Synthesis of Linear Ethyl 9-Methoxy-1*H*-benz[*f*]indole-2-carboxylate[1]

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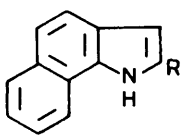
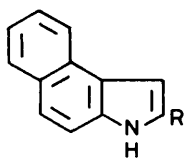
This paper describes a synthesis of genuine ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate (**6**). The genuine synthetic specimen has different physical properties from those of the indole reported as ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate, which was obtained by Fischer indolisation of ethyl pyruvate 2-(1-methoxy-2-naphthylhydrazone) (**9**) by Goldsmith and Lindwall.

Our synthetic method includes the Friedel–Crafts acylation of ethyl pyrrole-2-carboxylate (**13**) with phthalic anhydride and a new selective *N*-debenzylation of *N*-benzylindole derivatives having a methoxy group in their molecule with aluminium chloride in anisole at room temperature.

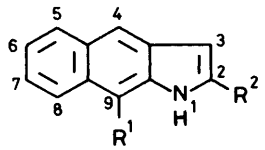
Apart from carbazole there are three isomeric benzindole skeletons,[2] benz[*g*]- (**1**), benz[*e*]- (**2**), and benz[*f*]- (**3**) indole derivatives. It is well known that Fischer indolisation[3] is an effective method for synthesis of the angular skeletons (**1**) and (**2**). For example, ethyl benz[*g*]indole-2-carboxylate[4] (**4**) and ethyl benz[*e*]indole-2-carboxylate[5] (**5**) have been prepared from ethyl pyruvate 1-and 2-naphthylhydrazone derivatives (**7**) and (**8**) by this method.



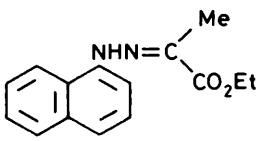
(**1**) R = H
(**4**) R = CO_2Et



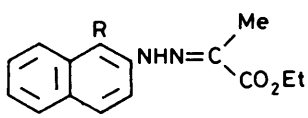
(**2**) R = H
(**5**) R = CO_2Et



(**3**) R^1 = R^2 = H
(**6**) R^1 = OMe, R^2 = CO_2Et

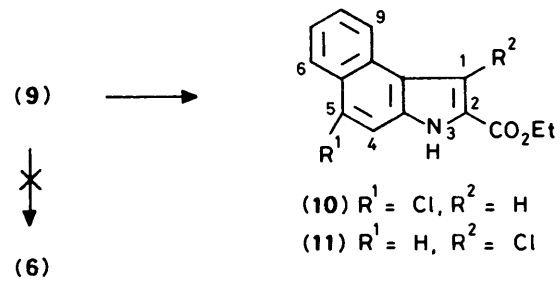


(**7**)



(**8**) R = H
(**9**) R = OMe

In 1953, Goldsmith and Lindwall[6] reported the synthesis of ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate (**6**), a linear derivative, by the Fischer indolisation of ethyl pyruvate 2-(1-methoxy-2-naphthylhydrazone) (**9**) using ethanolic hydrogen chloride as a reagent. However, results of our studies on the abnormal Fischer indolisation,[7] especially on naphthylhydrazone derivatives, [7b] cast doubt on their experimental results. We[8] rechecked their experiments and found that treatment of the starting naphthylhydrazone (**9**) under their conditions gave two indolic products (**10**) and (**11**) in yields of 74.6 and 2.2%, respectively. The structure of the major product, which had been claimed as a linear benz[*f*]indole derivative by Goldsmith and Lindwall, was revised to ethyl 5-chloro-3*H*-benz[*e*]indole-2-carboxylate (**10**), and the minor product was structurally established as ethyl 1-chloro-3*H*-benz[*e*]indole-2-carboxylate (**11**). It was also confirmed that linear benz[*f*]indole derivatives cannot be prepared by Fischer indolisation of 2-naphthylhydrazones having a variety of substituents at the C-1 position.[9] These findings prompted us to synthesize the genuine ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate (**6**). There are only a few reports[2] on the synthesis of simple benz[*f*]indole derivatives, though some benz[*f*]indole derivatives[10] (**3**) occur naturally.

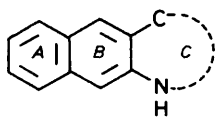


(**9**) → (**10**) R^1 = Cl, R^2 = H; (**11**) R^1 = H, R^2 = Cl
(**9**) ⇕ (**6**)

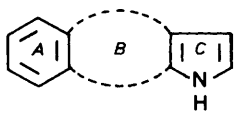
Scheme 1.

In synthesizing linear benz[*f*]indole derivatives (**3**), three pathways may be proposed with respect to the final ring-construction step: (i) the *C*-ring construction on an *AB*-ring moiety (naphthalene derivative) (mode A), (ii) the *B*-ring formation between a phenyl and a pyrrole residue (mode B), and (iii) building up the ring *A* on a *BC*-ring portion, indole nucleus, (mode C).

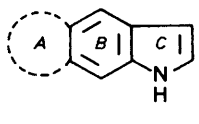
Most of the reported synthetic sequences for linear benz[*f*]-indole derivatives belong to mode A, including the ring contraction of a benzoquinoline derivative,[11] the ring construction of the pyrrole part from 2,3-disubstituted naphthalene derivatives,[12] and introduction of a pyrrole ring on the quinone part of a naphthoquinone derivative.[13] Synthesis of linear benz[*f*]-indole derivatives through mode C has, to our knowledge, not been attempted.



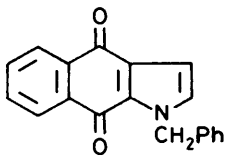
Mode A



Mode B



Mode C



(12)

In 1970, Suvorov *et al.*[14] synthesized a benz[*f*]indole derivative, 1-benzyl-4,9-dioxo-4,9-dihydro-1*H*-benz[*f*]indole (**12**), from a pyrrole derivative and phthalic anhydride in poor yield; this is the only report we know of which is classifiable as mode B synthesis. We therefore prepared the desired linear benz[*f*]-indole (**6**) *via* a new synthetic sequence belonging to mode B synthesis, and this method is expected to become widely applicable for linear benz[*f*]indole derivatives.

Since pyrrole itself is known to be susceptible to electrophilic attack at C-2 to give the 2-substituted product,[15] while Friedel–Crafts acylation of methyl pyrrole-2-carboxylate with acetic anhydride[16] takes place predominantly at the C-4 position in good yield, ethyl pyrrole-2-carboxylate (**13**) was treated with phthalic anhydride with aluminium chloride as catalyst to give the desired keto acid (**14**) (see Scheme 2). Confirmation of occurrence of the acylation at C-4 of the pyrrole ring comes from precise examination of the ^{1}H n.m.r. spectrum of the end product (**6**) in our project using the shift reagent tris(dipivaloylmethanato)europium [Eu(dpm)$_3$] (*vide infra*).

Reduction of the ketonic function of the keto acid (**14**) to a methylene group was successfully achieved by treatment with triethylsilane in trifluoroacetic acid (TFA),[17] without reduction of the carboxy and ester groups, to give the NH methylene acid (**15**).

Treatment of the NH methylene acid (**15**) with trifluoroacetic anhydride (TFAA) in TFA[18] gave the NH cyclised product (**16**). Although, at this point, we could not determine whether the cyclisation had taken place at the C-3 or the C-5 position of the pyrrole ring of the NH methylene acid (**15**), the structure of the NH cyclised product (**16**) was tentatively assigned to the desired linear indole derivative because the C-3 position was supposed to be deactivated against electrophilic attack by the presence of the carboxylate group at C-2. The evidence for the confirmation of the linear benz[*f*]indole structure will be discussed later.

In 1971, MacDowell and Wisowaty[19] reported the synthesis of the 4,9-dihydronaphtho[2,3-*b*]thiophene (**20a**) and discussed equilibrium of the product (**20a**) with its enol tautomer (**20b**) by determination of their ^{1}H n.m.r. spectra in several solvents. This suggested that the NH cyclised product (**16**) existed in a tautomeric mixture, and we therefore measured its ^{1}H n.m.r. spectrum in deuteriochloroform and in [$^2H_6$]dimethyl sulphoxide in detail.

In deuteriochloroform, the ^{1}H n.m.r. spectrum of the NH cyclised product (**16**) shows a 2 H singlet at δ 4.19 and a 2 H quartet at δ 4.30, ascribable to the C-4 benzylic protons and the methylene protons of the ethyl ester of the keto form (**16a**), respectively; there was no signal due to the C-4 aromatic proton of the enol form (**16b**), demonstrating that the NH cyclised product (**16**) exists only in a keto form (**16a**) in deuteriochloroform.

On the other hand, in [$^2H_6$]dimethyl sulphoxide, the spectrum shows a singlet at δ 4.22 and two quartets at δ 4.33 and δ 4.41 by their relative intensities in the proportions 2.6:2.6:1. Since the two more intensive signals were assignable to the C-4 benzylic protons and the methylene protons of the ethyl ester of the keto form (**16a**), the less intensive quartet should be allocated to the methylene signal of the ethyl ester in the enol form (**16b**). This illustrates that the NH cyclised product (**16**) is present in a tautomeric mixture of the keto and enol forms (**16a**) and (**16b**) in [$^2H_6$]dimethyl sulphoxide in the ratio of 2.6:1. This deduction is supported by the fact that, in the ^{13}C n.m.r. spectrum, the NH cyclised product (**16**) in [$^2H_6$]dimethyl sulphoxide shows thirty signals, which is twice the number of carbon atoms in that product. It is of interest that, in the ^{1}H n.m.r. spectrum after addition of deuterium oxide to the solution of the NH cyclised product (**16**), the signal observed in pure [$^2H_6$]dimethyl sulphoxide as a singlet at δ 4.22 disappeared, and the ratio of the two quartets at δ 4.33 and δ 4.41 was changed to 1:3.8 from 2.6:1. The disappearance of the singlet at δ 4.22 was explainable by supposing that the C-4 methylene protons were replaced with deuterium due to the equilibrium between the two tautomeric forms (**16a**) and (**16b**). Consequently, in our experiment there was 3.8 times more of the enol form (**16b**) of the NH cyclised product (**16**) than the keto form (**16a**) in a solution of [$^2H_6$]dimethyl sulphoxide containing deuterium oxide.

Since the above spectral diagnosis of the equilibrium between two tautomeric forms (**16a**) and (**16b**) inferred that the NH cyclised product (**16**) inclines to the enol form (**16b**) in polar and/or protic solvents, we attempted selective *O*-methylation of the NH cyclised product (**16**) with dimethyl sulphate with sodium ethoxide in ethanol and obtained yellow needles of compound (**6**), m.p. 144—145 °C, and yellow prisms of compound (**18**), m.p. 155—159 °C, in 31 and 5% yield, respectively.

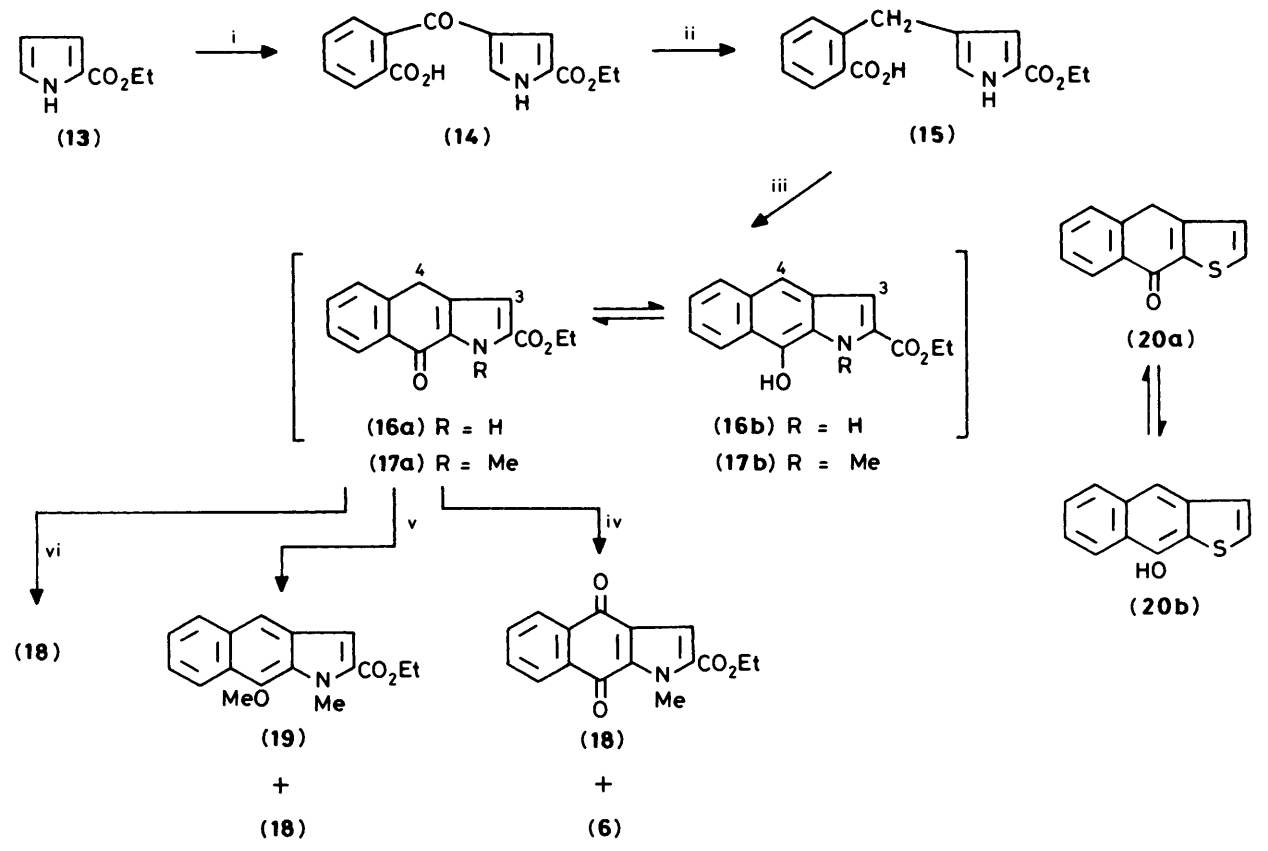
The fact that the former was the desired ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate (**6**) was suggested by elemental analysis ($C_{16}H_{15}NO_3$) and by its spectral data, but conclusive proof was obtained by the alternative synthesis of the desired product (**6**) through the *N*-benzyl cyclised product (**23**) (*vide infra*).

In contrast, elemental analysis of the second product (**18**), revealed its molecular formula to be $C_{16}H_{13}NO_4$, indicating that it is an oxidative product of a methylated derivative of the NH cyclised product (**16**). In the ^{1}H n.m.r. spectrum, this material (**18**) shows a 3 H singlet at δ 4.43 due to an *N*-methyl group. Moreover, the presence of a quinone moiety in the molecule was supported by observation of other spectral data ($\nu_{max.}$ 1 665 and 1 655 cm^{-1} and $\lambda_{max.}$ 268, 327, and 365 nm). These data allowed us to conclude that the second product was indeed the *N*-methyl quinone derivative (**18**).

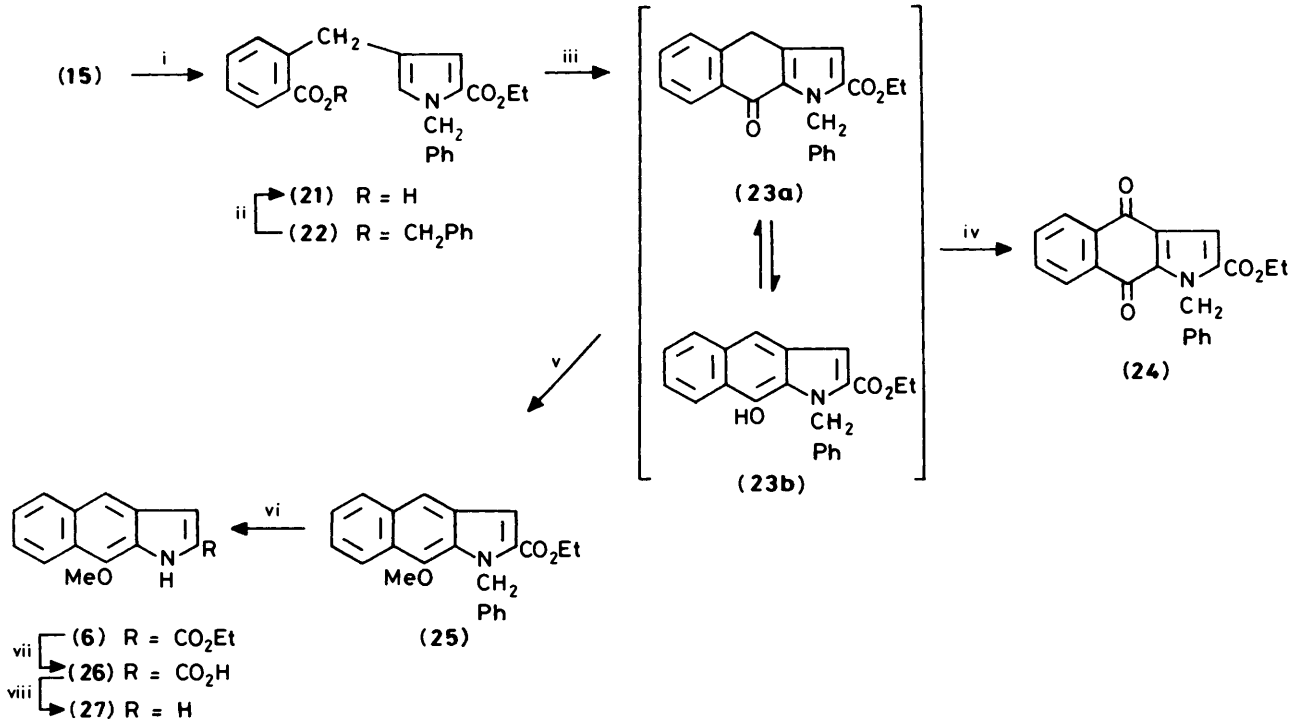
We also attempted to methylate the NH cyclised product (**16**) with dimethyl sulphate and potassium carbonate in *N*,*N*-dimethylformamide (DMF). The NH cyclised product (**16**) gave another labile compound, (**19**), together with *N*-methyl quinone derivative (**18**) in 46 and 25% yield, respectively. In the ^{1}H n.m.r. spectrum, the labile compound (**19**) showed two new 3 H singlets ascribable to *N*- and *O*-methyl groups (δ 4.02 and δ 4.39). Analysis of the high-resolution mass spectrum of the *N*,*O*-dimethyl derivative (**19**) disclosed that its molecular formula was $C_{17}H_{17}NO_3$, indicating that it is ethyl 9-methoxy-1-methyl-1*H*-benz[*f*]indole-2-carboxylate.

Further, treatment of the NH cyclised product (**16**) with diazomethane provided only the *N*-methyl quinone (**18**) in 34% yield.

It should be emphasised here that the resulting products were dependent upon the polarity of the solvents used in the methyl-



Scheme 2. *Reagents:* i, Phthalic anhydride, $AlCl_3$. ii, Et_3SiH–CF_3CO_2H. iii, $(CF_3CO)_2O$–CF_3CO_2H. iv, Me_2SO_4, EtONa. v, Me_2SO_4, K_2CO_3. vi, CH_2N_2· Et_2O



Scheme 3. *Reagents:* i, NaH, $PhCH_2Cl$; ii, H_2–Pd–C; iii, $(CF_3CO)_2O$–CF_3CO_2H; iv, DDQ–DMF; v, Me_2SO_4, K_2CO_3; vi, $AlCl_3$-anisole; vii, KOH–EtOH; viii, Cu-chromite-quinoline

ation of the NH cyclised product (**16**). Furthermore, since this experimental evidence cannot be explained by fairly rapid *N*-methylation of the NH cyclised product (**16**), probably through the keto form (**16a**), the possibility that the partially methylated product mentioned above is the *N*-methyl derivative (**17**) of the NH cyclised product (**16**) cannot be excluded from our considerations. Thus, we achieved an alternative synthesis of the desired product (**6**) *via* a more structurally definite pathway.

Treatment of the NH methylene acid (**15**) with sodium hydride followed by benzyl chloride gave the desired *N*-benzyl methylene acid (**21**) along with its benzyl ester (**22**) in 49 and 15% yield, respectively. Catalytic reduction of the latter product (**22**) easily gave the desired product (**21**).

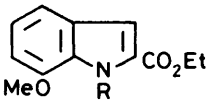
Cyclisation of the *N*-benzyl methylene acid (**21**) in a similar manner to that of the methylene acid (**15**) gave the desired *N*-benzyl cyclised product (**23**). Measurements of ^1H and ^{13}C n.m.r. spectra of the N-benzyl cyclised product (**23**) in solution disclosed that it exists in only the keto form (**23a**) in deuteriochloroform, but in an equimolar mixture of the tautomeric isomers (**23a**) and (**23b**) in [$^2H_6$]dimethyl sulphoxide (see Scheme 3).

It should be added here that, during the measurement of the n.m.r. spectrum in [$^2H_6$]dimethyl sulphoxide, we occasionally found that the *N*-benzyl cyclised product (**23**) was gradually converted into a different material. After a solution of the *N*-benzyl cyclised product (**23**) in DMSO was left at room temperature for 22 h, the resulting yellow prisms, m.p. 169—171 °C, were obtained in 25% yield. The molecular formula of this material (**24**) was established as $C_{22}H_{17}NO_4$ on the basis of elemental analysis and measurement of its mass spectrum. The ^1H n.m.r. spectrum showed the methylene signal of an *N*-benzyl group at δ 7.09, and the presence of a quinone moiety in the molecule was shown by observation of other spectral data ($\nu_{max.}$ 1 675 and 1 660 cm^{-1}; $\lambda_{max.}$ 267, 325, and 370 nm). These data allowed us to propose that the final product was the *N*-benzyl quinone (**24**), formation of which could be explained by air oxidation.

In order to examine whether the air oxidation of the *N*-benzyl cyclised product (**23**) took place on the keto form (**23a**) or the enol form (**23b**), two oxidative experiments using chemical reagents were carried out. Oxidation of the *N*-benzyl cyclised product (**23**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which is commonly used for benzylic oxidation [20] or for oxidative methoxylation,[20a] gave the *N*-benzyl quinone (**24**) in 96% yield. In contrast, treatment of a solution of the same product (**23**) in aqueous acetonitrile with cerium(IV) ammonium nitrate [21] (CAN), which is well known as a reagent for synthesis of *p*-quinone derivatives from phenolic compounds, resulted in quantitative recovery of the starting material. These experimental facts suggested that air oxidation of the *N*-benzyl cyclised product (**23**) took place on the keto form (**23a**) but not on the enol form (**23b**).

Formation of the air oxidation product (**24**) was clearly observed during the measurement of the ^1H or ^{13}C n.m.r. spectrum of the *N*-benzyl cyclised product (**23**) in [$^2H_6$]dimethyl sulphoxide but, in the case of the NH cyclised product (**16**), these spectra could be measured in the same solvent without formation of any by-product. Thus, we may conclude that the *N*-benzyl cyclised product (**23**) is more labile to air oxidation than is the NH cyclised compound (**16**). As described above, the *N*-methyl quinone (**18**) was formed during the methylation of the NH cyclised product (**16**). These phenomena may be rationalised by assuming a high susceptibility of the *N*-alkyl cyclised products (**23**) and (**17**) to air oxidation. In other words, the *N*-alkylation causes the NH cyclised product (**16**) to be labile to air oxidation.

Treatment of the *N*-benzyl cyclised product (**23**) with dimethyl sulphate and potassium carbonate in DMF gave the

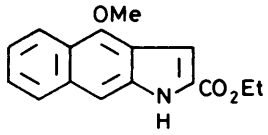


(**28**) R = CH_2Ph

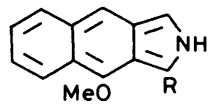
(**29**) R = H

N-benzyl derivative (**25**) of the desired linear benz[*f*]indole (**6**).

In a previous paper,[22] we reported selective debenzylation of ethyl 1-benzyl-7-methoxyindole-2-carboxylate (**28**) by treatment with aluminium chloride in anisole, which acted as a solvent and a trapping reagent of the benzyl cation, at room temperature. We applied the method to the *N*-benzyl derivative (**25**) and obtained the desired genuine ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate (**6**), m.p. 143—144 °C, in good yield. This material was completely identical with the sample prepared by partial *O*-methylation of the NH cyclised product (**16**). Further, our material (**6**) shows different physical and chemical properties from those Goldsmith described [6] for his product; *e.g.* m.p. 229—230 °C.



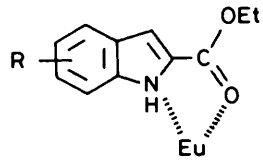
(**30**)



(**31**) R = CO_2Et

(**32**) R = H

To exclude even the slight possibility that our synthesized benz[*f*]indole derivative (**6**) might be the 4-methoxybenz[*f*]-indole (**30**) or the 9-methoxybenz[*f*]isoindole (**31**) derivative, we will discuss its structure in detail. If an electrophilic attack of phthalic anhydride to ethyl pyrrole-2-carboxylate (**13**) had taken place at the C-5 position followed by cyclisation at C-4, the former compound (**30**) could have been formed; if the attack had taken place at C-4 followed by cyclisation at C-3, the latter compound (**31**) might have been produced.



(**33**)

In an earlier paper,[23] we showed that use of the shift reagent technique using tris(dipivaloylmethanato)europium [Eu(dpm)$_3$] in the measurement of ^1H n.m.r. spectra is a strong tool for establishing the position of the methoxy group of ethyl indole-2-carboxylate derivatives (**33**; R = OMe). We also showed that the europium atom co-ordinates with both the nitrogen of the indole nucleus and the oxygen atom of the ester carbonyl group of ethyl indole-2-carboxylate derivatives (**33**), although indole itself [24] did not complex with the europium shift reagent. The Figure shows tris(dipivaloylmethanato)europium [Eu(dpm)$_3$]-induced shifts of several protons of our synthesized benz[*f*]indole ethyl ester (**6**), ethyl 7-methoxyindole-2-carboxylate [23] (**29**), and ethyl 4-methoxyindole-2-carboxylate [23] (**34**). At first glance, the values of the proton shifts of our benz[*f*]indole (**6**) appeared to resemble those of the 7-methoxyindole (**29**) but not those of the 4-methoxyindole (**34**). These data persistently refute the possibility that our benz[*f*]indole

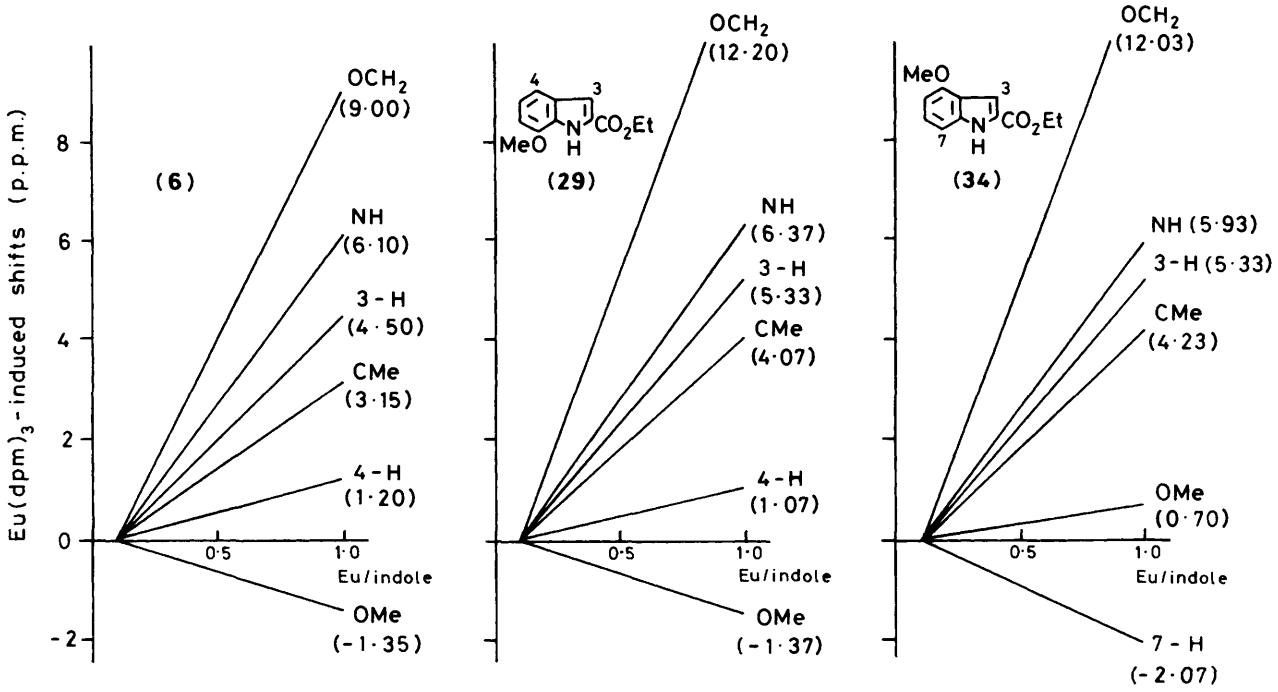


Figure. Comparison of the measured Eu(dpm)$_3$-induced shifts of ethyl 9-methoxy-1*H*-benz[*f*]indole (**6**), ethyl 7-methoxyindole-2-carboxylate (**29**), and ethyl 4-methoxyindole-2-carboxylate (**34**). These values are described by their *S*-value[23] [chemical shift corresponding to 1 mol equiv. of Eu(dpm)$_3$]

ethyl ester (**6**) might be the homologue of ethyl 4-methoxyindole-2-carboxylate (**34**), *i.e.*, ethyl 4-methoxy-1*H*-benz[*f*]-indole-2-carboxylate (**30**), and support the validity of the structure as that of ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate (**6**).

Finally, in order to exclude the other structural possibility of the 9-methoxybenz[*f*]isoindole derivative (**31**), we examined the signal pattern of the pyrrole ring of the parent skeleton of our compound. The desired 9-methoxy-1*H*-benz[*f*]indole (**27**) was prepared from the ester (**6**) by hydrolysis followed by decarboxylation.[25] In the ^{1}H n.m.r. spectrum, the benz[*f*]indole (**27**) shows a 1 H multiplet at δ 6.70. After addition of deuterium oxide this signal changed to a doublet (*J* 3.5 Hz). This evidence indicates that the signal is ascribable to the C-3 proton of benz[*f*]indole derivative* (**27**), and not to the proton of the isoindole (**32**), because the two signals of C-1 and C-3 of an isoindole skeleton should be recognizable as two independent singlets.

Consequently, we may say that the desired genuine ethyl 9-methoxy-1*H*-benz[*f*]indole-2-carboxylate (**6**) has been successfully synthesized.

Experimental

M.p.s were determined on a Yanagimoto micro-melting hot-stage apparatus and are uncorrected. I.r. spectra were recorded in Nujol mulls on a Shimadzu IR-400 spectrometer. U.v. spectra were measured with a Hitachi 340 spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Hitachi R-24B (60 MHz) (unless otherwise stated) and a JEOL GX-400 (400 MHz) spectrometer, and ^{13}C n.m.r. spectra on a JEOL GX-400 (100.4 MHz) in deuteriochloroform (unless otherwise stated), with tetramethylsilane as internal reference. Mass spectra were measured with a JEOL JMS-01-SG-2 spectrometer using a direct inlet system. For column chromatography, Merck silica gel 60 (70—230 mesh) was used, while for t.l.c. Merck silica gel 60F$_{254}$ was used.

2-[(5-*Ethoxycarbonylpyrrol*-3-*yl*)*carbonyl*]*benzoic Acid* (**14**).—Phthalic anhydride (5.87 g) was added to an ice-cooled suspension of aluminium chloride (12.4 g) in 1,2-dichloroethane (30 ml). After addition of a solution of ethyl pyrrole-2-carboxylate[26] (**13**) (3.01 g) in 1,2-dichloroethane (30 ml), the mixture was refluxed for 30 min and poured into a mixture of water (500 ml) and 1M sulphuric acid (100 ml). The suspension was extracted with ethyl acetate. The organic layer was extracted with 5% aqueous sodium hydroxide. The alkaline aqueous layer was then acidified with conc. hydrochloric acid and extracted with ethyl acetate. This extract was washed with water, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. Recrystallisation of the residue from ethanol–water gave the *title acid* as needles (5.84 g, 94%), m.p. 187—190 °C (Found: C, 62.7; H, 4.5; N, 4.6. $C_{15}H_{13}NO_5$ requires C, 62.7; H, 4.6; N, 4.9%); $\nu_{max.}$ 3 230 (NH), and 1 720 and 1 655 cm^{-1} (CO); δ_H[(CD$_3$)$_2$SO] 1.28 (3 H, t, *J* 8 Hz, CMe), 4.28 (2 H, q, *J* 8 Hz, OCH$_2$), 6.91 and 7.29 (each 1 H, m, pyrrole 4- and 2-H), 7.35—8.1 (4 H, m, ArH), and 12.45 (1 H, br s, NH); *m/z* 287 (*M*$^+$, 44%), 166 (63), and 120 (100).

2-[(5-*Ethoxycarbonylpyrrol*-3-*yl*)*methyl*]*benzoic Acid* (**15**).—Triethylsilane[17] (2.15 ml) was added to a solution of the keto acid (**14**) (1.00 g) in TFA (12.6 ml). The reaction mixture was stirred at room temperature for 24 h and evaporated to dryness under reduced pressure at room temperature. The residue was dissolved in ethyl acetate, and the solution was washed with water, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with chloroform–methanol (10:1) to give the *title*

* The signal of the C-2 proton was buried in a complex pattern of signals due to the aromatic protons.

acid as prisms (940 mg, 99%), m.p. 160.5—161.5 °C, which were recrystallised from ethanol–water (Found: C, 65.6; H, 5.5; N, 4.9. $C_{15}H_{15}NO_4$ requires C, 65.9; H, 5.5; N, 5.1%); $\nu_{max.}$ 3 300 (NH) and 1 670 cm^{-1} (CO); δ_H 1.30 (3 H, t, *J* 8 Hz, CMe), 4.25 (2 H, q, *J* 8 Hz, OCH_2), 4.27 (2 H, s, $ArCH_2Ar'$), 6.70—8.25 (6 H, m, ArH), and 9.70 (1 H, br s, NH); *m/z* 273 (M^+, 73%), 244 (37), 182 (63), and 133 (100).

Ethyl 9-Oxo-4,9-dihydro-1H-benz[f]indole-2-carboxylate (**16**).—TFAA[18] (0.1 ml) was added to an ice-cooled solution of the NH methylene acid (**15**) (137 mg) in TFA (1 ml). The mixture was stirred at room temperature for 25 min and evaporated to dryness under reduced pressure. The residue was dissolved in ethyl acetate. The organic layer was washed with water, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with benzene–ethyl acetate (20:1) to give the *title compound* as pale yellow prisms* (109 mg, 85%), m.p. 192—195 °C (decomp.) (Found: C, 70.3; H, 5.1; N, 5.3. $C_{15}H_{13}NO_3$ requires C, 70.6; H, 5.1; N, 5.5%); $\nu_{max.}$ 3 210 (NH) and 1 710 cm^{-1} (CO); δ_H[400 MHz; $(CD_3)_2SO$] [keto form (**16a**)] 1.33 (3 H, t, *J* 7 Hz, CMe), 4.22 (2 H, s, 4-H_2), 4.30 (2 H, q, *J* 7 Hz, OCH_2), 6.93 (1 H, s, 3-H), 7.49 (1 H, dt, *J* 2 and 7 Hz, 6- or 7-H), 7.59 (1 H, dd, *J* 2 and 7 Hz, 5-H), 7.63 (1 H, dt, *J* 2 and 7 Hz, 7- or 6-H), 8.21 (1 H, dd, *J* 2 and 7 Hz, 8-H), and 12.85 (1 H, br s, NH); [enol form (**16b**)] 1.39 (3 H, t, *J* 7 Hz, CMe), 4.41 (2 H, q, *J* 7 Hz, OCH_2), 7.25—7.33 (3 H, m, 3-, 6-, and 7-H), 7.77 (1 H, s, 4-H), 7.86 (1 H, dd, *J* 2 and 7 Hz, 5-H), 8.21 (1 H, dd, *J* 2 and 7 Hz, 8-H), 9.80 (1 H, br s, OH), and 11.08 (1 H, br s, NH); δ_C[$(CD_3)SO$] [keto form (**16a**)] 14.01 (q, C*Me*), 27.49 (t, C-4), 60.13 (t, OCH_2), 112.39 (d), 125.34 (d), 125.94 (d), 127.97 (s), 128.79 (d), 130.64 (s), 131.12 (d), 132.13 (s), and 140.46 (s, ArC), 159.42 (s, OC=O), and 174.01 (s, CC=O); [enol form (**16b**)] 14.14 (q, C*Me*), 60.50 (t, OCH_2), 106.84 (d), 109.60 (d), 119.33 (s), 120.59 (d), 121.82 (d), 122.26 (d), 123.72 (s), 127.20 (d), and 135.90 (s, ArC), and 160.35 (s, OC=O) (other aromatic carbons were not assignable as to whether they arose from the keto or enol form): 128.90 (s), 128.94 (s), 129.55 (s), and 129.78 (s). Each signal of the keto or enol form was assigned by observing changes of their intensities with the addition of deuterium oxide. The ratio of the keto and enol forms was 2.6:1, which was determined by the relative intensities of the C-4 and ester methylenes of the keto form (**16a**) and ester methylene of the enol form (**16b**). Addition of deuterium oxide changed their relative intensities to the ratio 1:3.8; *m/z* 255 (M^+, 52%), 209 (30), 183 (31), 182 (100), and 181 (39).

Attempted Methylation of Ethyl 9-Oxo-4,9-dihydro-1H-benz[f]indole-2-carboxylate (**16**).—(a) *With dimethyl sulphate and sodium ethoxide.* Dimethyl sulphate (0.038 ml) was added to a solution of the NH cyclised product (**16**) (101 mg) in ethanol (6 ml) containing sodium ethoxide (27 mg) at room temperature. The whole solution was stirred for 12 h at room temperature, poured into ice–water, and extracted with ethyl acetate. The extract was washed with saturated brine, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The crude residue (112 mg) was chromatographed on silica gel with hexane–ethyl acetate (5:1).

The first eluate gave *ethyl 1-methyl-4,9-dioxo-4,9-dihydro-1H-benz[f]indole-2-carboxylate* (**18**) as yellow prisms (6 mg, 5%), m.p. 161—162.5 °C, which were recrystallised from hexane–ethyl acetate (Found: C, 68.0; H, 4.5; N, 5.0. $C_{16}H_{13}NO_4$ requires C, 67.8; H, 4.6; N, 4.9%); $\nu_{max.}$ 1 725, 1 665, and 1 655 cm^{-1} (CO); $\lambda_{max.}$(EtOH) 268, 327, and 365 nm (log ε 4.82, 3.76, and 3.54); δ_H 1.40 (3 H, t, *J* 7 Hz, CMe), 4.37 (2 H, q, *J* 7 Hz, OCH_2), 4.43 (3 H, s, NMe), 7.43 (1 H, s, 3-H), and 7.60—7.85, 8.10—8.30 (each 2 H, m, ArH); *m/z* 283 (M^+, 100%), 254 (68), 238 (36), and 244 (98).

The second eluate gave *ethyl 9-methoxy-1H-benz[f]indole-2-carboxylate* (**6**) as yellow needles (33 mg, 31%), m.p. 144—145 °C, which were recrystallised from ethanol (Found: C, 71.4; H, 5.6; N, 5.3. $C_{16}H_{15}NO_3$ requires C, 71.4; H, 5.6; N, 5.2%); $\nu_{max.}$ 3 340 (NH) and 1 695 cm^{-1} (CO); δ_H(400 MHz) 1.46 (3 H, t, *J* 7 Hz, CMe), 4.13 (3 H, s, OMe), 4.46 (2 H, q, *J* 7 Hz, OCH_2), 7.35 (1 H, dt, *J* 1 and 8 Hz, 6- or 7-H), 7.38 (1 H, d, *J* 2 Hz, 3-H), 7.44 (1 H, dt, *J* 1 and 8 Hz, 7- or 6-H), 7.94 (1 H, dd, *J* 1 and 8 Hz, 5- or 8-H), 8.03 (1 H, s, 4-H), 8.18 (1 H, dd, *J* 1 and 8 Hz, 8- or 5-H), and 8.84 (1 H, br s, NH); *m/z* 269 (M^+, 72%), 223 (95), and 208 (100).

(b) *With dimethyl sulphate and potassium carbonate.* A solution of the NH cyclised product (**16**) (52 mg) in DMF (1 ml) was added to anhydrous potassium carbonate (138 mg). Dimethyl sulphate (0.029 ml) was then added to the above ice-cooled mixture. The reaction mixture was stirred at room temperature for 1 h, poured into ice–water, and extracted with ethyl acetate. The extract was washed successively with 5% hydrochloric acid, 5% aqueous sodium hydrogen carbonate, and saturated brine, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with hexane–ethyl acetate (3:1).

The first eluate gave *ethyl 9-methoxy-1-methyl-1H-benz[f]-indole-2-carboxylate* (**19**) as dark yellow needles† (27 mg, 46%), m.p. 66—70 °C (Found: M^+, 283.1212. $C_{17}H_{17}NO_3$ requires *M*, 283.1209); $\nu_{max.}$ 1 710 cm^{-1} (CO); δ_H 1.42 (3 H, t, *J* 8 Hz, CMe), 4.02 (3 H, s, OMe), 4.39 (2 H, q, *J* 8 Hz, OCH_2), 4.40 (3 H, s, NMe), 7.18—7.60 (3 H, m, ArH), and 7.75—8.30 (3 H, m, ArH); *m/z* 283 (M^+, 100%), 268 (89), and 240 (31).

The second eluate gave compound (**18**) as pale orange needles (15 mg, 25%), m.p. 159.5—161 °C, which were recrystallised from ethyl acetate–hexane. This compound was identical with the quinone (**18**) described above.

(c) *With diazomethane.* A solution of an excess of diazomethane in diethyl ether was added to an ice-cooled solution of the NH cyclised product (**16**) (51 mg) in ethyl acetate (20 ml). After being kept at 0 °C for 5 h, the mixed solution was evaporated to dryness under reduced pressure. The residue was purified by chromatography on silica gel with benzene–ethyl acetate (20:1). Recrystallisation of the crude product from hexane–ethyl acetate gave yellow prisms (19 mg, 34%), m.p. 161—162 °C. This compound was identical with the quinone (**18**) described above.

2-[(1-*Benzyl-5-ethoxycarbonylpyrrol-3-yl*)*methyl*]*benzoic Acid* (**21**).—An ice-cooled solution of the NH methylene acid (**15**) (647 mg) in DMSO (40 ml) was added to 50% sodium hydride in oil (287 mg) under argon and the mixture was stirred for 0.5 h. Benzyl chloride (0.685 ml) was added to the stirred solution. The whole mixture was stirred at 50 °C for 0.5 h, poured into a mixture of crushed ice and conc. hydrochloric acid, and extracted with diethyl ether. The extract was shaken with aqueous sodium carbonate and separated into an organic layer (the neutral extraction) and an alkaline aqueous layer. The alkaline solution was acidified with dil. hydrochloric acid and extracted with ethyl acetate. This extract was washed with water, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with chloroform–methanol (10:1) and recrystallised from ethanol–water to give the *title compound* as

* This material gradually decomposed during recrystallisation (from ethanol–ethyl acetate) or even in the solid state. The sample for elemental analysis was obtained only by careful column chromatography.

† This material gradually decomposed during recrystallisation.

fine needles (420 mg, 49%), m.p. 132.5—134.5 °C (Found: C, 72.6; H, 5.85; N, 3.7. $C_{22}H_{21}NO_4$ requires C, 72.7; H, 5.8; N, 3.85%); $\nu_{max.}$ 1 690 cm^{-1} (CO); δ_H 1.23 (3 H, t, *J* 8 Hz, CMe), 4.17 (2 H, q, *J* 8 Hz, OCH_2), 4.23 (2 H, s, $ArCH_2Ar'$), 5.47 (2 H, s, NCH_2), 6.60—7.10 (10 H, m, ArH), 8.03 (1 H, dif d, *J* 8 Hz, 6-H of benzoic acid), and 8.70 (1 H, br s, OH); *m/z* 363 (M^+, 59%), 290 (31), 272 (57), 133 (47), and 91 (100).

The neutral extract was washed with water, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The crude residue was chromatographed on silica gel with benzene as eluant to give ethyl 1-benzyl-4-(2-benzyloxycarbonylbenzyl)pyrrole-2-carboxylate (**22**) as an oil (159 mg, 15%); δ_H 1.22 (3 H, t, *J* 8 Hz, CMe), 4.14 (2 H, s, $ArCH_2Ar'$), 4.15 (2 H, q, *J* 8 Hz, OCH_2Me), 5.23 and 5.40 (each 2 H, s, CH_2Ph), 6.55 and 6.75 (each 1 H, d, *J* 2 Hz, pyrrole 2- and 4-H), and 6.90—8.02 (14 H, m, ArH); *m/z* 453 (M^+, 20%), 362 (66), 133 (43), and 91 (100).

Without further purification, the benzyl ester (**22**) was hydrogenated over 10% Pd/C (107 mg) in ethanol (4 ml) at room temperature for 45 min. The catalyst was filtered off and the filtrate was evaporated to dryness under reduced pressure to give the *N*-benzyl methylene acid (**21**) as needles, m.p. 120—123 °C (96 mg; total 516 mg, 60%).

In the benzylation reactions the product ratio of the *N*-benzyl methylene acid (**21**) and its benzyl ester (**22**) was not constant. Sometimes only the *N*-benzyl methylene acid (21) was obtained.

Ethyl 1-Benzyl-9-oxo-4,9-dihydro-1H-benz[f]indole-2-carboxylate (**23**).—TFAA (0.12 ml) was added to an ice-cooled solution of the *N*-benzyl methylene acid (**21**) (210 mg) in TFA (2 ml). The mixture was stirred at room temperature for 1 h under argon and then evaporated to dryness under reduced pressure. The residue was dissolved in ethyl acetate, and washed successively with 5% aqueous sodium hydrogen carbonate and saturated brine. The organic layer was dried over magnesium sulphate and evaporated to dryness under reduced pressure. The crude residue was chromatographed on silica gel with benzene to give the *title compound* as needles (160 mg, 80%), m.p. 158.5—160 °C, which were recrystallised from benzene (Found: C, 76.7; H, 5.5; N, 3.8. $C_{22}H_{19}NO_3$ requires C, 76.5; H, 5.5; N, 4.1%); $\nu_{max.}$ 1 715 and 1 645 cm^{-1} (CO); δ_H(400 MHz) 1.32 (3 H, t, *J* 7 Hz, CMe), 4.18 (2 H, s, 4-H_2), 4.29 (2 H, q, *J* 7 Hz, OCH_2), 6.36 (2 H, s, NCH_2), 7.03 (1 H, s, 3-H), 7.10—7.28 (5 H, m, Ph), 7.42 (1 H, t, *J* 7 Hz, 6- or 7-H), 7.45 (1 H, dd, *J* 2 and 7 Hz, 5-H), 7.53 (1 H, dt, *J* 2 and 7 Hz, 7- or 6-H), and 8.31 (1 H, dd, *J* 2 and 7 Hz, 8-H); δ_C 14.17 (q, *CMe*), 28.22 (t, C-4), 49.19 (t, NCH_2), 60.53 (t, OCH_2), 114.43 (d, ArC), 126.02 (d, ArC of benzyl group), 126.14 (d), 126.29 (d), and 126.57 (d) (each ArC), 127.74 (d, ArC of benzyl group), 128.11 (d), 128.35 (s), 129.37 (s), 130.65 (s), 131.09 (d), 133.50 (s), 138.40 (s), and 139.43 (s) (each ArC), 160.12 (s) (OC=O), and 176.00 (s) (CC=O); δ_H[400 MHz; $(CD_3)_2SO$] [keto form (**23a**)] 1.25 (3 H, t, *J* 7 Hz, CMe), 4.24 (2 H, q, *J* 7 Hz, OCH_2), 4.27 (2 H, s, 4-H_2), 6.25 (2 H, s, NCH_2), 6.99 (2 H, d, *J* 7 Hz, 2- and 6-H of benzyl group), 7.09 (1 H, s, 3-H), 7.11—7.35 (3 H, m, ArH), 7.48 (1 H, dt, *J* 2 and 7 Hz, 6- or 7-H), 7.59 (1 H, dd, *J* 2 and 7 Hz, 5-H), 7.64 (1 H, dt, *J* 2 and 7 Hz, 7- or 6-H), and 8.14 (1 H, dd, *J* 2 and 7 Hz, 8-H); [enol form (**23b**)] 1.29 (3 H, t, *J* 7 Hz, CMe), 4.29 (2 H, q, *J* 7 Hz, OCH_2), 6.30 (2 H, s, NCH_2), 6.94 (2 H, d, *J* 7 Hz, 2- and 6-H of benzyl group), 7.11—7.35 (5 H, m, ArH), 7.47 (1 H, s, 3-H), 7.86 (1 H, s, 4-H), 7.89 (1 H, dd, *J* 2 and 7 Hz, 5-H), 8.23 (1 H, dd, *J* 2 and 7 Hz, 8-H), and 9.86 (1 H, s, OH); δ_C[$(CD_3)_2SO$] [keto form (**23a**)] 13.86 (q, *CMe*), 27.53 (t, C-4), 48.49 (t, NCH_2), 60.30 (t, OCH_2), 159.39 (t, OC=O), and 175.11 (s, CC=O); [enol form (**23b**)] 13.92 (q, *CMe*), 48.62 (t, NCH_2), 60.27 (t, OCH_2), and 160.31 (s, OC=O). (Other carbons were not assignable as to whether they arose from the keto or enol form): 110.64, 111.22, 114.49, 120.68, 121.51, 122.29, 122.41, 125.18, 125.28, 125.46, 125.50, 125.91, 126.02, 126.12, 126.99, 127.39, 127.59, 127.66, 127.80, 127.81, 128.05, 128.57, 128.59, 128.92, 131.01, 131.18, 131.31, 132.58, 137.29, 138.30, 139.77, and 139.81. The ratio of the keto and enol forms was 1:1, which was determined by the relative intensities of the signals for the C-4 and ester methylenes of the keto form (**23a**) and the ester methylene of the enol form (**23b**); *m/z* 345 (M^+, 71%), 272 (55), 210 (83), 135 (41), and 91 (100).

Ethyl 1-Benzyl-4,9-dioxo-4,9-dihydro-1H-benz[f]indole (**24**).—(a) *Formation in dimethyl sulphoxide solution.* A solution of the *N*-benzyl cyclised product (**23**) (50 mg) in DMSO (4 ml) was stirred at room temperature for 22 h. The mixture was poured into water and extracted with ethyl acetate. The extract was washed with water, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The oily residue (49 mg) was chromatographed on silica gel with hexane–ethyl acetate (5:1) to give the starting material (**23**) (6 mg, 12% recovery) and the *title quinone* as yellow prisms (13 mg, 25%), m.p. 167—172 °C, in order of elution. The latter compound was identical with an authentic sample of the quinone (**24**) prepared in the next step.

(b) *Alternative synthesis* via DDQ *oxidation.* DDQ (44 mg) was added to a solution of *N*-benzyl cyclised product (**23**) (66 mg) in a mixture of DMF (4 ml) and methanol (0.5 ml), and the mixture was stirred at room temperature for 2 days. The reaction mixture was poured into water and extracted with ethyl acetate. The extract was washed successively with 5% sodium hydrogen carbonate and saturated brine, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The oily residue was purified by column chromatography on silica gel with benzene to give a pale yellow solid (62 mg, 96%), m.p. 167—171 °C. Recrystallisation of the solid from ethanol gave the *title quinone* as yellow prisms, m.p. 169—171 °C (Found: C, 73.8; H, 4.8; N, 3.9. $C_{22}H_{17}NO_4$ requires C, 73.5; H, 4.8; N, 3.9%); $\nu_{max.}$ 1 710, 1 675, and 1 660 cm^{-1} (CO); $\lambda_{max.}$(EtOH) 267, 325, and 370 nm (log ε 4.70, 3.75, and 3.45); δ_H[$(CD_3)_2SO$] 1.26 (3 H, t, *J* 7 Hz, CMe), 4.26 (2 H, q, *J* 7 Hz, OCH_2), 6.18 (2 H, s, NCH_2), 7.09 (2 H, d, *J* 7 Hz, 2′- and 6′-H), 7.21—7.33 (3 H, m, 3′-, 4′-, and 5′-H), 7.40 (1 H, s, 3-H), 7.82—7.89 (2 H, m, 6- and 7-H), and 8.05—8.13 (2 H, m, 5- and 8-H); *m/z* 359 (M^+, 47%), 345 (67), 272 (32), 224 (34), 210 (55), 135 (63), and 91 (100).

Ethyl 1-Benzyl-9-methoxy-1H-benz[f]indole-2-carboxylate (**25**).—A solution of the *N*-benzyl cyclised product (**23**) (518 mg) in DMF (17 ml) was added to ice-cooled anhydrous potassium carbonate (630 mg). After addition of dimethyl sulphate (0.142 ml) under argon, the reaction mixture was stirred at room temperature for 1 h, poured into ice–water, acidified with 10% hydrochloric acid, and extracted with diethyl ether. The extract was washed successively with water, 5% aqueous sodium hydrogen carbonate, and saturated brine, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with hexane–ethyl acetate (10:1) to give the *title compound* as yellow prisms (430 mg, 80%), m.p. 83—86 °C, which were recrystallised from ethanol (Found: C, 76.7; H, 5.9; N, 3.8. $C_{23}H_{21}NO_3$ requires C, 76.9; H, 5.9; N, 3.9%); $\nu_{max.}$ 1 710 cm^{-1} (CO); δ_H 1.33 (3 H, t, *J* 7 Hz, CMe), 3.82 (3 H, s, OMe), 4.32 (2 H, q, *J* 7 Hz, OCH_2), 6.23 (2 H, s, NCH_2), 6.75—7.62 (8 H, m, ArH), and 7.75—8.32 (3 H, m, ArH); *m/z* 359 (M^+, 100%), 344 (50), 222 (48), and 91 (77).

Ethyl 9-Methoxy-1H-benz[f]indole-2-carboxylate (**6**).—A solution of the *N*-benzylbenz[f]indole (**25**) (266 mg) in anisole (4.5 ml) was added to ice-cooled aluminium chloride[22] (411 mg). After being stirred at room temperature under argon for 3

h, the reaction mixture was poured into ice–water and extracted with benzene. The organic layer was washed successively with dil. hydrochloric acid, 5% aqueous sodium hydrogen carbonate, and saturated brine, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with hexane–dichloromethane (1:2) to give the *title compound* as yellow needles (144 mg, 72%), m.p. 143—144 °C, which were recrystallised from ethanol (Found: C, 71.25; H, 5.7; N, 5.2. Calc. for $C_{16}H_{15}NO_3$: C, 71.4; H, 5.6; N, 5.2%). This compound was identical with the desired compound (**6**) prepared from the NH cyclised product (**16**) by direct methylation.

It should be added that the debenzylation in benzene gave a complex mixture of products.

Measurement of the ^{1}H *N.m.r. Spectrum of Ethyl* 9-*Methoxy*-1H-*benz*[f]*indole-2-carboxylate* (**6**) *using Shift Reagent, and Treatment of the Data.*—The following procedure was based on that in a previous paper.[23] To a solution of sample (**6**) (8.8 mg) in deuteriochloroform (0.3 ml) was added tris(dipivaloylmethanato)europium [Eu(dpm)$_3$] portionwise (5 × 0.1 mol equiv.) to become, successively, 0.1, 0.2, 0.3, 0.4, and 0.5 mol equiv. to this sample. The induced shifts (p.p.m.) with molar fraction [Eu(dpm)$_3$]/[the sample] were plotted, and a good straight line was obtained for each proton. The *S*-values, imaginary induced shifts at 1:1 complex of [Eu(dpm)$_3$]:[the sample], were estimated by extrapolation of the lines drawn over the above range, and compared with those of ethyl 7-(**29**) and 4-(**34**) methoxyindole-2-carboxylates (see the Figure). The values of the *S*-values of the benz[f]indole (**6**) resembled those[23] of the 7-methoxyindole (**29**) but not those[23] of the 4-methoxyindole (**34**).

9-*Methoxy*-1H-*benz*[f]*indole* (**27**).—A solution of the ester (**6**) (50 mg) in ethanol (3 ml) containing potassium hydroxide (83 mg) was stirred at 60 °C for 4 h. The reaction mixture was poured into water, acidified with 10% hydrochloric acid, and extracted with ethyl acetate. The extract was washed with saturated brine, dried over magnesium sulphate, and evaporated to dryness under reduced pressure to give the crude carboxylic acid (**26**) as a yellow solid, m.p. 194—209 °C (Found: M^+, 241.0748. $C_{14}H_{11}NO_3$ requires M, 241.0739); $\nu_{max.}$ 3 420 (NH) and 1 680 cm^{-1} (CO); δ_H 4.13 (3 H, s, OMe), 7.2—8.3 (6 H, m, ArH), and 9.15 (1 H, br s, NH or OH); *m/z* 241 (M^+, 72%), 223 (56), 222 (37), and 208 (100).

A mixture of the crude carboxylic acid (**26**) and copper chromite (7 mg) in quinoline[25c,27] (1 ml) was heated at 200 °C for 45 min. The reaction mixture was poured into ice–water and extracted with ethyl acetate. The extract was washed successively with 5% hydrochloric acid, 5% sodium hydrogen carbonate, and saturated brine, dried over magnesium sulphate, and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with hexane–dichloromethane (1:1) to give a pale pink solid [20 mg, 55% from the ester (**6**)], m.p. 113.5—124 °C, as an unstable substance, which was recrystallised from diethyl ether–hexane to afford the *title compound* (Found: M^+, 197.0848. $C_{13}H_{11}NO$ requires M, 197.0842); $\nu_{max.}$ 3 310 cm^{-1} (NH); δ_H 4.12 (3 H, s, OMe), 6.70 (1 H, m, 3-H), and 7.20—8.35 (7 H, m, ArH and NH); δ_H(CDCl$_3$ + D$_2$O) 4.12 (3 H, s, OMe), 6.64 (1 H, d, *J* 3.5 Hz, 3-H), and 7.20—8.35 (6 H, m, ArH); *m/z* 197 (M^+, 58%) and 182 (100).

References

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