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The Synthesis and Attempted Ring Closure of Ethyl 3-(Aminomethyl)-7,8,12,13,17,18-hexaethylporphyrin-2-carboxylate

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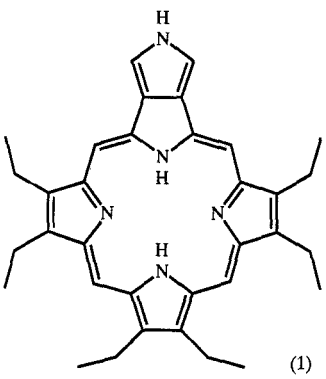
Abstract

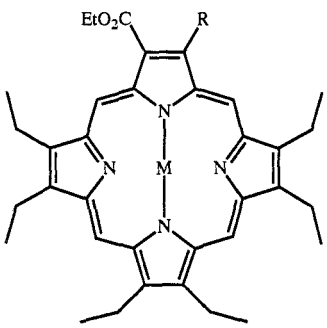
A synthesis of the porphyrin amino ester derivative (4) is described. All attempts to convert (4) into a fused pyrroloporphyrin were unsuccessful, with the corresponding 2-formylporphyrin (5) being formed instead.

Introduction

Only a very few examples of the isolation and/or synthesis of porphyrins containing an aromatic ring fused to one of the porphyrin pyrrolic rings have been reported.[1–3] These were all concerned with benzo-fused porphyrins. We were interested in preparing *pyrrolo-fused* porphyrins, e.g. (1), with a view to exploring their chemistry and electrochemistry. The chemistry described herein presents our first attempts to prepare such systems. Our approach involved leaving construction of the 'extra' pyrrole ring until after the synthesis of the porphyrin nucleus. We intended to achieve this by incorporating the elements of the extra pyrrole ring into a dipyrrylmethane precursor. The pyrrole-forming



(1)



	M	R
(2)	Zn	$CH_2NPhthal$
(3)	H, H	$CH_2NPhthal$
(4)	H, H	CH_2NH_2
(5)	H, H	CH=O

[1] Baker, E. W., Yen, T. F., Dickie, J. P., Rhodes, R. E., and Clarke, L. F., *J. Am. Chem. Soc.*, 1967, **89**, 3631.
[2] Kaur, S., Chicarelli, M. I., and Maxwell, J. R., *J. Am. Chem. Soc.*, 1986, **108**, 1347.
[3] Clezy, P. S., and Leung, C. W. F., *Aust. J. Chem.*, 1993, **46**, 1705.

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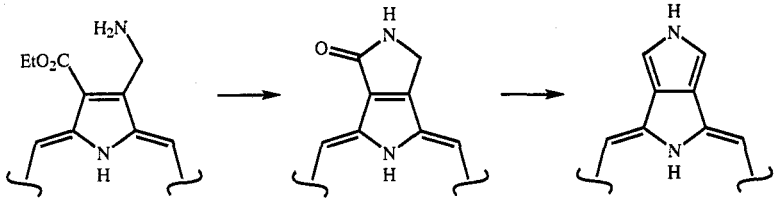
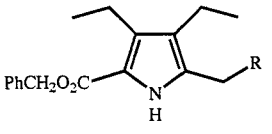
process we had hoped to use involved closing a suitable γ-amino ester to the corresponding γ-lactam followed by reduction and dehydration (Scheme 1). The evidence is now clear that these cyclizations are difficult, if not impossible, where the γ-amino ester is attached to either a pyrrole ring[4] or, from this work, a porphyrin.



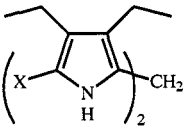
Scheme 1

Results and Discussion

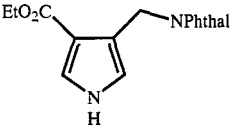
The porphyrin synthesis adopted in this work was based on Kenner's modification[5] of the acid-catalysed coupling of dipyrrylmethanes developed by MacDonald.[6] In order to ensure good solubility for the porphyrins, ethyls were employed as the six remaining β-pyrrolic substituents. This necessitated the synthesis of the new dipyrrylmethane (11), effected by reacting pyrrole (10)[4] with 5-(acetoxymethyl)pyrrole (7)[7] in the presence of montmorillonite clay. The desired product (11) was obtained in 51% yield after recrystallization. A by-product, tripyrrylmethane (13), was also formed in 26% yield. Dipyrrylmethane (11) was



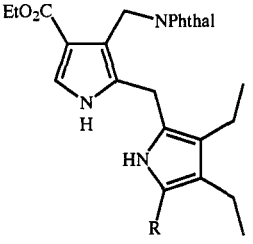
(6) R = H
(7) R = OAc



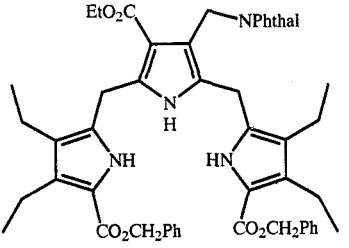
(8) X = $PhCH_2O_2C$
(9) X = OCH



(10)



(11) R = CO_2CH_2Ph
(12) R = H



(13)

[4] Arnold, D. P., Brown, R. F. C., Nitschinsk, L. J., Perlmutter, P., and Tope, H. K., *Aust. J. Chem.*, 1994, **47**, 975.
[5] Caraleiro, J. A. S., Gonsalves, A. M. d'A. R., Kenner, G. W., and Smith, K. M., *J. Chem. Soc., Perkin Trans. 1*, 1974, 1771,
[6] Arsenault, G. P., Bullock, E., and MacDonald, S,. F., *J. Am. Chem. Soc.*, 1960, **82**, 4384.
[7] Johnson, A. W., Kay, I. T., Markham, E., Price, R., and Shaw, K. B., *J. Chem. Soc.*, 1959, 3416.

converted into the α,α'-unsubstituted derivative (12) by hydrogenation of the benzyl ester followed by rapid acid-catalysed decarboxylation. The crude product was then coupled, without isolation, to the known α,α'-diformyldipyrrylmethane (9)[8] by using toluenesulfonic acid in methanol followed by treatment with zinc acetate dihydrate. Porphyrin (2) was isolated in 31% yield after recrystallization. Demetallation was achieved by treatment of (2) with ethanolic sulfuric acid at room temperature for 3 days, a procedure providing porphyrin (3) in 83% yield. Hydrazinolysis of the phthalimide protecting group gave the porphyrin amino ester (4) in rather low yield (25%). As discussed below the poor yield was attributed to the thermal instability of (4).

It now remained to attempt the ring closure to form a γ-lactam. Heating a solution of (4) in benzene at reflux gave, after repeated chromatographic purification, a new green product, the 3-formylporphyrin (5). Repeating this reaction, but with pyridine present, gave similar results. This compound was also identified in the mother liquors of attempted recrystallizations of (4). As it proved impossible to obtain an analytically pure sample of (5) the assignment of its structure rests on spectroscopic evidence only. High-resolution f.a.b. mass spectroscopy gave an MH^+ at m/z 579·3343 which corresponds well to the expected value for (5) (m/z 579·3555). Also the ^1H n.m.r. spectrum contained five resonances in the region δ 9·5–12·0. Four of these can be attributed to the four *meso*-protons and the fifth to the aldehydic proton. However, it was not possible to make more specific assignments. Finally the visible region of the electronic absorption spectrum of (5) was characterized by a relatively intense band at 581 nm. This rather unusual absorption has been observed in other porphyrins containing two electron-withdrawing groups in the same pyrrolic ring.[9] Hence all the spectroscopic evidence is consistent with the proposed structure for (5).

A likely precursor to the aldehyde (5) is an imine, which could be hydrolysed by atmospheric moisture or on chromatography. The reaction was run under nitrogen for 4 days, but on such a small scale (14 mg) that it is difficult to be certain that oxygen was not directly involved in the oxidation of the porphyrin–CH_2NH_2 system. An alternative is that hydride transfer from the methylene group to the porphyrin ring (at, say, C 5) occurs. The resulting aldiminium cation could then be easily hydrolysed to a formyl group, and the reduced porphyrin ring could then be oxidized during chromatography. The exact nature of the role of the porphyrin ring in this transformation awaits elucidation. However, its presence is apparently necessary as the corresponding 4-(aminomethyl)-3-(ethoxycarbonyl)pyrrole is quite stable under similar conditions.[4]

Experimental

Microanalyses were performed by NAL, Australian Microanalytical Service, Melbourne, the Research School of Chemistry, Australian National University, Canberra, and Chemical and Microanalytical Services, Pty Ltd, Melbourne. Electronic absorption specta were measured with a Hitachi 150-20 spectrophotometer, and infrared spectra were measured with Jasco IRA-1 or Jasco A-100 spectrometers, or with a Digilab FTS-60 or a Perkin–Elmer 1600 Fourier-transform spectrophotometer. ^1H n.m.r. spectra were recorded with Bruker AC-200 or Bruker AM-300 spectrometers. Low-resolution e.i. mass spectra were recorded with

[8] Dolphin, D., Paine, J. B., and Woodward, R. B., *J. Org. Chem.*, 1976, **41**, 2826.
[9] Chaudhry, I. A., and Clezy, P. S., *Aust. J. Chem.*, 1982, **35**, 1185.

either a VG Micromass 7070F spectrometer or a VG TRIO-1 spectrometer, operated at 70 eV with a source temperature of 200°. Accurate mass determinations were made by using electron impact with a JEOL DX303 spectrometer operated at 70 eV with a source temperature of 150°. Low-resolution positive-ion fast atom bombardment (f.a.b.) mass spectra were obtained with a VG-ZAB-2HF mass spectrometer using argon atoms of 8 keV energy. The samples were dissolved in dichloromethane and mixed with the matrix of 3-nitrobenzyl alcohol. High-resolution f.a.b. mass spectra were obtained with a VG Analytical ZAB-HS-2HF spectrometer with 8 keV xenon atoms generated with an IonTech saddle field gun. The samples were dissolved in dichloromethane and mixed with the matrix of 3-nitrobenzyl alcohol or dithiothreitol/dithioerythritol. Polyethylene glycol 600 was added for mass calibration. The accuracy of the high-resolution f.a.b. measurements is typically ±15 ppm near m/z 600. Machery–Nagel plastic sheets coated with silica gel G/UV_{254} or aluminium oxide N/UV_{254} were used for analytical thin-layer chromatography (t.l.c.). Column chromatography was carried out using Merck silica gel 60 (70–230 mesh, No. 7734) or Merck neutral aluminium oxide (activity I, 70–230 mesh, No. 1077). Flash chromatography was performed using Merck silica gel 60 (No. 9385). Radial chromatography was performed with a 7924T Chromatotron, from Harrison Research, California. The glass rotor was coated with Merck silica gel 60 PF_{254} (No. 7749).

3,3′,4,4′-Tetraethyl-2-2′-dipyrrylmethane-5,5′-dicarbaldehyde (9)

Benzyl 3,4-diethyl-5-methylpyrrole-2-carboxylate (6) was oxidized with lead tetraacetate,[7] and the 5-acetoxymethyl product (7) was converted into the dipyrrylmethane (8) in ethanol/HCl.[10] Hydrogenolysis of the esters (Pd/C), and decarboxylation of the diacid in boiling dimethylformamide followed by formylation with benzoyl chloride/dimethylformamide[11] gave the title dicarbaldehyde (9), in 53% yield from the dibenzyl ester (8), as pale tan crystals, m.p. 178–180° (lit.[8] 179·5–180·5°).

Ethyl 5′-Benzyloxycarbonyl-3′,4′-diethyl-3-phthalimidomethyl-2,2′-dipyrrylmethane-4-carboxylate (11) and the Tripyrrylmethane (13)

Ethyl 4-(phthalimidomethyl)pyrrole-3-carboxylate (10)[4] (0·45 g, 1·5 mmol) was dissolved in dichloromethane (60 ml). Montmorillonite clay K10 (2·00 g) and benzyl 5-(acetoxymethyl)-3,4-diethylpyrrole-2-carboxylate (7)[7] were added with stirring, and the mixture was heated under reflux for 1 h. The mixture was filtered (Celite pad) and the filtrate was evaporated. Radial chromatography on silica (2 mm) with gradient elution (diethyl ether/light petroleum 55:45 through to 70:30) separated the two components of R_F 0·58 (0·15 g) and R_F 0·35 (0·54 g). The component of R_F 0·58 was recrystallized from dichloromethane/light petroleum to give *ethyl 2,5-bis[(5-benzyloxycarbonyl-3,4-diethylpyrrol-2-yl)methyl]-4-(phthalimidomethyl)pyrrole-3-carboxylate* (13) (0·04 g) as colourless microcrystals, m.p. 197–198° (Found: C, 71·5; H, 6·6; N, 6·6. $C_{50}H_{52}N_4O_8$ requires C, 71·8; H, 6·3; N, 6·7%). ν_{max} (KBr) 3260m (NH), 1765w and 1700s (imide), 1650s cm^{-1} (ester). ^1H n.m.r. δ (300 MHz, (D_6)acetone) 10·36, br s, NH; 10·00, br s, NH; 9·93, br s, NH; 7·79–7·66, symm. m, 4H, phthalimide ring; 7·44–7·29, m, 2×$C_6\mathbf{H}_5CH_2$; 5·20, br s, 2×$C_6H_5C\mathbf{H}_2$; 5·00, s, CH_2N; 4·25, q, J 7·0 Hz, $OC\mathbf{H}_2CH_3$; 4·15, s, (pyrrolyl)$_2CH_2$; 4·02, s, (pyrrolyl)$_2CH_2$; 2·66, q, 2·62, q, 2·33, q, 2·30, q, J 7·4–7·5 Hz, 4×$C\mathbf{H}_2CH_3$; 1·25, t, J 7·0 Hz, $OCH_2C\mathbf{H}_3$; 1·04, t×2, 0·92, t, 0·88, t, J 7·4–7·5 Hz, 4×$CH_2C\mathbf{H}_3$. Mass spectrum: m/z 836 (M, 1%), 790 (2), 761 (2), 745 (16), 91 (100). The component of R_F 0·35 was identified as ethyl 5′-benzyloxycarbonyl-3′,4′-diethyl-3-phthalimidomethyl-2,2′-dipyrrylmethane-4-carboxylate (11) (0·54 g, 68%) by spectroscopic methods. Recrystallization from dichloromethane/light petroleum gave the *dipyrrylmethane* (11) as fine colourless crystals, m.p. 162–165°, raised to 166–167° on further recrystallization (Found: C, 70·1; H, 5·8; N, 7·3. $C_{33}H_{33}N_3O_6$ requires C, 69·8; H, 5·9; N, 7·4%). ν_{max} (mull) 3360w and 3290m (NH), 1775w and 1715s (imide), 1660s (ester), 1590w, 1530w cm^{-1}. ^1H n.m.r. δ (200 MHz, $CDCl_3$) 9·51, br s, NH; 8·05, br s, NH; 7·60, s, 4H, phthalimide; 7·46–7·28, m, 6H, $C_6\mathbf{H}_5CH_2$ and H 5; 5·29, s, $C_6H_5C\mathbf{H}_2$; 4·99, s, CH_2N; 4·22, q, J 7·1 Hz, $OC\mathbf{H}_2CH_3$; 4·06, s, (pyrryl)$_2CH_2$; 2·72, q, J 7·4 Hz, and 2·46, J 7·5 Hz, 2×$C\mathbf{H}_2CH_3$; 1·24, t,

[10] Johnson, A. A., and Price, R., *J. Chem. Soc.*, 1960, 1649.
[11] Chong, R., Clezy, P. S., Liepa, A. J., and Nichol, A. W., *Aust. J. Chem.*, 1969, **22**, 229.

J 7·1 Hz, OCH_2CH_3; 1·13, t, *J* 7·4 Hz, and 1·11, t, *J* 7·5 Hz, $2\times CH_2CH_3$. Mass spectrum: *m/z* 567 (M, 2%), 522 (3), 477 (11), 476 (28), 459 (11), 431 (16), 430 (45), 91 (100).

[2-Ethoxycarbonyl-7,8,12,13,17,18-hexaethyl-3-(phthalimidomethyl)porphyrinato]zinc(II) *(2)*

A solution of ethyl 5′-benzyloxcarbonyl-3′,4′-diethyl-3-phthalimidomethyl-2,2′-dipyrrylmethane-4-carboxylate (11) (227 mg, 0·40 mmol) in ethanol (60 ml), containing a trace of triethylamine, was hydrogenated at room temperature over 10% Pd/C for 9 days. The catalyst was filtered off, and the filtrate and washings were evaporated. Trifluoroacetic acid (5 ml) was added to the residue under nitrogen, and the mixture was stirred for 2 min and then evaporated under vacuum (0·2 mm). Dichloromethane (30 ml) was added and the solution was washed (water; saturated $NaHCO_3$) and dried (Na_2SO_4). The filtered solution (containing dipyrrylmethane (12)) was diluted to 140 ml with dichloromethane, and 3,3′,4,4′-tetraethyl-2,2′-dipyrrylmethane-5,5′-dicarbaldehyde (9) (106 mg, 0·34 mmol) was added. The solution was vigorously stirred in the dark and *p*-toluenesulfonic acid (455 mg, 2·40 mmol) in methanol (5·5 ml) was added. After 24 h a saturated solution of zinc acetate dihydrate in methanol (5·5 ml) was added and the mixture was stirred for a further 48 h. The solution was washed (water; saturated $NaHCO_3$), dried (Na_2SO_4) and evaporated. Dichloromethane (20 ml) was added to the residue. The solution was cooled and the purple crystalline product was collected and washed with dichloromethane/light petroleum (1:1). Recrystallization from chloroform/hexane gave *[2-ethoxycarbonyl-7,8,12,13,17,18-hexaethyl-3-(phthalimidomethyl)porphyrinato]zinc*(II) (2) (81 mg, 31%) as purple microcrystals, m.p. 310–315° (dec.) (Found: C, 65·9; H, 5·8; N, 8·6. $C_{44}H_{45}N_5O_4Zn.\frac{1}{3}CHCl_3$ requires C, 65·5; H, 5·6; N, 8·6%). λ_{max} ($CHCl_3$) (log ϵ): 410 (5·35), 509sh (3·55), 528sh (3·87), 543 (4·02), 587 nm (4·43). ν_{max} (KBr) 2970m, 2935w, 2870w, 1775w and 1715s (imide), 1675s (ester), 1655w, 1560w, 1545w, 1520w, 1510w cm^{-1}. ^1H n.m.r. δ (200 MHz, $CDCl_3$/(D_6)dimethyl sulfoxide) 10·92, s, 10·47, s, 9·90, s, and 9·89, s, 4×methine H; 7·83–7·79, m, and 7·64–7·59, m, phthalimide ring; 6·82, s, CH_2N; 5·04, q, *J* 7·2 Hz, OCH_2CH_3; 4·12–3·97, m, $6\times CH_2CH_3$; 1·96–1·81, m, $6\times CH_2CH_3$ and $1\times OCH_2CH_3$. Low-resolution f.a.b. mass spectrum: *m/z* 779 (5%), 778 (8), 777 (16), 776 (26), 775 (51), 774 (47), 773 (73), 772 (M+1, 62), 771 (M, 100), 770 (19), 769 (5) ($C_{44}H_{45}N_5O_4Zn$ requires *m/z* 779 (0·32%), 778 (1·68), 777 (6·95), 776 (22·27), 775 (50·55), 774 (40·35), 773 (70·74), 772 (51·65), 771 (100)).

Demetallation of Zinc Complex (2) to give Ethyl 7,8,12,13,17,18-Hexaethyl-3-(phthalimidomethyl)porphyrin-2-carboxylate (3)

The (porphyrinato)zinc(II) complex (2) (52 mg) was suspended in chloroform (3·0 ml), and stirred with 5% v/v sulfuric acid in ethanol (75 ml) in the dark for 3 days. Water (100 ml) was added and the product was extracted with chloroform (2×80 ml; 1×20 ml). The extract was washed (water; saturated $NaHCO_3$), dried (Na_2SO_4) and evaporated. Flash chromatography on silica with benzene/chloroform/diethyl ether (gradient elution, 60:39:1 to 60:37:3) separated a major component of R_F 0·44 (zinc complex R_F 0·33). Recrystallization of the major fraction from chloroform/hexane gave the *title porphyrin* (3) (40 mg, 83%) as purple needles which softened at 210–216° and melted at 237–239° (Found: C, 72·8; H, 6·5; N, 9·2. $C_{44}H_{47}N_5O_4.\frac{1}{5}CHCl_3$ requires C, 72·4; H, 6·5; N, 9·5%). λ_{max} ($CHCl_3$) (log ϵ): 410 (5·28), 513 (3·98), 552 (4·26), 576 (4·01), 632 nm (3·07). ν_{max} (KBr) 3315w (NH), 2965m, 2930m, 2870w, 1770w and 1715s (imide), 1700sh (ester), 1610w, 1580w, 1535w cm^{-1}. ^1H n.m.r. δ (200 MHz, $CDCl_3$) 11·00, s, 10·64, s, 9·97, s, and 9·96, s, 4×methine H; 7·84–7·73, m, and 7·60–7·49, m, phthalimide ring; 6·77, CH_2N; 5·07, q, *J* 7·2 Hz, OCH_2CH_3; 4·33–3·90, m, $6\times CH_2CH_3$; 1·98–1·82, m, $6\times CH_2CH_3$, $1\times OCH_2CH_3$; 3·24, br s, 2×NH. Mass spectrum: *m/z* 711 (12%), 710 (50), 709 (M, 100), 332 (11), 331 (25), 79 (10).

Ethyl 3-(Aminomethyl)-7,8,12,13,17,18-hexaethylporphyrin-2-carboxylate (4)

The 3-(phthalimidomethyl)porphyrin-2-carboxylate (3) (20 mg, 0·028 mmol), hydrazine hydrate (0·09 ml, 1·86 mmol) and ethanol (6 ml) were sonicated in an ultrasonic bath for 8 h and then stirred in the dark at 20° for 36 h. The mixture was evaporated, and the residue was treated with water (15 ml) and dilute acetic acid (to pH 5). The solution was extracted with dichloromethane (2×10 ml), basified to pH 10 with concentrated ammonia, and reextracted with dichloromethane (3×10 ml). The last three extracts were combined,

dried (Na_2SO_4) and evaporated, and the residue was chromatographed on neutral alumina (activity I, 63–200 μm, 250 by 25 mm) with gradient elution (chloroform/diethyl ether/benzene, 6:2:2 with a trace of pyridine, to methanol/chloroform/diethyl ether/benzene, 6:60:20:14, and methanol/chloroform, 1:1). Fractions containing a component of R_F 0·3 (6:2:2 solvent above) were evaporated, and the residue was recrystallized from chloroform/ethanol to give *ethyl 3-(aminomethyl)-7,8,12,13,17,18-hexaethylporphyrin-2-carboxylate* (4) as a dark green-purple solid (4 mg, 25%), m.p. 227–237° (Found (high-resolution f.a.b. mass spectrum): *m/z* 580·364±0·009. $C_{36}H_{46}N_5O_2$ (M+1) requires *m/z* 580·365). λ_{max} (4% v/v chloroform in methanol) (log ϵ): 406 (5·09), 513 (3·73), 554 (4·10), 578 (3·84), 632 nm (3·19). ν_{max} (KBr) 3430br,w, 3320w, 3150br,vw (NH_2 and internal NH), 2965s, 2930s, 2805br,w, 2715br,w, 2600br,vw, 1705s (C=O), 1670br(sh),w, 1615w, 1585w, 1525m cm^{-1}. ^1H n.m.r. δ (300 MHz, $CDCl_3$/(D_6)dimethyl sulfoxide) 11·19, s, 10·39, s, 10·01, s, and 9·98, s, 4×methine H; 9·13, br s, 2·8H (RNH_3^+?); 5·80, s, CH_2N; 4·98, q, *J* 7·1 Hz, OCH_2CH_3; 4·31–4·08, m, 4×CH_2CH_3; 3·98, q, *J* 7·4 Hz, 2×CH_2CH_3; 1·98–1·86, m, 6×CH_2CH_3, 1×OCH_2CH_3; 3·45, s, 2×NH. Mass spectrum (c.i.): *m/z* 582 (1%), 581 (10), 580 (M+1, 19), 567 (13), 566 (50), 565 (100), 533 (10), 71 (12), 57 (26), 56 (11), 55 (14). The mother liquors from recrystallization of (4) contained some starting material (3) and a green component of R_F 0·8 later identified as the 3-formyl compound (5) and probably derived from decomposition of (4).

Ethyl 7,8,12,13,17,18-Hexaethyl-3-formylporphyrin-2-carboxylate (5)

Ethyl 3-(aminomethyl)-7,8,12,13,17,18-hexaethylporphyrin-2-carboxylate (4) (14 mg) was heated under reflux and under nitrogen in benzene (60 ml) for 4 days. The benzene was evaporated and the residue was subjected to flash chromatography on silica with gradient elution (chloroform/diethyl ether/benzene, 60:20:20, to chloroform/diethyl ether/benzene/methanol, 60:20:18:2). At least five components were present but after a second chromatography the major component, R_F 0·8, was isolated as a green solid (2·5 mg), m.p. 200–210°, identified as *ethyl 7,8,12,13,17,18-hexaethyl-3-formylporphyrin-2-carboxylate* (5) (Found (high-resolution f.a.b. mass spectrum): *m/z* 579·334±0·009. $C_{36}H_{43}N_4O_3$ (M+1) requires *m/z* 579·3335). λ_{max} ($CHCl_3$) (log ϵ): 311 (4·07), 340 (4·19), 370 (4·24), 426 (4·78), 533 (3·42), 581 (4·00), 610sh (3·82), 652sh nm (3·40). ν_{max} (KBr) 3320w (NH), 2960s, 2930s, 2870m, 1695s (ester), 1660s (CH=O), 1615w, 1590w, 1510s cm^{-1}. ^1H n.m.r. δ (200 MHz, $CDCl_3$) 11·75, s, 11·15, s, 11·05, s, 9·79, s (2H), 4×methine H and CH=O; 4·95, q, *J* 7·1 Hz, OCH_2CH_3; 4·19–3·85, m, 6×CH_2CH_3; 1·97–1·79, m, 6×CH_2CH_3, 1×OCH_2CH_3; 2·79, br s, 2×NH.

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