmetrical structure; it is the first reported example of a pyrrolo[3,2-*f*; 4,5-*f*']diindole.



16a $R^1 = CO_2CH_2Ph$; $R^2 = H$
b $R^1 = CO_2Me$; $R^2 = H$
c $R^1 = CO_2Et$; $R^2 = Me$
d $R^1 = Me$; $R^2 = CO_2Et$
e $R^1 = Me$; $R^2 = CO_2Me$



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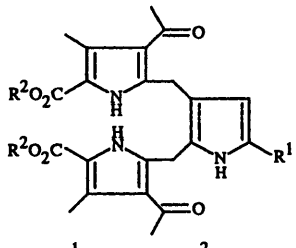
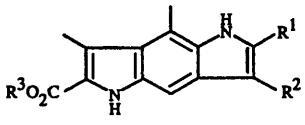
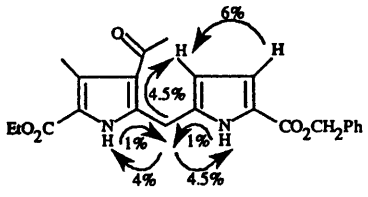


18a $R^1 = CO_2CH_2Ph$; $R^2 = Et$
b $R^1 = CO_2Me$; $R^2 = Et$
c $R^1 = CO_2CH_2Ph$; $R^2 = CH_2Ph$
d $R^1 = CO_2Me$; $R^2 = CH_2Ph$



22a $R^1 = CO_2Me$; $R^2 = H$; $R^3 = Et$
b $R^1 = CO_2Et$; $R^2 = Me$; $R^3 = Et$
c $R^1 = Me$; $R^2 = CO_2Et$; $R^3 = Et$
d $R^1 = CO_2CH_2Ph$; $R^2 = H$; $R^3 = CH_2Ph$
e $R^1 = CO_2Me$; $R^2 = H$; $R^3 = CH_2Ph$
f $R^1 = CO_2Et$; $R^2 = Me$; $R^3 = CH_2Ph$
g $R^1 = Me$; $R^2 = CO_2Et$; $R^3 = CH_2Ph$
h $R^1 = R^2 = H$; $R^3 = Et$



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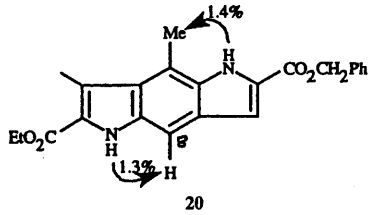

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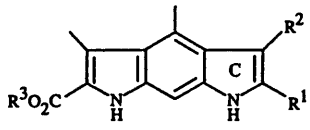
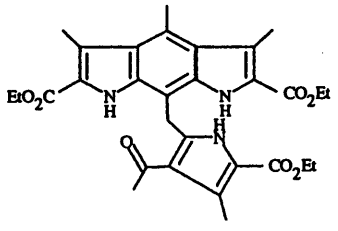


21a $R^1 = CO_2Me$; $R^2 = H$; $R^3 = Et$
b $R^1 = CO_2Et$; $R^2 = Me$; $R^3 = Et$
c $R^1 = Me$; $R^2 = CO_2Et$; $R^3 = Et$
d $R^1 = Me$; $R^2 = CO_2Me$; $R^3 = Et$
e $R^1 = Me$; $R^2 = H$; $R^3 = Et$
f $R^1 = Et$; $R^2 = H$; $R^3 = Et$
g $R^1 = CO_2CH_2Ph$; $R^2 = H$; $R^3 = CH_2Ph$
h $R^1 = CO_2Me$; $R^2 = H$; $R^3 = CH_2Ph$
i $R^1 = CO_2Et$; $R^2 = Me$; $R^3 = CH_2Ph$
j $R^1 = Me$; $R^2 = CO_2Et$; $R^3 = CH_2Ph$
k $R^1 = R^2 = H$; $R^3 = Et$



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The immediate goal, however, of the 2,3-unsubstituted pyrrolo[3,2-*f*]indole **21k** was achieved by careful regiospecific hydrolysis and decarboxylation of the *N*-methoxycarbonylpyrroloindole **33** with potassium hydroxide in THF at reflux (73% yield). The product **21k** showed in its ^1H NMR spectrum the replacement of the methyl singlet at δ 3.99 in **33** by a second NH singlet at δ 10.56. The acid **39a** was obtained in 69% yield by treatment of **33** with sodium hydroxide in aqueous methanol.

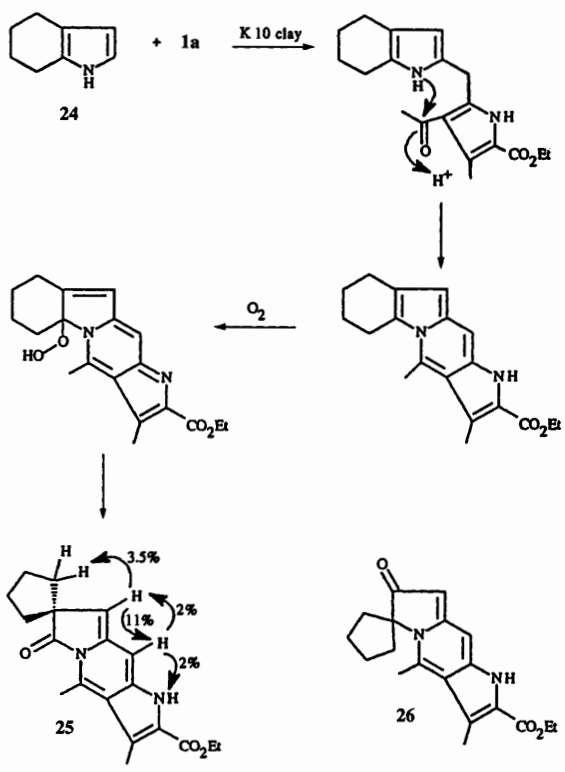
Formylation of the pyrroloindole **21k** under Vilsmeier conditions gave the 8-formyl compound **39b**. This was unexpected in the light of earlier work[9,12] on the completely unsubstituted system, which gave 3-substituted products of electrophilic substitution. Similar formylation of the *N*-methoxycarbonyl derivative **33** gave the 8-formyl-1-methoxycarbonylpyrroloindole **39c** (36.5%).

Experimental

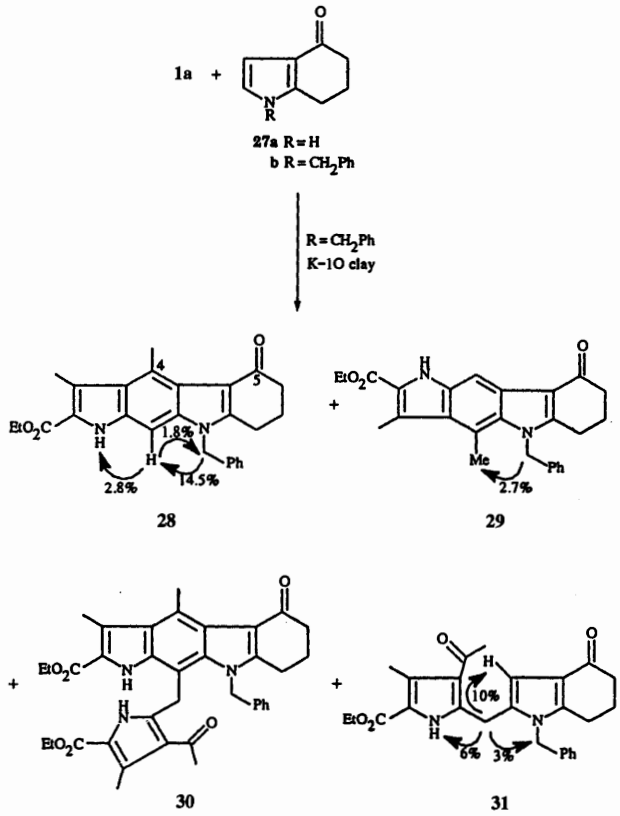
IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer; ^1H NMR spectra were obtained on a Bruker WM 360-NMR spectrometer at 360 MHz. *J* Values are given in Hz. EI mass spectra were run on a VG Platform II, Fisons Instrument. UV spectra were measured in ethanol on a Perkin-Elmer Lambda 2 UV–VIS spectrophotometer. 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 2,6-ethoxycarbonyl-8-formyl-3,5-dimethylpyrrolo-[3,2-*f*]indole 15

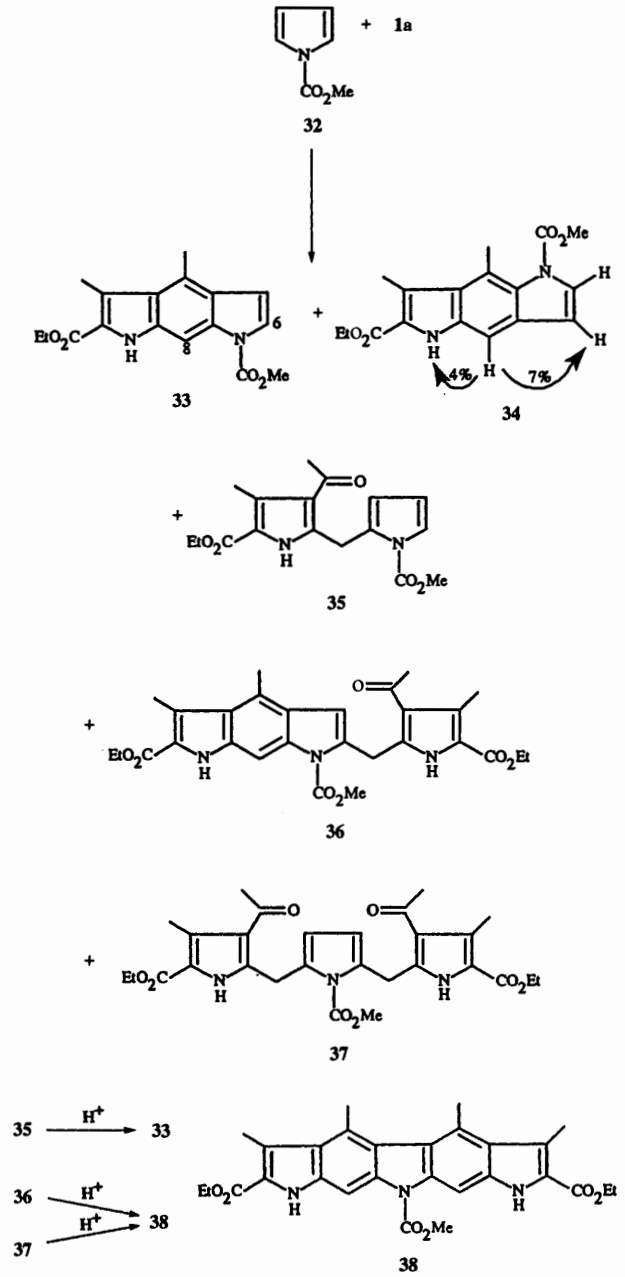
5,5′-Diethoxycarbonyl-4,4′-dimethyl-2,2′-dipyrrolylmethane[10] **14a** (0.095 g, 0.3 mmol) was added to a solution of *N*-methylformanilide (0.037 cm^3, 0.3 mmol) and phosphorus oxychloride (0.041 cm^3, 0.45 mmol) in trichloroethane (1 cm^3), and the mixture was gently heated under reflux for 2 h. After cooling, aqueous sodium acetate (0.13 g in 1.5 cm^3 water) 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 (1%; 3 × 10 cm^3) and water (3 × 10 cm^3) and then evaporated under reduced pressure to give a yellow solid. The solid was suspended in ethanol (10 cm^3) and the mixture was heated to 75 °C, filtered and washed with warm ethanol to give the *pyrrolo*[3,2-f]*indole* **15** as a yellow solid (0.036 g, 33.7%), mp 256–259 °C (Found: C, 63.8; H, 5.45; N, 7.6. $C_{19}H_{20}N_2O_5$



Scheme 2



Scheme 3



Scheme 4

requires C, 64.03; H, 5.66; N, 7.86%); δ_H([$^2H_6$]DMSO) 11.25 (2 H, br s, 2 × NH), 10.84 (1 H, s, CHO), 8.45 (1 H, s, 4-H), 4.35 (4 H, q, 2 × OCH_2CH_3), 2.62 (6 H, s, 2 × CH_3) and 1.36 (6 H, t, 2 × OCH_2CH_3); saturation of the CHO proton at δ 10.84 enhanced the signal due to 1-NH and 7-NH at δ 11.25 (4%), saturation of the singlet 4-H at δ 8.45 enhanced the signal due to 3-CH_3 and 5-CH_3 at δ 2.62 (1.5%) and saturation of the 3-CH_3 and 5-CH_3 at δ 2.62 enhanced the signal due to 4-H at δ 8.45 (13%); *m/z* 356 (100%, M^+), 327 (2), 350 (50) and 282 (18). Removal of the solvent from the filtrate gave an off-white solid which was crystallised from ethanol to yield the starting dipyrrolylmethane **14a** (0.029 g, 30.5%); δ_H($CDCl_3$) 9.03 (2 H, br s, 2 × NH), 5.90 (2 H, d, *J* 2.8, 3-H and 3′-H), 4.28 (4 H, q, 2 × OCH_2CH_3), 3.90 (2 H, s, CH_2), 2.31 (6 H, s, 2 × CH_3) and 1.34 (6 H, t, 2 × OCH_2CH_3).

Synthesis of the pyrrolo[2,3-*f*]indoles 20, 22a–g and 34 and pyrrolo[3,2-*f*]indoles 19, 21a–j and 33

General procedure. A solution of the 5-acetoxymethyl-4-acetylpyrrole (1.5 mmol) and the 2,3-unsubstituted pyrrole (1.5

mmol) in 1,2-dichloroethane (15 cm^3) was heated under reflux and stirred with Montmorillonite clay (1.5 g) for 18–24 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, eluted with ethyl acetate in dichloromethane, gave the corresponding pyrrolo[2,3-*f*]-indoles, pyrrolo[3,2-*f*]indoles, 2-(pyrrolylmethyl)pyrroles and 2,3-(dipyrrolylmethyl)pyrroles.

6-Benzoxycarbonyl-2-ethoxycarbonyl-3,4-dimethylpyrrolo-[2,3-*f*]indole 20 and 6-benzoxycarbonyl-2-ethoxycarbonyl-3,4-dimethylpyrrolo[3,2-*f*]indole 19. These compounds were obtained from benzyl pyrrole-2-carboxylate **16a** and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Chromatographic separation yielded the starting pyrrole **16a** (0.076 g, 24.8%), the [2,3-f] *isomer* **20** as a yellow solid (0.021 g, 3.6%), mp 218–220 °C (Found: C, 70.9; H, 5.9; N, 7.3. $C_{23}H_{22}N_2O_4$ requires C, 70.75; H, 5.68; N, 7.18%); δ_H([$^2H_6$]DMSO) 11.18 (1 H, s, 5-NH), 10.97 (1 H, s, 1-NH), 7.52 (2 H, d, *J* 7, *o*-ArH), 7.36–7.48 (4 H, m, *m*- and *p*-ArH and 8-H), 7.23 (1 H, d, *J* 1.5, 7-H), 5.41 (2 H, s, OCH_2Ph), 4.35 (2 H, q, OCH_2CH_3), 2.93 (3 H, s, 4-CH_3), 2.85 (3 H, s, 3-CH_3) and 1.38 (3 H, t, OCH_2CH_3); saturation of the 5-NH proton at δ 11.18 enhanced the signal due to 4-CH_3 at δ 2.93 (1.4%) and saturation of the 1-NH at δ 10.97 enhanced the signal due to 8-H at δ 7.46 (1.3%); *m*/*z* 390 (100%, M^+), 344 (71), 282 (59), 236 (60), 228 (27), 209 (21) and 91 (78); ν_{max}(Nujol)/cm^{-1} 3400, 3350, 1725 and 1680; and the [3,2-f] *isomer* **19** as a yellow solid (0.032 g, 5.5%), mp 179–182 °C; δ_H([$^2H_6$]DMSO) 11.36 (1 H, s, 7-NH), 10.95 (1 H, s, 1-NH), 7.52 (2 H, d, *J* 7, *o*-ArH), 7.48–7.37 (3 H, m, *m*- and *p*-ArH), 7.34 (1 H, br s, 5-H), 7.19 (1 H, s, 8-H), 5.39 (2 H, s, CH_2Ph), 4.35 (2 H, q, OCH_2CH_3), 2.89 (3 H, s, 4-CH_3), 2.84 (3 H, s, 3-CH_3) and 1.37 (3 H, t, OCH_2CH_3); saturation of the 8-H proton at δ 7.19 enhanced the signals due to 7-NH at δ 11.36 (0.7%) and 1-NH at δ 10.95 (0.7%) and saturation of the 4-CH_3 at δ 2.89 enhanced the signal due to 5-H at δ 7.34 (4.3%); *m*/*z* 390 (4%, M^+), 344 (7), 306 (5), 282 (5), 236 (6), 209 (15), 154 (18), 127 (19) and 91 (100) (Found: M^+, 390.1580. $C_{23}H_{22}N_2O_4$ requires *M*, 390.1579). Also obtained were the 2-(*pyrrolylmethyl*)*pyrrole* **17** as off-white crystals from dichloromethane–light petroleum (0.151 g, 24.7%), mp 130–132 °C; δ_H([$^2H_6$]DMSO) 11.96 (1 H, s, 1-NH), 11.65 (1 H, s, 1′-NH), 7.45–7.31 (5 H, m, ArH), 6.70 (1 H, m, 4′-H), 5.75 (1 H, dd, *J* 4 and 2.6, 3′-H), 5.27 (2 H, s, CH_2Ph), 4.28 (2 H, q, OCH_2CH_3), 4.20 (2 H, s, 2-CH_2), 2.50 (concealed by DMSO, $COCH_3$), 2.34 (3 H, s, 4′-CH_3) and 1.31 (3 H, t, OCH_2CH_3); saturation of the 2-CH_2 singlet at δ 4.20 enhanced the signals due to 3′-H at δ 5.75 (4.5%), 1-NH at δ 11.96 (4.5%) and 1′-NH at δ 11.65 (4%); *m*/*z* 408 (14%, M^+), 317 (100), 271 (97) and 91 (47) (Found: M + NH_4^+, 426.2029. $C_{23}H_{24}N_2O_5$ + NH_4 requires 426.2028); and the 2,3-*di*(*pyrrolylmethyl*)*pyrrole* **18a** as colourless crystals from benzene–light petroleum (0.128 g, 27.7%), mp 164–166 °C (Found: C, 66.5; H, 6.2; N, 6.7. $C_{34}H_{37}N_3O_8$ requires C, 66.33; H, 6.06; N, 6.83%); δ_H($CDCl_3$) 10.50 (1 H, br s, 1-NH), 9.10 (2 H, br s, 2 × NH), 7.42–7.20 (5 H, m, ArH), 6.65 (1 H, d, *J* 2.5, 4-H), 5.23 (2 H, s, CH_2Ph), 4.32 (2 H, q, OCH_2CH_3), 4.13 (2 H, s, 2-CH_2), 4.08 (2 H, s, 3-CH_2), 2.60 and 2.59 (2 × 3 H, s, 2 × CH_3), 2.55 and 2.54 (2 × 3 H, 2 s, 2 × $COCH_3$), 1.36 (3 H, t, OCH_2CH_3) and 1.35 (3 H, t, OCH_2CH_3); *m*/*z* (%) 408 (47), 317 (77), 271 (67) and 91 (100); Electrospray 616 (4, M + H), 204 (100, M + $3H^+$/3).

Cyclisation of the 2-(*pyrrolylmethyl*)*pyrrole* **17**.—A solution of the 2-(pyrrolylmethyl)pyrrole **17** (0.083 g, 0.2 mmol) in 1,2-dichloroethane (5 cm^3) was heated under reflux and stirred with Montmorillonite clay (0.25 g) for 18 h. The reaction was followed 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 an oil. Chromatographic separation of the oil eluting with (0–15%) ethyl acetate in dichloromethane yielded the *pyrrolo*[3,2-f]-*indole* **19** as a yellow solid (0.028 g, 36%) which was identical in all respects to the pyrrolo[3,2-*f*]indole **19** of the previous experiment.

2-Ethoxycarbonyl-6-methoxycarbonyl-3,4-dimethylpyrrolo-[2,3-*f*]indole 22a and 2-ethoxycarbonyl-6-methoxycarbonyl-3,4-dimethylpyrrolo[3,2-*f*]indole 21a. These compounds were obtained from methyl pyrrole-2-carboxylate **16b** and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Chromatographic separation gave the [2,3-f] *isomer* **22a** as yellow crystals from dichloromethane–light petroleum (0.026 g, 5.6%), mp 245–248 °C; δ_H([$^2H_6$]DMSO) 11.16 (1 H, s, 5-NH), 11.00 (1 H, s, 1-NH), 7.45 (1 H, s, 8-H), 7.20 (1 H, s, 7-H), 4.37 (2 H, q, OCH_2CH_3), 3.91 (3 H, s, OCH_3), 2.95 (3 H, s, 3-CH_3), 2.88 (3 H, s, 4-CH_3) and 1.37 (3 H, t, OCH_2CH_3); saturation of the 1-NH at δ 11.00 enhanced the signal due to 8-H at δ 7.45 (3.9%) and saturation of the 5-NH at δ 11.16 enhanced the signal due to 4-CH_3 at δ 2.88 (2%); *m*/*z* 314 (81%, M^+), 282 (55), 268 (89), 236 (100), 208 (56), 179 (50), 153 (48), 118 (56), 90 (82) and 77 (72) (Found: M^+, 314.1267. $C_{17}H_{18}N_2O_4$ requires *M*, 314.1266); and the [3,2-f] *isomer* **21a** as yellow crystals from dichloromethane–light petroleum (0.052 g, 11.0%), mp 242–245 °C; δ_H([$^2H_6$]DMSO) 11.36 (1 H, s, 7-NH), 10.92 (1 H, s, 1-NH), 7.33 (1 H, s, 8-H), 7.24 (1 H, s, 5-H), 4.36 (2 H, q, OCH_2CH_3), 3.89 (3 H, s, OCH_3), 2.92 (3 H, s, 3-CH_3), 2.87 (3 H, s, 4-CH_3) and 1.37 (3 H, t, OCH_2CH_3); *m*/*z* 314 (60%, M^+), 282 (50), 268 (62), 236 (60), 208 (60), 179 (55), 165 (34), 152 (52), 134 (48), 127 (56) and 118 (100) (Found: M^+, 314.1267. $C_{17}H_{18}N_2O_4$ requires *M*, 314.1266). Further elution gave the 2-(*pyrrolylmethyl*)*pyrrole* **14b** as off-white crystals from dichloromethane–light petroleum (0.080 g, 16.1%), mp 160–162 °C (Found: C, 61.6; H, 6.3; N, 8.5. $C_{17}H_{20}N_2O_5$ requires C, 61.43; H, 6.07; N, 8.43%); δ_H($CDCl_3$) 10.40 (1 H, s, 1-NH), 9.78 (1 H, s, 1′-NH), 6.79 (1 H, dd, *J* 4 and 2.5, 4′-H), 6.09 (1 H, dd, *J* 4 and 2.5, 3′-H), 4.30 (2 H, q, OCH_2CH_3), 4.22 (2 H, s, 2-CH_2), 3.80 (3 H, s, OCH_3), 2.58 and 2.50 (2 × 3 H, s, $COCH_3$ and 4-CH_3) and 1.33 (3 H, t, OCH_2CH_3); *m*/*z* 332 (6%, M^+), 300 (55), 271 (54), 254 (66), 227 (61), 211 (55), 183 (65), 155 (59), 128 (66), 106 (85), 94 (45), 78 (66) and 43 (100); and the 2,3-*di*-(*pyrrolylmethyl*)*pyrrole* **18b** as off-white crystals from benzene–light petroleum (0.166 g, 41.1%), mp 203–206 °C (Found: C, 62.2; H, 6.2; N, 7.7. $C_{28}H_{33}N_3O_8$ requires C, 62.32; H, 6.16; N, 7.79%); δ_H($CDCl_3$) 11.08 (1 H, s, 1-NH), 9.42 (1 H, s, 2-pyr-NH), 9.13 (1 H, s, 3-pyr-NH), 6.63 (1 H, d, *J* 2, 4-H), 4.33 (2 H, q, OCH_2CH_3), 4.32 (2 H, q, OCH_2CH_3), 4.13 (2 H, s, 2-CH_2), 4.11 (2 H, s, 3-CH_2), 3.77 (3 H, s, OCH_3), 2.61 and 2.59 (2 × 3 H, 2 s, 2 × $COCH_3$), 2.57 (6 H, s, 2 × CH_3), 1.37 (3 H, t, OCH_2CH_3) and 1.36 (3 H, t, OCH_2CH_3); *m*/*z* 539 (2%, M^+), 331 (28), 285 (18), 253 (6), 162 (12) and 43 (100).

2,6-Diethoxycarbonyl-3,4,7-trimethylpyrrolo[2,3-*f*]indole 22b and 2,6-diethoxycarbonyl-3,4,5-trimethylpyrrolo[3,2-*f*]indole 21b. These compounds were obtained from ethyl 3-methylpyrrole-2-carboxylate[13] **16c** and the 5-acetoxymethyl-4-acetylpyrrole **1a**. The chromatographic separation yielded the *pyrrolo*[2,3-f]*indole* **22b** as a yellow solid (0.015 g, 2.9%), mp 260–262 °C (Found: C, 66.45; H, 6.5; N, 7.9. $C_{19}H_{22}N_2O_4$ requires C, 66.65; H, 6.48; N, 8.18%); δ_H([$^2H_6$]DMSO) 11.00 (1 H, s, 5-NH), 10.57 (1 H, s, 1-NH), 7.38 (1 H, s, 8-H), 4.38 (2 H, q, OCH_2CH_3), 4.36 (2 H, q, OCH_2CH_3), 2.91 and 2.86 (2 × 3 H, s, 4-CH_3 and 3-CH_3), 2.34 (3 H, s, 7-CH_3), 1.40 (3 H, t, OCH_2CH_3) and 1.38 (3 H, t, OCH_2CH_3); *m*/*z* (CI) 343 (25%, M^+ + H), 329 (4), 297 (8), 111 (20), 99 (32), 87 (39), 71 (36) and 47 (100); the 8-(*pyrrolylmethyl*)*pyrrolo*[3,2-f]*indole* **23** as a yellow solid (0.043 g, 10.4%), mp 221–224 °C (Found: C, 65.7; H, 6.6; N, 7.6. $C_{30}H_{35}N_3O_7$ requires C, 65.56; H, 6.42; N, 7.65%); δ_H($CDCl_3$) 9.20 (2 H, br s, 1-NH and 7-NH), 8.92 (1 H, br s, pyr-NH), 4.54 (2 H, s, 8-CH_2), 4.36 (4 H, q, 2- and 6-$CO_2CH_2CH_3$), 4.18 (2 H, q, pyr-$CO_2CH_2CH_3$), 3.14 (3 H, s, 4-CH_3), 2.92 (6 H, s, 3-CH_3 and 5-CH_3), 2.62 and 2.56 (2 × 3 H,

2 s, $COCH_3$ and pyr-CH_3), 1.41 (6 H, t, 2- and 6-$CO_2CH_2CH_3$) and 1.24 (3 H, t, pyr-$CO_2CH_2CH_3$); *m/z* 549 (3%, M^+), 503 (3), 457 (2), 411 (2), 369 (2), 207 (3), 126 (5) and 43 (100); and the *pyrrolo*[3,2-f]*indole* **21b** as a yellow solid (0.035 g, 6.8%), mp 285–288 °C (Found: C, 66.9; H, 6.5; N, 8.25. $C_{19}H_{22}N_2O_4$ requires C, 66.65; H, 6.48; N, 8.18%); δ_H([$^2H_6$]DMSO) 11.21 (2 H, s, 2 × NH), 7.47 (1 H, s, 8-H), 4.30 (4 H, q, 2 × OCH_2CH_3), 3.05 (3 H, s, 4-CH_3), 2.80 (6 H, s, 3-CH_3 and 5-CH_3) and 1.31 (6 H, t, 2 × OCH_2CH_3).

2,7-Diethoxycarbonyl-3,4,6-trimethylpyrrolo[2,3-*f*]indole 22c and 2,5-diethoxycarbonyl-3,4,6-trimethylpyrrolo[3,2-*f*]indole 21c. These compounds were obtained from ethyl 2-methylpyrrole-3-carboxylate **16d**[14,15] and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Chromatographic separation yielded the starting pyrrole **16d** (0.067 g, 29.2%), the [2,3-*f*] isomer **22c** as a colourless solid (0.032 g, 6.2%), mp 269 °C (decomp.); δ_H([$^2H_6$]DMSO) 11.34 (1 H, s, 5-NH), 11.00 (1 H, s, 1-NH), 7.80 (1 H, s, 8-H), 4.33 (2 H, q, 7-OCH_2CH_3), 4.26 (2 H, q, 2-OCH_2CH_3), 2.85 (6 H, s, 3-CH_3 and 4-CH_3), 2.69 (3 H, s, 6-CH_3), 1.39 (3 H, t, 7-OCH_2CH_3) and 1.37 (3 H, t, 2-OCH_2CH_3); saturation of the singlet 8-H at δ 7.80 enhanced the signal due to 1-NH at δ 11.00 (2.3%); *m/z* 342 (75%, M^+), 296 (100), 268 (6), 223 (7) and 195 (5) (Found: M^+, 342.1580. $C_{19}H_{22}N_2O_4$ requires *M*, 342.1579); λ_{max}(EtOH)/nm (log ε_{max}/dm^3 mol^{-1} cm^{-1}) 378 (3.56), 365sh (3.53), 329 (3.83), 304 (3.99) and 259 (3.74); the [3,2-f] *isomer* **21c** as a colourless solid (0.072 g, 14%), mp 216–216.5 °C (Found: C, 66.8; H, 6.7; N, 8.2. $C_{19}H_{22}N_2O_4$ requires C, 66.65; H, 6.48; N, 8.18%); δ_H([$^2H_6$]DMSO) 11.30 (1 H, s, 7-NH), 10.91 (1 H, s, 1-NH), 7.12 (1 H, s, 8-H), 4.35 (2 H, q, 5-OCH_2CH_3), 4.28 (2 H, q, 2-OCH_2CH_3), 2.90 and 2.87 (2 × 3 H, 2 s, 4-CH_3 and 3-CH_3), 2.54 (3 H, s, 6-CH_3), 1.36 (3 H, t, OCH_2CH_3) and 1.34 (3 H, t, OCH_2CH_3); saturation of the 8-H proton at δ 7.12 enhanced the signals due to 7-NH at δ 11.30 (2.4%) and 1-NH at δ 10.91 (1.8%), *m/z* (%) 342 (64, M^+), 296 (100), 250 (5) and 149 (9); λ_{max}(EtOH)/nm (log ε_{max}/dm^3 mol^{-1} cm^{-1}) 340 (4.10), 327 (4.53), 270 (4.46); and the starting pyrrole **1a** (0.043 g, 10.8%).

2-Ethoxycarbonyl-3,4,6-trimethylpyrrolo[3,2-*f*]indole 21e and 2-ethoxycarbonyl-5-methoxycarbonyl-3,4,6-trimethylpyrrolo[3,2-*f*]indole 21d. These compounds were obtained from methyl 2-methylpyrrole-3-carboxylate **16e** and the 5-acetoxymethyl-4-acetylpyrrole **1a**. Chromatographic separation gave the *pyrrolo*[3,2-f]*indole* **21e** as a pale yellow solid (0.007 g, 1.7%), mp 213–216 °C (decomp.); δ_H([$^2H_6$]DMSO) 10.70 (1 H, s, 1-NH), 10.41 (1 H, s, 7-NH), 7.03 (1 H, s, 8-H), 6.14 (1 H, s, 5-H), 4.33 (2 H, q, OCH_2CH_3), 2.85 (3 H, s, 3-CH_3), 2.78 (3 H, s, 4-CH_3), 2.37 (3 H, s, 6-CH_3) and 1.35 (3 H, t, OCH_2CH_3); saturation of the 8-H proton at δ 7.03 enhanced the signals due to 1-NH at δ 10.71 (3.5%) and 7-H at δ 10.41 (3%) and saturation of the 5-H proton at δ 6.14 enhanced the signals due to 4-CH_3 at δ 2.78 (2%) and 6-CH_3 at δ 2.37 (0.6%); *m/z* 270 (49%, M^+), 224 (100) and 106 (17) (Found: M^+, 270.1387. $C_{16}H_{18}N_2O_2$ requires *M*, 270.1368); and starting pyrrole **16e** (0.0625 g, 30%). Further elution gave the *pyrrolo*[3,2-f]*indole* **21d** as a colourless solid (0.038 g, 7.8%), mp 247–250 °C (Found: C, 66.1; H, 6.4; N, 8.5. $C_{18}H_{20}N_2O_4$ requires C, 65.84; H, 6.14; N, 8.53%); δ_H([$^2H_6$]DMSO) 11.33 (1 H, s, 7-NH), 10.91 (1 H, s, 1-NH), 7.21 (1 H, s, 8-H), 4.35 (2 H, q, OCH_2CH_3), 3.78 (3 H, s, OCH_3), 2.88 and 2.87 (2 × 3 H, 2 s, 4-CH_3 and 3-CH_3), 2.53 (concealed by DMSO, 6-CH_3) and 1.37 (3 H, t, OCH_2CH_3); *m/z* 328 (64%, M^+), 297 (5), 282 (100), 250 (6), 221 (6) and 194 (17); and the starting pyrrole **1a** (0.021 g, 5.3%).

2-Ethoxycarbonyl-6-ethyl-3,4-dimethylpyrrolo[3,2-*f*]indole 21f. This compound was obtained from 2-ethylpyrrole and the 5-acetoxymethyl-4-acetylpyrrole **1a**, as a yellow solid (0.045 g, 10.6%), mp 140–145 °C (decomp.); δ_H($CDCl_3$) 8.30 (1 H, br s, 1-NH), 7.60 (1 H, br s, 7-NH), 7.00 (1 H, s, 8-H), 6.28 (1 H, s, 5-H), 4.00 (2 H, q, OCH_2CH_3), 2.92 and 2.90 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3), 2.78 (2 H, q, CH_2CH_3), 1.42 (3 H, t, OCH_2CH_3) and 1.36 (3 H, t, CH_2CH_3); *m/z* 284 (95%, M^+), 254 (12), 238 (100), 210 (25), 195 (71), 181 (22), 168 (21), 158 (18) and 115 (25) (Found: M^+, 284.1525. $C_{17}H_{20}N_2O_2$ requires *M*, 284.1525); also obtained was the starting pyrrole **1a** (0.253 g, 63.2%).

2,6-Dibenzoxycarbonyl-3,4-dimethylpyrrolo[2,3-*f*]indole 22d and 2,6-dibenzoxycarbonyl-3,4-dimethylpyrrolo[3,2-*f*]indole 21g. These compounds were obtained from benzyl pyrrole-2-carboxylate **16a** and the 5-acetoxymethyl-4-acetylpyrrole **1b**. The chromatographic separation gave the [2,3-f] *isomer* **22d** as yellow crystals from ethyl acetate–light petroleum (0.029 g, 4.2%), mp 210–212 °C (Found: C, 73.5; H, 5.3; N, 6.1. $C_{28}H_{24}N_2O_4$ requires C, 73.62; H, 5.49; N, 6.36%); δ_H([$^2H_6$]DMSO) 11.17 (1 H, s, 5-NH), 11.02 (1 H, s, 1-NH), 7.57–7.34 (11 H, m, 2 × ArH and 8-H), 7.23 (1 H, d, *J* 1.5, 7-H), 5.42 and 5.40 (2 × 2 H, 2 s, 2 × CH_2Ph), 2.93 and 2.87 (2 × 3 H, s, 4-CH_3 and 3-CH_3); *m/z* 452 (68%, M^+), 344 (58), 236 (17) and 91 (100); and the [3,2-f] *isomer* **21g** as yellow crystals from dichloromethane–light petroleum (0.054 g, 8.0%), mp 184–186 °C (Found: C, 73.7; H, 5.6; N, 6.3. $C_{28}H_{24}N_2O_4$ requires C, 73.62; H, 5.49; N, 6.36%); δ_H([$^2H_6$]DMSO) 11.36 (1 H, s, 7-NH), 10.99 (1 H, s, 1-NH), 7.52 (4 H, d, *J* 7, *o*-ArH), 7.46–7.37 (7 H, m, *m*- and *p*-ArH and 8-H), 7.23 (1 H, br s, 5-H), 5.40 (4 H, s, 2 × CH_2Ph), 2.91 and 2.86 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3); *m/z* 452 (55%, M^+), 344 (59), 236 (10) and 91 (100). Next to be eluted was the 2-*(pyrrolylmethyl)pyrrole* **14c** as pale yellow crystals from dichloromethane–light petroleum (0.156 g, 22.1%), mp 141–143 °C (Found: C, 71.6; H, 5.6; N, 5.8. $C_{28}H_{26}N_2O_5$ requires C, 71.47; H, 5.57; N, 5.95%); δ_H($CDCl_3$) 10.22 (1 H, s, 1-NH), 9.25 (1 H, s, 1′-NH), 7.48–7.28 (10 H, m, ArH), 6.83 (1 H, dd, *J* 2.5 and 4, 4′-H), 6.05 (1 H, dd, *J* 2.5 and 4, 3′-H), 5.28 and 5.26 (2 × 2 H, 2 s, 2 × CH_2Ph), 4.13 (2 H, s, 2-CH_2), 2.58 and 2.49 (2 × 3 H, 2 s, $COCH_3$ and 4-CH_3); *m/z* 470 (6%, M^+), 379 (45), 271 (32), 91 (100), 65 (61) and 43 (38); similarly obtained was the 2,3-*di(pyrrolylmethyl)pyrrole* **18c** as an oil (0.139 g, 25.1%); δ_H($CDCl_3$) 11.18 (1 H, s, 1-NH), 10.46 (1 H, s, 2-pyr-NH), 9.31 (1 H, s, 3-pyr-NH), 7.42–7.27 (15 H, m, ArH), 6.61 (1 H, d, *J* 2, 4-H), 5.31, 5.29 and 5.22 (3 × 2 H, 2 s, 3 × CH_2Ph), 4.13 (2 H, s, 2-CH_2), 4.05 (2 H, s, 3-CH_2), 2.57 and 2.55 (2 × 3 H, 2 s, 2 × $COCH_3$), 2.51 and 2.37 (2 × 3 H, 2 s, 2 × CH_3); saturation of the singlet 2-CH_2 at δ 4.13 enhanced the signals due to 1-NH at δ 11.18 (10%) and 2-pyr-NH at δ 10.46 (8%) and saturation of the 3-CH_3 at δ 4.05 enhanced the signals due to 4-H at δ 6.61 (8%) and 3-pyr NH at δ 9.31 (10%); *m/z* 739 (2%, M^+), 108 (95), 91 (72) and 79 (100) (Found: M^+, 739.2890. $C_{44}H_{41}N_3O_8$ requires *M*, 739.2893).

2-Benzoxycarbonyl-6-methoxycarbonyl-3,4-dimethylpyrrolo-[2,3-*f*]indole 22e and 2-benzoxycarbonyl-6-methoxycarbonylpyrrolo[3,2-*f*]indole 21h. These compounds were obtained from methyl pyrrole-2-carboxylate **16b** and the 5-acetoxymethyl-4-acetylpyrrole **1b**. The chromatographic separation yielded the starting pyrrole **16b** (0.038 g, 20.4%), the [2,3-f] *isomer* **22e** as a yellow solid (0.044 g, 7.8%), mp 262–265 °C (Found: C, 70.0; H, 5.4; N, 7.3. $C_{22}H_{20}N_2O_4$ requires C, 70.20; H, 5.36; N, 7.44%); δ_H([$^2H_6$]DMSO) 11.09 (1 H, s, 5-NH), 10.98 (1 H, s, 1-NH), 7.49 (2 H, d, *J* 7.5, *o*-ArH), 7.42–7.34 (4 H, m, *m*- and *p*-ArH and 8-H), 7.14 (1 H, d, *J* 2, 7-H), 5.37 (2 H, s, CH_2Ph), 3.86 (3 H, s, OCH_3), 2.90 and 2.84 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3); *m/z* 376 (22%, M^+), 344 (8), 268 (26), 236 (18), 209 (12), 127 (12) and 91 (100); and the [3,2-f] *isomer* **21h** as a yellow solid (0.104 g, 18.4%), mp 225–227 °C; δ_H([$^2H_6$]DMSO) 11.32 (1 H, s, 1-NH), 10.94 (1 H, s, 7-NH), 7.49 (2 H, d, *J* 7.5, *o*-ArH), 7.48–7.28 (3 H, m, *m*- and *p*-ArH), 7.28 (1 H, d, *J* 1, 5-H), 7.18 (1 H, s, 8-H), 5.36 (2 H, s, CH_2Ph), 3.84 (3 H, s, OCH_3), 2.86 and 2.83 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3); *m/z* 376 (18%, M^+), 268 (30), 236 (14), 209 (11), 91 (100) and 77 (13) (Found: M^+, 376.1433. $C_{22}H_{20}N_2O_4$ requires *M*, 376.1423). Further elution gave the starting pyrrole **1b** (0.017 g, 3.5%), the 2-(*pyrrolylmethyl*)-

pyrrole **14d** as an off-white solid (0.086 g, 14.6%), mp 163–165 °C; $\delta_H(CDCl_3)$ 10.24 (1 H, br s, 1-NH), 9.47 (1 H, br s, 1-NH), 7.38–7.28 (5 H, m, ArH), 6.78 (1 H, m, 4'-H), 6.06 (1 H, m, 3'-H), 5.27 (2 H, s, CH_2Ph), 4.16 (2 H, s, 2-CH_2), 3.79 (3 H, s, OCH_3), 2.59 and 2.51 (2 × 3 H, 2 s, $COCH_3$ and 4-CH_3); *m/z* 394 (72%, M^+), 379 (12), 362 (20), 303 (60), 285 (46), 271 (40), 254 (42), 227 (23), 211 (22), 155 (25), 128 (22), 106 (22), 91 (100), 71 (43) and 65 (63) (Found: M^+, 394.1529. $C_{22}H_{22}N_2O_5$ requires *M*, 394.1529); and the 2,3-*di*(*pyrrolylmethyl*)*pyrrole* **18d** as a colourless solid (0.063 g, 12.6%), mp 185–188 °C; $\delta_H(CDCl_3)$ 11.13 (1 H, br s, 1-NH), 10.41 (1 H, br s, 2-pyr-NH), 9.06 (1 H, br s, 3-pyr-NH), 7.41–7.31 (10 H, m, ArH), 6.60 (1 H, d, *J* 2.7, 4-H), 5.32 (4 H, s, 2 × CH_2Ph), 4.13 (2 H, s, 2-CH_2), 4.08 (2 H, s, 3-CH_2), 3.59 (3 H, s, OCH_3), 2.58 and 2.56 (2 × 3 H, 2 s, 2 × $COCH_3$), 2.55 and 2.40 (2 × 3 H, 2 s, 2 × CH_3); *m/z* (FAB) 664 (M + H) [Found: M + H (FAB) 664.2630. $C_{38}H_{37}N_3O_5$ + H requires 664.2659].

2-Benzoxycarbonyl-6-ethoxycarbonyl-3,4,7-trimethylpyrrolo[2,3-*f*]indole 22f and 2-benzoxycarbonyl-6-ethoxycarbonyl-3,4,5-trimethylpyrrolo[3,2-*f*]indole 21i. These compounds were obtained from ethyl 3-methylpyrrole-2-carboxylate **16c** and the 5-acetoxymethyl-4-acetylpyrrole **1b**. Chromatographic separation gave the starting pyrrole **16c** (0.043 g, 18.9%), the [2,3-f] *isomer* **22f** as yellow crystals from benzene–light petroleum (0.041 g, 7.7%), mp 232–235 °C (Found: C, 71.0; H, 6.1; N, 6.8. $C_{24}H_{24}N_2O_4$ requires C, 71.27; H, 5.98; N, 6.93%); δ_H([$^2H_6$]DMSO) 11.00 (1 H, s, 1-NH), 10.54 (1 H, s, 5-NH), 7.50 (2 H, d, *J* 7, *o*-ArH), 7.43–7.32 (4 H, m, *m*- and *p*-ArH and 8-H), 5.38 (2 H, s, CH_2Ph), 4.34 (2 H, q, OCH_2CH_3), 2.88 and 2.84 (2 × 3 H, 2 s, 4-CH_3 and 3-CH_3), 2.52 (3 H, s, 7-CH_3) and 1.36 (3 H, t, OCH_2CH_3); *m/z* 404 (65%, M^+), 358 (33), 296 (34), 250 (27), 223 (17), 193 (12), 91 (100), 71 (13) and 65 (32); and the [3,2-f] *isomer* **21i** as a yellow solid (0.171 g, 28.9%), mp 181–184 °C (Found: C, 71.4; H, 6.1; N, 6.8. $C_{24}H_{24}N_2O_4$ requires C, 71.27; H, 5.98; N, 6.93%); δ_H([$^2H_6$]DMSO) 10.87 (1 H, s, 1-NH), 10.82 (1 H, s, 7-NH), 7.49 (2 H, d, *J* 7, *o*-ArH), 7.42–7.32 (3 H, m, *m*- and *p*-ArH), 7.14 (1 H, s, 8-H), 5.36 (2 H, s, CH_2Ph), 4.30 (2 H, q, OCH_2CH_3), 3.05 (3 H, s, 4-CH_3), 2.85 and 2.84 (2 × 3 H, 2 s, 3-CH_3 and 5-CH_3) and 1.33 (3 H, t, OCH_2CH_3); *m/z* 404 (68%, M^+), 358 (37), 296 (40), 250 (23), 223 (12), 193 (15), 91 (100), 71 (18) and 65 (43). Further elution gave the starting pyrrole **1b** (0.018 g, 3.7%) and the 2,3-*di*(*pyrrolylmethyl*)*pyrrole* **14e** as an off-white solid (0.066 g, 12.8%), mp 86–89 °C; $\delta_H(CDCl_3)$ 10.24 (1 H, s, 1-NH), 10.19 (1 H, s, 2-pyr-NH), 8.66 (1 H, s, 3-pyr-NH), 7.40–7.30 (10 H, m, ArH), 5.28 and 5.24 (2 × 2 H, 2 s, CH_2Ph), 4.28 (2 H, q, OCH_2CH_3), 4.09 (2 H, s, 2-CH_2), 4.04 (2 H, s, 3-CH_2), 2.57 and 2.53 (2 × 3 H, 2 s, 2 × $COCH_3$), 2.47 (6 H, s, 2 × 4'-CH_3), 2.24 (3 H, s, 4-CH_3) and 1.34 (3 H, t, OCH_2CH_3).

2-Benzoxycarbonyl-7-ethoxycarbonyl-3,4,6-trimethylpyrrole[2,3-*f*]indole 22g and 2-benzoxycarbonyl-5-ethoxycarbonyl-3,4,6-trimethylpyrrolo[3,2-*f*]indole 21j. These compounds were obtained from ethyl 2-methylpyrrole-2-carboxylate **16d** and the 5-acetoxymethyl-4-acetylpyrrole **1b**. Chromatographic separation gave the starting pyrrole **16d** (0.046 g, 20.0%), the [2,3-f] *isomer* **22g** as a yellow solid (0.014 g, 2.3%), mp 114–120 °C (Found: C, 71.0; H, 5.7; N, 6.7. $C_{24}H_{24}N_2O_4$ requires C, 71.27; H, 5.98; N, 6.93%); δ_H([$^2H_6$]DMSO) 11.31 (1 H, s, 1-NH), 11.04 (1 H, s, 5-NH), 7.78 (1 H, s, 8-H), 7.51–7.33 (5 H, m, ArH), 5.36 (2 H, s, CH_2Ph), 4.25 (2 H, q, OCH_2CH_3), 2.83 and 2.82 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3), 2.67 (3 H, s, 6-CH_3) and 1.35 (3 H, t, OCH_2CH_3); *m/z* 404 (22%, M^+), 359 (3), 296 (13) and 91 (100); and the [3,2-f] *isomer* **21j** as a yellow solid (0.171 g, 28.2%), mp 199–202 °C (Found: C, 71.5; H, 6.2; N, 6.7. $C_{24}H_{24}N_2O_2$ requires C, 71.27; H, 5.98; N, 6.93%); δ_H([$^2H_6$]DMSO) 11.27 (1 H, s, 1-NH), 10.92 (1 H, s, 7-NH), 7.51–7.32 (5 H, m, ArH), 7.10 (1 H, s, 8-H), 5.36 (2 H, s, CH_2Ph), 4.24 (2 H, q, OCH_2CH_3), 2.86 and 2.85 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3), 2.58 (3 H, s, 6-CH_3) and 1.31 (3 H, t, OCH_2CH_3); *m/z* 404 (68%, M^+), 359 (10), 296 (50) and 91 (100). Next to be eluted was the 2-(*pyrrolylmethyl*)*pyrrole* **14f** as colourless crystals from dichloromethane–light petroleum (0.034 g, 5.4%), mp 194–196 °C (Found: C, 68.05; H, 6.45; N, 6.5. $C_{24}H_{26}N_2O_5$ requires C, 68.23; H, 6.20; N, 6.63%); $\delta_H(CDCl_3)$ 9.55 (1 H, br s, 1-NH), 9.05 (1 H, br s, 1'-NH), 7.41–7.33 (5 H, m, ArH), 6.34 (1 H, d, *J* 2.5, 3'-H), 5.29 (2 H, s, CH_2Ph), 4.23 (2 H, q, OCH_2CH_3), 3.96 (2 H, s, 2-CH_2), 2.60 and 2.54 (2 × 3 H, 2 s, $COCH_3$ and 4-CH_3), 2.44 (3 H, s, 5'-CH_3) and 1.31 (3 H, t, OCH_2CH_3); *m/z* 422 (2%, M^+), 91 (100), 77 (5), 65 (12) and 43 (18).

2-Ethoxycarbonyl-5-methoxycarbonyl-3,4-dimethylpyrrolo[2,3-*f*]indole 34 and 2-ethoxycarbonyl-7-methoxycarbonyl-3,4-dimethylpyrrolo[3,2-*f*]indole 33. These compounds were obtained from *N*-carbomethoxypyrrole **32** (8.0 mmol) and the 5-acetoxymethyl-4-acetylpyrrole **1a** (8.0 mmol). Chromatographic separation gave the starting pyrrole **32** (0.145 g, 14.5%), the [2,3-f] *isomer* **34** as colourless crystals from dichloromethane–light petroleum (0.026 g, 1.0%), mp 163–165 °C (Found: C, 64.7; H, 5.8; N, 8.8. $C_{17}H_{18}N_2O_4$ requires C, 64.95; H, 5.77; N, 8.91%); δ_H([$^2H_6$]DMSO) 11.33 (1 H, s, NH), 7.64 (1 H, d, *J* 3.5, 6-H), 7.38 (1 H, s, 8-H), 6.72 (1 H, d, *J* 3.5, 7-H), 4.35 (2 H, q, OCH_2CH_3), 3.95 (3 H, s, OCH_3), 2.86 (3 H, s, 3-CH_3), 2.75 (3 H, s, 4-CH_3) and 1.37 (3 H, t, OCH_2CH_3); saturation of the singlet 8-H at δ 7.38 enhanced the signals due to NH at δ 11.29 (4%) and 7-H at δ 6.72 (7%); *m/z* 314 (57%, M^+), 268 (100), 240 (18), 209 (19), 195 (25), 181 (52), 154 (42) and 127 (28); and the [3,2-f] *isomer* **33** as colourless solid (0.603 g, 24%); mp 197–200 °C (Found: C, 64.8; H, 5.55; N, 8.7. $C_{17}H_{18}N_2O_4$ requires C, 64.92; H, 5.77; N, 8.91%); δ_H([$^2H_6$]DMSO) 11.37 (1 H, s, NH), 8.03 (1 H, s, 8-H), 7.58 (1 H, d, *J* 3.5, 6-H), 6.88 (1 H, d, *J* 3.5, 5-H), 4.35 (2 H, q, OCH_2CH_3), 3.99 (3 H, s, OCH_3), 2.86 (6 H, s, 2 × CH_3) and 1.36 (3 H, t, OCH_2CH_3); saturation of the singlet 8-H at δ 8.03 enhanced the signal due to NH at δ 11.37 (6%) and saturation of the 5-H proton at δ 6.88 enhanced the signal due to 4-CH_3 at δ 2.86 (3%); *m/z* 314 (53%, M^+), 268 (100), 240 (13), 209 (21), 195 (12), 181 (12), 154 (13) and 127 (16). Futher elution gave the 2-(*pyrrolylmethyl*)*pyrrole* **35** as a colourless solid (0.159 g, 6.0%), mp 172–175 °C (Found: C, 61.4; H, 6.2; N, 8.4. $C_{17}H_{20}N_2O_5$ requires C, 61.43; H, 6.07; N, 8.43%); $\delta_H(CDCl_3)$ 9.53 (1 H, br s, NH), 7.21 (1 H, dd, *J* 3.5 and 2, 5'-H), 6.26 (1 H, m, 4'-H), 6.13 (1 H, m, 3'-H), 4.56 (2 H, s, 2-CH_2), 4.31 (2 H, q, OCH_2CH_3), 3.95 (3 H, s, OCH_3), 2.59 and 2.47 (2 × 3 H, 2 s, $COCH_3$ and 4-CH_3) and 1.35 (3 H, t, OCH_2CH_3); *m/z* 332 (28%, M^+), 289 (92), 243 (100), 227 (22), 185 (28), 77 (24), 59 (35) and 43 (100); the 6-(*pyrrolylmethyl*)*pyrrolo*[3,2-f]*indole* **36** as off-white crystals from ethanol (0.159 g, 7.6%), mp 218–222 °C (Found: C, 64.2; H, 5.9; N, 7.9. $C_{28}H_{31}N_3O_7$ requires C, 64.48; H, 5.99; N, 8.06%); δ_H([$^2H_6$]DMSO) 12.08 (1 H, s, pyr-NH), 11.32 (1 H, s, 1-NH), 8.01 (1 H, s, 8-H), 5.87 (1 H, s, 5-H), 4.59 (2 H, s, 6-CH_2), 4.34 (2 H, q, OCH_2CH_3), 4.28 (2 H, q, pyr-$CO_2CH_2CH_3$), 4.05 (3 H, s, OCH_3), 2.79 and 2.64 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3), 2.59 and 2.34 (2 × 3 H, 2 s, 4-CH_3 and $COCH_3$), 1.36 (3 H, t, OCH_2CH_3) and 1.33 (3 H, t, pyr-$CO_2CH_2CH_3$); *m/z* 521 (2%, M^+), 59 (100) and the *tripyrrane* **37** as colourless crystals after crystallisation from dichloromethane–light petroleum (0.129 g, 6%), mp 227–230 °C (Found: C, 62.3; H, 6.0; N, 7.6. $C_{28}H_{33}N_3O_8$ requires C, 62.32; H, 6.16; N, 7.79%); δ_H([$^2H_6$]DMSO) 11.95 (2 H, s, 2 × NH), 5.19 (2 H, s, 3-H and 4-H), 4.38 (4 H, s, 2 × CH_2), 4.24 (4 H, q, 2 × OCH_2CH_3), 4.01 (3 H, s, OCH_3), 2.50 (concealed by DMSO, 2 × $COCH_3$), 2.28 (6 H, s, 2 × CH_3) and 1.29 (6 H, t, OCH_2CH_3); *m/z* 539 (34%, M^+), 521 (34), 507 (8), 494 (13), 464 (15), 331 (99), 285 (85), 273 (40), 227 (58), 207 (46), 162 (87) and 59 (100).

Cyclisation of the 2-(*pyrrolylmethyl*)*pyrrole* **35**.—Toluene-*p*-sulfonic acid (100 mg) was added to the solution of the 2-(pyrrolylmethyl)pyrrole **35** (0.435 g, 1.3 mmol) in benzene (50 cm^3) using a Dean–Stark apparatus, and the reaction mixture was heated under reflux for 5 h. Evaporation of the solvent gave

a brown solid which was submitted to column chromatography on silica eluting with (0–10%) ethyl acetate in dichloromethane to give the *7-methoxycarbonylpyrrolo*[3,2-f']*indole* **33** as a colourless solid (0.358 g, 79.7%) which was identical in all respects to the pyrrolo[3,2-*f*]indole **33** of the previous experiment.

2'-Ethoxycarbonyl-6',7'-dihydro-3',4'-dimethylspiro[cyclopentane-1,7'-1'*H*-pyrrolo[3,2-*f*]indolizin]-6'-one 25

This compound, obtained from 4,5,6,7-tetrahydroindole **24** and the 5-acetoxymethyl-4-acetylpyrrole **1a**, gave yellow crystals from chloroform–light petroleum (0.0147 g, 3.0%), mp 223–226 °C; δ_H([$^2H_6$]DMSO) 11.00 (1 H, s, NH), 7.10 (1 H, s, 7-H), 6.36 (1 H, s, 8-H), 4.30 (2 H, q, O$CH_2$$CH_3$), 2.91 (3 H, s, 3-$CH_3$), 2.70 (3 H, s, 4-$CH_3$), 1.80 (6 H, m, 3 × CH_2), 1.55 (2 H, m, CH_2) and 1.33 (3 H, t, OCH$_2$$CH_3$); saturation of the singlet 8-H proton at δ 6.36 enhanced the signals due to NH at δ 11.00 (2%) and 7-H at δ 7.10 (2%) and saturation of the 7-H at δ 7.10 enhanced the signals due to the 8-H at δ 6.36 (11%) and the CH_2 at δ 1.55 (3.5%); *m*/*z* 326 (77%, M$^+$), 280 (72), 252 (37), 223 (61), 195 (15), 180 (10), 158 (15), 140 (22), 115 (18), 93 (42) and 43 (100) (Found: M$^+$, 326.1630. $C_{19}H_{22}N_2O_3$ requires *M*, 326.1630); ν_{max}(Nujol)/cm^{-1} 3310, 1668 and 1614; and the starting pyrrole **1a** (0.266 g, 66.4%).

Synthesis of 9-benzyl-2-ethoxycarbonyl-3,4-dimethyl-5-oxo-5,6,7,8-tetrahydropyrrolo[2,3-*b*]carbazole 28 and 5-benzyl-2-ethoxycarbonyl-3,4-dimethyl-9-oxo-6,7,8,9-tetrahydropyrrolo-[3,2-*b*]carbazole 29

The general procedure was followed using 1-benzyl-4-oxo-4,5,6,7-tetrahydroindole[16] **27a** (1.5 mmol) and 5-acetoxymethyl-4-acetylpyrrole **1a** (1.5 mmol). The *pyrrolo*[2,3-b]*carbazole* **28** was a colourless solid (0.099 g, 16.0%), mp 279–282 °C (Found: C, 75.5; H, 6.1, N, 6.7. $C_{26}H_{26}N_2O_3$ requires C, 75.34; H, 6.32; N, 6.76%); δ_H([$^2H_6$]DMSO) 11.00 (1 H, s, NH), 7.30–7.19 (3 H, m, *m*- and *p*-ArH), 7.06 (2 H, d, *J* 7, *o*-ArH), 7.02 (1 H, s, 10-H), 5.41 (2 H, s, CH_2Ph), 4.26 (2 H, q, OCH_2CH$_3$), 3.28 (3 H, s, 4-CH_3), 2.96 (2 H, t, *J* 6, 8-CH_2), 2.82 (3 H, s, 3-CH_3), 2.47 (concealed by DMSO, 6-CH_2), 2.06 (2 H, quintet, *J* 6, 7-CH_2) and 1.29 (3 H, t, OCH$_2$$CH_3$); saturation of the 10-H proton at δ 7.02 enhanced the signals due to NH at δ 11.01 (2.8%) and CH_2Ph at δ 5.41 (1.8%), saturation of the singlet CH_2Ph at δ 5.41 enhanced the signals due to 10-H at δ 7.02 (14.5%), 8-CH_2 at δ 2.96 (3.6%) and *o*-ArH at δ 7.06 (14.5%), and saturation of the 4-CH_3 proton at δ 3.28 enhanced the signal due to 3-CH_3 at δ 2.82 (3.3%); *m*/*z* 414 (40%, M$^+$), 368 (50), 277 (10), 249 (18), 221 (7), 193 (10) and 91 (100). The *10-pyrrolylmethylpyrrolo*[2,3-b]*carbazole* **30** was a colourless solid (0.028 g, 6.0%), mp 245–250 °C (Found: C, 71.3; H, 6.2; N, 6.6. $C_{37}H_{39}N_3O_6$ requires C, 71.48; H, 6.32; N, 6.76%); δ_H(CDCl$_3$) 8.88 (1 H, br s, pyr-NH), 8.25 (1 H, br s, 1-NH), 7.22–7.19 (3 H, m, *m*- and *p*-ArH), 6.76–6.74 (2 H, m, *o*-ArH), 5.26 (2 H, s, CH_2Ph), 4.52 (2 H, s, 10-CH_2), 4.32 (2 H, q, OCH_2CH$_3$), 4.10 (2 H, q, OCH_2CH$_3$), 3.33 (3 H, s, 4-CH_3), 2.90 (3 H, s, 3-CH_3), 2.78 (2 H, t, *J* 6, 8-CH_2), 2.60 (2 H, t, *J* 6, 6-CH_2), 2.50 (3 H, s, COCH$_3$), 2.42 (3 H, s, 4'-CH_3), 2.16 (2 H, quintet, *J* 6, 7-CH_2), 1.35 (2 H, t, OCH$_2$$CH_3$) and 1.22 (2 H, t, OCH$_2$$CH_3$); *m*/*z* (FAB) 622 (M$^+$ + H) and 621 (M$^+$). The *pyrrolo*[3,2-b]*carbazole* **29** was a colourless solid (0.021 g, 3.3%), mp 288 °C (decomp.) (Found: C, 75.2; H, 6.25; N, 6.5. $C_{26}H_{26}N_2O_3$ requires C, 75.34; H, 6.32; N, 6.76%); δ_H([$^2H_6$]DMSO) 11.12 (1 H, s, NH), 8.01 (1 H, s, 10-H), 7.33–7.21 (3 H, m, *m*- and *p*-ArH), 6.95 (2 H, d, *J* 7, *o*-ArH), 5.64 (2 H, s, CH_2Ph), 4.28 (2 H, q, OCH_2CH$_3$), 2.87 (2 H, t, *J* 6, 6-CH_2), 2.77 (3 H, s, 4-CH_3), 2.75 (3 H, s, 3-CH_3), 2.42 (2 H, t, *J* 6, 8-CH_2), 2.09 (2 H, quintet, *J* 6, 7-CH_2) and 1.31 (3 H, t, OCH$_2$$CH_3$); saturation of the CH_2Ph at δ 5.64 enhanced the signals due to 4-CH_3 at δ 2.77 (2.7%), 6-CH_2 at δ 2.87 (2.3%) and *o*-ArH at δ 6.95 (6.5%); *m*/*z* 414 (68%, M$^+$), 368 (60), 277 (19), 249 (15), 221 (9), 193 (11) and 91 (100). The *2-pyrrolylmethylindole* **31** was colourless crystals from benzene (0.064 g, 9.8%), mp 218–221 °C (Found: C, 72.5; H, 6.75; N, 6.3. $C_{26}H_{28}N_2O_4$ requires C, 72.20; H, 6.53; N, 6.48%); δ_H(CDCl$_3$) 8.68 (1 H, s, NH), 7.21–7.16 (3 H, m, *m*- and *p*-ArH), 6.73–6.69 (2 H, m, *o*-ArH), 6.42 (1 H, s, 3-H), 4.99 (2 H, s, CH_2Ph), 4.27 (2 H, q, OCH_2CH$_3$), 4.20 (2 H, s, 2-CH_2), 2.63 (2 H, t, *J* 6, 7-CH_2), 2.47 (2 H, t, *J* 6, 5-CH_2), 2.43 (3 H, s, 4'-CH_3), 2.32 (3 H, s, COCH$_3$), 2.12 (2 H, quintet, *J* 6, 6-CH_2) and 1.32 (3 H, t, OCH$_2$$CH_3$); saturation of the singlet 2-CH_2 at δ 4.20 enhanced the signals due to CH_2Ph at δ 4.99 (3%), 3-H at δ 6.42 (10%), NH at δ 8.68 (6%) and COCH$_3$ at δ 2.32 (2.5%) and saturation of the CH_2Ph proton at δ 4.49 enhanced the signals due to 7-CH_2 at δ 2.63 (4.5%), *o*-ArH at δ 6.71 (7.9%) and 2-CH_2 at δ 4.2 (4.5%); *m*/*z* 432 (60%, M$^+$), 389 (64), 343 (7), 269 (8) and 91 (100).

Synthesis of 2,7-diethoxycarbonyl-10-methoxycarbonyl-3,4,5,6-tetramethylpyrrolo[3,2-f; 4,5-f']diindole 38

From the 6-pyrrolylmethylpyrrolo[3,2-*f*]indole 36. To a solution of the 6-pyrrolylmethylpyrrolo[3,2-*f*]indole **36** (0.052 g, 0.1 mmol) in ethanol (10 cm^3) was added toluene-*p*-sulfonic acid (20 mg) and the reaction mixture was heated under reflux for 1.5 h. On cooling, the products were filtered and washed well with ethanol to yielded the *pyrrolo*[3,2-f; 4,5-f']*diindole* **38** as off-white crystals (0.043 g, 85.5%), mp > 300 °C (Found: C, 66.6; H, 6.0; N, 8.5. $C_{28}H_{29}N_3O_6$ requires C, 66.78; H, 5.81; N, 8.35%); δ_H([$^2H_6$]DMSO) 11.51 (2 H, s, 2 × NH), 8.18 (2 H, s, 9-H and 11-H), 4.37 (4 H, q, 2 × OCH_2CH$_3$), 4.09 (3 H, s, OCH$_3$), 2.91 (6 H, s, 4-CH_3 and 5-CH_3), 2.89 (6 H, s, 3-CH_3 and 6-CH_3) and 1.38 (6 H, t, 2 × OCH$_2$$CH_3$); *m*/*z* (FAB) 504 (M$^+$ + H) and 503 (M$^+$).

From the tripyrrane 37. The above procedure was followed using tripyrrane (0.054 g, 0.1 mmol) to yield the *pyrrolo*[3,2-f; 4,5-f']*diindole* **38** as off-white crystals (0.047 g, 93.4%) which were identical in all respects with the pyrrolodiindole **38** of the previous experiment.

Vilsmeier formylation of the pyrrolo[3,2-*f*]indoles 21k and 33

General procedure. The pyrrolo[3,2-*f*]indole (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 1.5 cm^{-3} water) 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 (1%; 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 (0–15%) ethyl acetate in dichloromethane to give the 8-formylpyrrolo[3,2-*f*]indole.

2-Ethoxycarbonyl-8-formyl-3,4-dimethylpyrrolo[3,2-*f*]indole 39b. Compound **39b** was obtained from the pyrrolo[3,2*f*]indole **21k** as a yellow solid (0.022, 25.8%), mp 281–284 °C; δ_H([$^2H_6$]DMSO) 11.61 (1 H, br s, 1-NH), 10.81 (1 H, br s, 7-NH), 10.72 (1 H, s, CHO), 7.35 (1 H, m, 6-H), 6.71 (1 H, m, 5-H), 4.38 (2 H, q, OCH_2CH$_3$), 2.94 (3 H, s, 4-CH_3), 2.87 (3 H, s, 3-CH_3) and 1.37 (3 H, t, OCH$_2$$CH_3$); *m*/*z* 284 (53%, M$^+$), 255 (24), 238 (50), 211 (45), 181 (85), 154 (100), 127 (95), 101 (47) and 77 (70) (Found: M$^+$, 284.1161. $C_{16}H_{16}N_2O_3$ requires *M*, 284.1161).

2-Ethoxycarbonyl-8-formyl-7-methoxycarbonyl-3,4-dimethylpyrrolo[3,2-*f*]indole 39c. Compound **39c** was obtained from the pyrrolo[3,2-*f*]indole **33** as a yellow solid (0.037 g, 36.1%), mp 155–158 °C; δ_H(CDCl$_3$) 10.93 (1 H, br s, NH), 10.79 (1 H, s, CHO), 7.54 (1 H, d, *J* 4, 6-H), 6.81 (1 H, d, *J* 4, 5-H), 4.41 (2 H, q, OCH_2CH$_3$), 4.05 (3 H, s, OCH$_3$), 2.93 (3 H, s, 4-CH_3), 2.92 (3 H, s, 3-CH_3) and 1.44 (3 H, t, OCH$_2$$CH_3$); *m*/*z* 342 (80%, M$^+$), 314 (32), 296 (37), 268 (72), 237 (40), 181 (49),

154 (46), 127 (48), 77 (29) and 59 (100) (Found: M^+, 342.1216. $C_{18}H_{18}N_2O_5$ requires M, 342.1216).

Synthesis of 2-ethoxycarbonyl-3,4-dimethylpyrrolo[3,2-*f*]indole 21k

To a solution of 5% potassium hydroxide (10 cm^3) in tetrahydrofuran (100 cm^3) was added the pyrrolo[3,2-*f*]indole **33** (0.314 g, 1.0 mmol) and the reaction mixture was heated at gentle reflux and stirred under nitrogen for 3 days. After evaporation of the solvent, water (20 cm^3) was added and the solution extracted with ether (3 × 20 cm^3). The combined extracts were washed with water, dried over magnesium sulfate and then evaporated under reduced pressure to give a brown solid. This was submitted to column chromatography eluting with (0–5%) ethyl acetate in dichloromethane to give the *pyrrolo*[3,2-f]*indole* **21k** as a colourless solid (0.187 g, 73%), mp 233–235 °C (Found: C, 70.5; H, 6.4; N, 11.05. $C_{15}H_{16}N_2O_2$ requires C, 70.29; H, 6.29; N, 10.93%); $\delta_H([^2H_6]DMSO)$ 10.72 (1 H, s, 1-NH), 10.56 (1 H, s, 7-NH), 7.23 (1 H, dd, *J* 3.4 and 2.4, 6-H), 7.13 (1 H, s, 8-H), 6.45 (1 H, m, 5-H), 4.32 (2 H, q, OCH_2CH_3), 2.85 and 2.84 (2 × 3 H, 2 s, 3-CH_3 and 4-CH_3) and 1.36 (3 H, t, OCH_2CH_3); *m/z* 256 (28%, M^+), 227 (5), 210 (100), 181 (99), 154 (89), 126 (63), 77 (42) and 63 (32).

Synthesis of 3,4-dimethylpyrrolo[3,2-*f*]indole-2-carboxylic acid 39a

A solution of the pyrrolo[3,2-*f*]indole **33** (0.108 g, 0.34 mmol) in 2 mol dm^{-3} sodium hydroxide (10 cm^3) and methanol (10 cm^3) was heated under reflux for 30 min. After cooling, the reaction mixture was neutralised by 1 mol dm^{-3} hydrochloric acid and extracted with diethyl ether (3 × 20 cm^3) and the combined extracts were washed with water and then evaporated under reduced pressure to give the *pyrrolo*[3,2-f]-*indole-2-carboxylic acid* **39a** as a yellow solid (0.54 g, 69.3%), mp 206–208 °C; $\delta_H([^2H_6]DMSO)$ 12.61 (1 H, br s, COOH), 10.68 (1 H, s, 7-NH), 10.56 (1 H, s, 1-NH), 7.25 (1 H, br s, 6-H), 7.12 (1 H, s, 8-H), 6.47 (1 H, br s, 5-H), 2.80 (6 H, s, 2 × CH_3); *m/z* 228 (8%, M^+), 210 (12), 183 (95), 154 (58), 123 (33), 77 (40) and 63 (100) (Found: M^+, 228.0899. $C_{13}H_{12}N_2O_2$ requires M, 228.0899).

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