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PORPHYRINS.

24.* IDENTIFICATION OF ISOMERIC MONOESTERS OF NATURAL PORPHYRINS BY PMR SPECTROSCOPY

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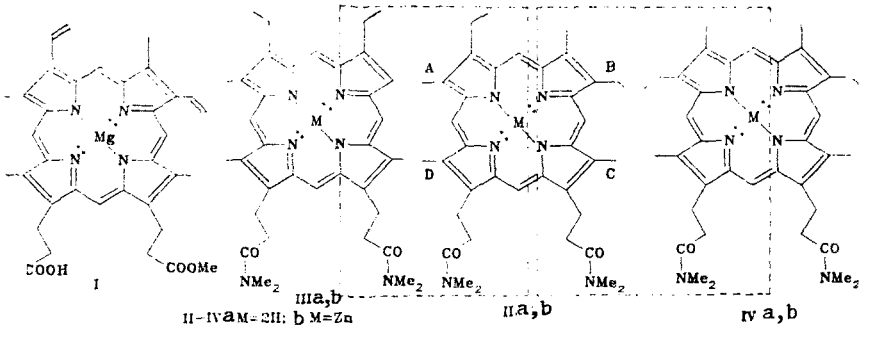
The monomethyl esters of mono(dimethylamides) and the bisdimethylamides of mesoporphyrin-IX, mesoporphyrin-III, and mesoporphyrin-XIII have been obtained, together with their zinc complexes. A relationship has been found between the chemical shifts of the signals for $CONMe_2$ in the PMR spectra and the positions of the substituents in the porphyrin ring, enabling a correct assignment to be made for the first time of these signals to the groups in positions 13^2 and 17^2 of the porphyrin ring, to establish the structures of the isomeric monomethyl esters of mesoporphyrin-IX, and to develop a method of identifying monoesters of natural porphyrins by converting them into the monoesters of the mono(dimethylamides) of mesoporphyrin-IX, followed by examination of their PMR spectra.

The first step in the biosynthesis of chlorophyll is the formation of the monomethyl ester of the magnesium complex of protoporphyrin-IX (I), in which the presence of an esterified propionic acid residue in ring C (position 13) has not been strictly identified, but has been assumed solely by analogy with the structure of chlorophyll [2]. For this reason, the correct identification of the isomeric monomethyl esters of porphyrin (I) is of considerable interest.



The broken lines identify identical fragments of the molecule in derivatives of mesoporphyrin-IX, mesoporphyrin-III, and mesoporphyrin-XIII.

*For Communication 23, see [1].

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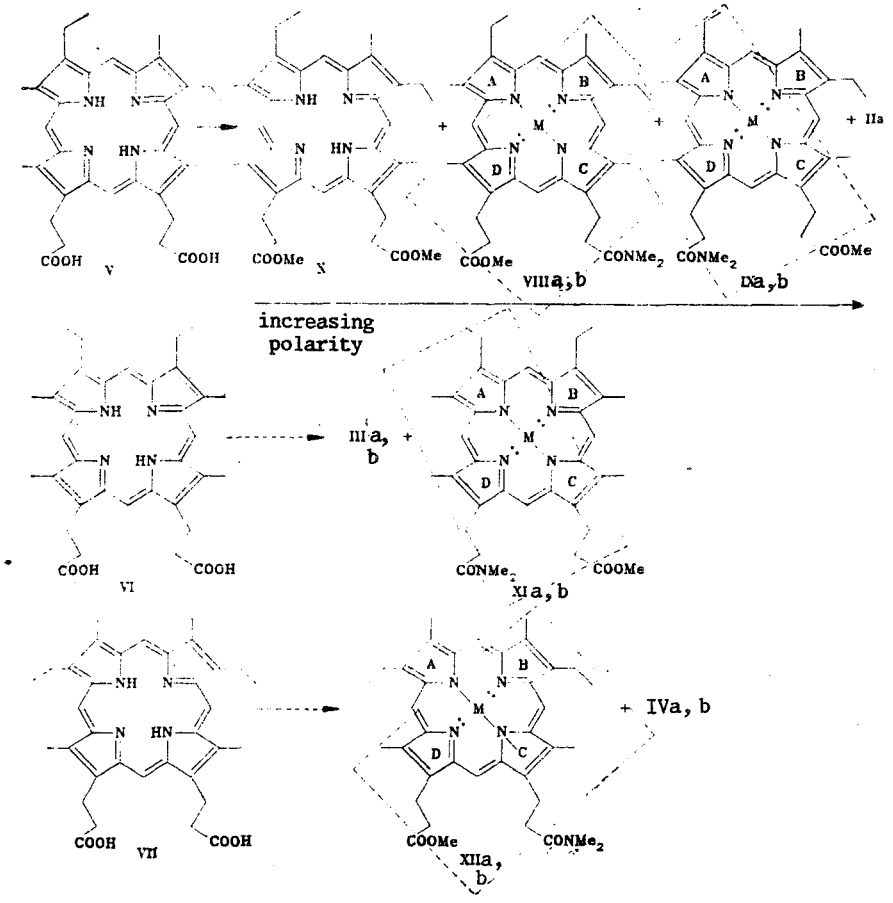
An examination of the PMR spectra of the unsymmetrical bis(dimethylamide) of mesoporphyrin-IX (IIa) showed that the signals for the amide methyl protons were present in the spectrum as four singlets (Table 1). The nonequivalence of the amide groups in (IIa) showed that the structures of the pyrrole rings A and B have a significant effect on the chemical shifts of the signals for the NMe_2 groups.

In order to confirm this, we synthesized the bis(dimethylamides) of mesoporphyrin-III (IIIa) and mesoporphyrin-XIII (IVa), which are symmetrical with respect to the amide residues. In the PMR spectra of these compounds, the singlet signals corresponding to the NMe_2 groups were two in number (Table 1), i.e., it was confirmed that the substituents in rings A and B affect the chemical shifts of the protons of the dimethylamide groups, and consequently there was a definite possibility of establishing the structures of the mono(dimethylamides) of mesoporphyrin-IX by comparing their PMR spectra with those of the monoamides of mesoporphyrin-III and mesoporphyrin-XIII.

The bis(dimethylamides) of mesoporphyrin-IX (IIa), mesoporphyrin-III (IIIa), and mesoporphyrin-XIII (IVa) were obtained by treatment of the starting porphyrins mesoporphyrin-IX (V), mesoporphyrin-III (VI), and mesoporphyrin-XIII (VII) with thionyl chloride followed by dimethylamine.



III, IV, VIII, IX, XI, XII a M=2H; b M=Zn

The broken lines identify identical fragments of the molecule in derivatives of mesoporphyrin-IX, mesoporphyrin-III, and mesoporphyrin-XIII.

A mixture of isomeric monomethyl esters of mono(dimethylamides) of porphyrin-IX (VIIIa and IXa) was obtained as follows. Porphyrin (Va) was esterified as described in [3]. As soon as the accumulation of hemiesters has reached a maximum, the porphyrins were isolated from the reaction mixture and treated with thionyl chloride, followed by dimethylamine. Separation of the reaction products on a column of silica gel gave (in order of mobility) the dimethyl ester of porphyrin-IX (X), a mixture of monoamides, and the bisamide (IIa). The mixture of isomeric monoamides was separated by preparative HPLC into the pure compounds (VIIIa) and (IXa).

TABLE 1. PMR Spectra of mono- and bis(Dimethylamides) of Mesoporphyrin-IX, Mesoporphyrin-III, and Mesoporphyrin-XIII

Compound	meso-H, s	CH_2CH_2COO, t	CH_2CH_3, q	ring CH_3 and OCH_3, s	CH_2CH_2COO, t	13-$N(CH_3)_2$, s	17-$N(CH_3)_2$, s	CH_2CH_3, t	NH, s
II a	10,11 (1H); 10,10 (2H); 10,09 (1H)	4,45 (4H)	4,10 (4H)	3,67 (3H); 3,66 (3H); 3,64 (6H)	3,28 (4H)	2,91 (3H); 2,66 (3H)	2,88 (3H); 2,60 (3H)	1,87 (6H)	−3,77 (2H)
III a	10,10 (2H); 10,09 (2H)	4,45 (4H)	4,10 (4H)	3,66 (6H); 3,63 (6H)	3,28 (4H)	2,87 (6H);	2,61 (6H)	1,87 (6H)	−3,75 (2H)
IV a	10,09 (4H)	4,44 (4H)	4,08 (4H)	3,64 (6H); 3,61 (6H)	3,26 (4H)	2,88 (6H);	2,62 (6H)	1,83 (6H)	−3,78 (2H)
VIIIa	10,08 (4H)	4,46 (2H); 4,42 (2H)	4,09 (4H)	3,67 (6H); 3,65 (9H)	3,26 (4H)	2,89 (3H); 2,62 (3H)	—	1,84 (6H)	−3,83 (2H)
IXa	10,09 (4H)	4,47 (2H); 4,43 (2H)	4,09 (4H)	3,64 (6H); 3,62 (6H); 3,61 (3H)	3,28 (4H)	—	2,88 (3H); 2,57 (3H)	1,84 (6H)	−3,81 (2H)
XIa	10,10 (4H)	4,44 (2H); 4,40 (2H)	4,08 (4H)	3,65 (6H); 3,62 (9H)	3,25 (4H)	2,86 (3H);	2,57 (3H)	1,85 (6H)	−3,76 (2H)
XIIa	10,10 (4H)	4,45 (2H); 4,41 (2H)	4,09 (4H)	3,65 (6H); 3,62 (9H)	3,27 (4H)	2,89 (3H);	2,61 (3H)	1,84 (6H)	−3,77 (2H)
II b	9,70 (1H); 9,65 (1H); 9,60 (1H); 9,59 (1H)	4,29 (2H); 4,26 (2H)	3,99 (2H); 3,93 (2H)	3,55 (3H); 3,51 (3H); 3,48 (3H); 3,46 (3H)	3,15 (2H); 3,12 (2H)	2,86 (3H); 2,59 (3H)	2,79 (3H); 2,45 (3H)	1,79 (3H); 1,76 (3H)	
IIIb	9,85 (1H); 9,80 (2H); 9,69 (1H)	4,32 (4H)	4,04 (4H)	3,56 (6H); 3,52 (6H)	3,16 (4H)	2,81 (6H);	2,49 (6H)	1,82 (6H)	
IVb	9,72 (2H); 9,70 (2H)	4,33 (4H)	3,93 (4H)	3,53 (6H); 3,49 (6H)	3,16 (4H)	2,83 (6H);	2,55 (6H)	1,75 (6H)	
VIIIb	9,74 (1H); 9,71 (1H); 9,66 (1H); 9,63 (1H)	4,32 (2H); 4,23 (2H)	3,98 (2H); 3,95 (2H)	3,72 (3H); 3,67 (3H); 3,64 (3H); 3,61 (6H)	3,14 (4H)	2,86 (3H); 2,53 (3H)	—	1,78 (3H); 1,76 (3H)	
IXb	9,78 (1H); 9,75 (1H); 9,69 (1H); 9,68 (1H)	4,27 (4H)	3,96 (4H)	3,64 (3H); 3,58 (3H); 3,56 (3H); 3,53 (3H); 3,50 (3H)	3,14 (4H)	—	2,80 (3H); 2,40 (3H)	1,78 (6H)	
XIb	9,68 (1H); 9,67 (1H); 9,65 (2H)	4,32 (2H); 4,26 (2H)	3,94 (4H)	3,64 (3H); 3,55 (6H); 3,52 (3H); 3,49 (3H)	3,15 (2H); 3,16 (2H)	2,80 (3H); 2,42 (3H)		1,77 (6H)	
XIIb	9,70 (1H); 9,68 (1H); 9,67 (2H)	4,33 (2H); 4,28 (2H)	3,94 (2H); 3,91 (2H)	3,63 (3H); 3,53 (6H); 3,48 (3H); 3,47 (3H)	3,17 (2H); 3,16 (2H)	2,86 (3H); 2,52 (3H)		1,75 (6H)	

Similarly, from mesoporphyrin-III (VI) there was obtained porphyrin (XIa), and from mesoporphyrin-XIII (VII), porphyrin (XIIa).

The zinc complexes of (IIb-IVb), (VIIIb), (IXb), (XIb), and (XIIb) were obtained by reacting the porphyrins (IIa-IVa), (VIIIa), (IXa), (XIa), and (XIIa) with zinc acetate in chloroform–methanol (3:1).

In the porphyrin (XIa), the structures of the pyrrole rings A and C, which are adjacent to ring D, which contains an amide residue, are identical with porphyrin (IXa). Since the effects of the substituents in the 'inverted' ring B on the chemical shifts of the $N-CH_3$ protons are reduced as a result of their steric remoteness, porphyrin (XIa) provides a model for isomer (IXa). Similarly, porphyrin (XIIa) is a model for (VIIIa).

Similar reasoning in the case of bis(dimethylamides) (IIa-IVa) leads to the conclusion that the chemical environment of the $CONMe_2$ group in the symmetrical amide (IIIa) is similar to that of the $CONMe_2$ group in the 17^2 position in (IIa), while the $CONMe_2$ group in the 13^2 position in this compound is similar to that of the same groups in the amide (IVa).

In the PMR spectra of porphyrins (XIa) and (XIIa), the signals for the protons of the $N-CH_3$ amide protons in (XIIa) are shifted to lower field relative to the same signals in (XIa). In the isomeric porphyrins (VIIIa) and (IXa), the relative positions of the signals for the $CONMe_2$ group were found to be the same (Table 1). The signals for the less polar isomer were seen at lower field, and for the more polar, at higher field. Since the low-field shift is characteristic of the model porphyrin (XIIa), and the high-field shift corresponds to (XIa), it may be concluded that the less polar isomer of the monomethyl ester of the mono(dimethylamide) of mesoporphyrin-IX is (VIIIa), and the more polar is (IXa).

In the PMR spectrum of the diamide (IIa), the protons of the $CONMe_2$ group are seen as two pairs of singlets. In the symmetrical porphyrins (IIIa) and (IVa), the $CONMe_2$ protons are present as a single pair of signals only, this lying at lower field in (IVa) than in (IIIa) (Table 1). It follows that in the bis(dimethylamide) (IIa), the low-field pair of signals corresponds to the $CONMe_2$ group in the 13^2 position, and the high-field pair to the same group in the 17^2 position of the porphyrin ring.

The PMR spectral characteristics observed for the porphyrins (a shift in the $CONMe_2$ signals to lower field in the amide derivatives of mesoporphyrin-XIII relative to the signals for mesoporphyrin-III, and a corresponding shift in the signals for the $CONMe_2$ group in the 13^2 position relative to the signals for this group in the 17^2 position for mono- and bis(dimethylamide) derivatives of mesoporphyrin-XI), are also characteristic of the zinc complexes (IIb-IVb), (VIIIb), (IXb), (XIb), and (XIIb) (Table 1), confirming that this is a true effect, and excludes the possibility of a chance coincidence of the chemical shifts of the $CONMe_2$ groups in the model compounds and those in question here.

To summarize, the following principal conclusions may be drawn: 1) structure (VIIIa) is assigned to the isomer of the monomethyl ester of mesoporphyrin-IX mono(dimethylamide) which is less polar and has a low-field shift of the signals for the protons of the $CONMe_2$ groups, whereas the more polar isomer, in which the signals for the $CONMe_2$ groups are shifted to high field, has the structure (IXa); 2) in the PMR spectrum of the diamide (IIa), of the two groups of signals corresponding to the dimethylamido-group in the 13^2 position, and that shifted to higher field to the dimethylamido group in the 17^2 position; and 3) the structure of the naturally-occurring monomethyl ester of protoporphyrin-IX may be established by hydrogenation to the corresponding mesoporphyrin, conversion of the free ethoxycarbonyl substituent to the dimethylamide, and examination of its PMR spectrum.

EXPERIMENTAL

Absorption spectra were obtained on a Specord UV-VIS in chloroform, IR spectra in KBr disks on a Perkin-Elmer 398, and PMR spectra on a Bruker WM-250, internal standard TMS, as solutions in $CDCl_3$. The R_f values were measured on Silufol plates in the system chloroform–ethanol (9:1). Separation of isomers (VIIIa) and (IXa) was effected on an Altex 111A chromatograph using a preparative Lobar column (25 × 310 mm) and an Ultrasphere Si analytical column (4.6 × 250 mm), with a Hitachi UV detector operating at 400 nm. Mesoporphyrin-IX (V) was obtained by hydrogenating naturally-occurring protohemin in formic acid over a palladium catalyst [4]. Mesoporphyrin-III (VI) was prepared as described in [5]. Mesoporphyrin-XIII (VII) was synthesized as described in [6]. The porphyrins were crystallized as in [7]. The PMR spectra of the products and their zinc complexes are given in Table 1.

2,7,12,18-Tetramethyl-3,8-diethyl-13,17-bis(2-N,N-dimethylaminocarbonylethyl)porphyrin (IIa). Mesoporphyrin-IX (V) (563 mg; 1 mmole) was dissolved in a mixture of 20 ml (275 mmole) of thionyl chloride and 0.2 ml (2.6 mmole) of dimethylformamide. After 30 min, the solution was evaporated to dryness, and the residue dissolved in 100 ml of methylene chloride, cooled to 0°C, and 2 ml (41 mmole) of dimethylamine added. After 1 h the solvent was evaporated to dryness, and the residue dissolved in 200 ml of methylene chloride, washed with 50 ml of water, dried over Na_2SO_4, and passed through an alumina column (d = 5 cm, h = 3 cm). The solvent was removed to dryness, and the residue crystallized from a mixture of methylene chloride and heptane. Yield 584 mg (94%). R_f 0.42, λ_{max} ($\varepsilon \cdot 10^{-3}$): 400 (145), 499 (13.2), 535 (9.5), 568 (6.5), 621 nm (4.7). IR spectrum: 1655 (C=O), 3315 cm^{-1} (N–H). Found: C 73.6; H 7.8; N 13.3%. $C_{38}H_{48}N_6O_2$. Calculated: C 73.5; H 7.8; N 13.5%.

2,8,12,18-Tetramethyl-3,8-diethyl-13,17-bis(2-N,N-dimethylaminocarbonylethyl)porphyrin (IIIa) was obtained from mesoporphyrin-III (VI) as for porphyrin (IIa). Yield 89%. R_f 0.31. λ_{max} ($\varepsilon \cdot 10^{-3}$): 401 (184), 502 (13.2), 537 (9.3), 569 (6.2), 623 nm (4.3). IR spectrum: 1635 (C=O), 3315 cm^{-1} (N–H). Found: C 73.4; H 7.8; N 13.3%. $C_{38}H_{48}N_6O_2$. Calculated: C 73.5; H 7.8; N 13.5%.

3,7,12,18-Tetramethyl-2,8-diethyl-13,17-bis(2-N,N-dimethylaminocarbonylethyl)porphyrin (IVa) was obtained from mesoporphyrin-XIII (VII) as for (IIa). Yield 90%. R_f 0.54. λ_{max} ($\varepsilon \cdot 10^{-3}$): 400 (100), 501 (9.5), 534 (6.7), 569 (4.4), 622 nm (3.3). IR spectrum: 1640 (C=O), 3305 cm^{-1} (N–H). Found: C 73.5; H 7.8; N 13.4%. $C_{38}H_{48}N_6O_2$. Calculated: C 73.5; H 7.8; N 13.5%.

2,7,12,18-Tetramethyl-3,8-diethyl-13,17-bis(2-N,N-dimethylaminocarbonylethyl)porphyrin, Zinc Complex (IIb). 93 mg (0.15 mmole) of porphyrin IIa and 220 mg (1 mmole) of $Zn(OAc)_2 \cdot H_2O$ were boiled in a mixture of 100 ml of chloroform-methanol (3:1) for 10 min, then cooled, washed with water (2 × 50 ml) dried over Na_2SO_4, filtered and passed through an alumina column (d = 3 cm, h = 1 cm). The solvent was removed to dryness, and the residue crystallized from a mixture of chloroform–hexane. Yield 99 mg (97%). R_f 0.37. λ_{max} ($\varepsilon \cdot 10^{-3}$): 404 (259), 535 (15.8) 571 nm (19.3). IR spectrum: 1604, 1645 cm^{-1} (C=O). Found: C 66.7; H 6.8; N 12.2%. $C_{38}H_{46}N_6O_2Zn$. Calculated: C 66.7; H 6.8, N 12.2%.

2,8,12,18-Tetramethyl-3,8-diethyl-13,17-bis(2-N,N-dimethylaminocarbonylethyl)porphyrin Zinc Complex (IIIb) was obtained from (IIIa) as for complex (IIb). Yield 98%. R_f 0.43. λ_{max} ($\varepsilon \cdot 10^{-3}$): 404 (265), 537 (13.1), 573 nm (16.8). IR spectrum: 1600, 1640 cm^{-1} (C=O). Found: C 66.5; H 6.8; N 12.2%. $C_{38}H_{46}N_6O_2Zn$. Calculated: C 66.7; H 6.8; N 12.2%.

3,7,12,18-Tetramethyl-2,8-diethyl-13,17-bis(N,N-dimethylaminocarbonylethyl)porphyrin Zinc Complex (IVb) was obtained from (IVa) as for complex (IIb). Yield 91%. R_f 0.51. λ_{max} ($\varepsilon \cdot 10^{-3}$): 404 (236), 536 (9.6), 571 nm (11.4). IR spectrum: 1600, 1640 cm^{-1} (C=O). Found: C 66.5; H 6.8; N 12.2%. $C_{38}H_{46}N_6O_2Zn$. Calculated: C 66.7; H 6.8; N 12.2%.

2,7,12,18-Tetramethyl-3,8-diethyl-13(17)-(2-methoxycarbonylethyl)-17(13)-(2-N,N-dimethylaminocarbonylethyl)porphyrins (VIIIa) and (IXa). Mesoporphyrin-IX (V) was dissolved in a mixture (50 ml) of tetrahydrofuran, methanol, and concentrated sulfuric acid (1:0.1:0.01). After 45 min 7.84 ml of 10% aqueous NaOH was added to pH 7-8. The solvent was evaporated to dryness, and the residue washed with 100 ml of water, dried, and dissolved in 20 ml (275 mmole) of thionyl chloride with the addition of 0.2 ml (2.6 mmole) of dimethylformamide. After 0.5 h, the solution was evaporated to dryness, and the residue dissolved in 100 ml of methylene chloride, cooled to 0°C, and 2 ml (41 mmole) of dimethylamine added. After 1 h, the solvent was removed to dryness, the residue washed with 100 ml of water, dried, dissolved in 50 ml of methylene chloride, and chromatographed on a column of silica gel (d = 3.5, h = 40 cm) in the system methylene chloride–acetone (95:5). Three fractions were obtained. Fraction 1 was evaporated to dryness, and the residue crystallized from a mixture of methylene chloride and methanol to give 155 mg (26%) of (X), R_f 0.89. IR spectrum: 1740 (C=O), 3323 cm^{-1} (N–H). Fraction 2 was evaporated to dryness, and the residue crystallized from methylene chloride–heptane to give 195 mg (32%) of a mixture of porphyrins (VIIIa) and (IXa). R_f 0.71. λ_{max} ($\varepsilon \cdot 10^{-3}$): 402 (180), 501 (13.1), 536 (9.5), 571 (6.4), 623 nm (4.5). IR spectrum: 1645 (amide C=O), 1735 (ester C=O), 3310 cm^{-1} (N–H). Found: C 73.2; H 7.5; N 11.5%. $C_{37}H_{45}N_5O_3$. Calculated: C 73.1; H 7.5; N 11.5%.

The isomeric porphyrins (VIIIa) and (IXa) were separated by double chromatography on a Lobar preparative column. A total of 30 mg of porphyrins was separated, in quantities of 10 mg. The eluent was chloroform containing 0.5% of ethanol, rate of elution 6 ml/min. The

fractions containing more than 70% of one of the isomers were separated, evaporated to dryness, and subjected to repeated chromatography. The combined fractions containing 90% or more of isomer (VIIIa) were evaporated to dryness, and the residue crystallized from heptane to give 8 mg of 2,7,12,18-tetramethyl-3,8-diethyl-13-(2-N,N-dimethylaminocarbonylethyl)-17-(2-methoxycarbonylethyl)porphyrin (VIIIa). A control separation was carried out on an Ultrasphere Si analytical column, the eluent being a mixture of purified chloroform and hexane (3:2), rate of elution 1 ml/min, emergence time of (VIIIa) 18.11 min, emergence time for traces of the isomeric porphyrin (IXa) 19.16 min, isomer ratio 0.91:0.09. Similarly, there was obtained 6 mg of 2,7,12,18-tetramethyl-3,8-diethyl-13-(2-methoxycarbonylethyl)-17-(2-N,N-dimethylaminocarbonyl)porphyrin (IX). Control separation showed its isomeric purity to be 89%.

Fraction 3 was evaporated to dryness, and the residue crystallized from a mixture of methylene chloride and heptane to give 211 mg (34%) of (IIa), identical on TLC and IR spectroscopy to that obtained earlier.

2,8,12,18-Tetramethyl-3,7-diethyl-13-(2-methoxycarbonylethyl)-17-(2-N,N-dimethylaminocarbonylethyl)porphyrin (XIa) was obtained from mesoporphyrin-III (VI) as for (VIIIa) and (IXa). Yield 31%. R_f 0.67. λ_{max} ($\varepsilon \cdot 10^{-3}$): 401 (174), 500 (12.2), 535 (7.5), 570 (5.5), 622 nm (3.1). IR spectrum: 1640 (amide C=O), 1735 (ester C=O), 3310 cm^{-1} (N—H). Found: C 72.3; H 7.4; N 11.5%. $C_{37}H_{45}N_5O_5$. Calculated: C 73.1; H 7.5; N 11.5%.

3,7,12,18-Tetramethyl-2,8-diethyl-13-(2-N,N-dimethylaminocarbonylethyl)porphyrin (XIIa), was obtained from mesoporphyrin-XII (VII) as for (VIIIa) and (IXa). Yield 32%. R_f 0.7. λ_{max} ($\varepsilon \cdot 10^{-3}$) 401 (92), 500 (8.5), 534 (6.1), 569 (4.0), 622 nm (2.8). IR spectrum: 1642 (amide C=O), 1735 (ester C=O), 3310 cm^{-1} (N—H). Found: C 72.6; H 7.6; N 11.5%. $C_{37}H_{45}N_5O_5$. Calculated: C 73.1; H 7.5; N 11.5%.

Zinc complexes of 2,7,12,18-tetramethyl-3,8-diethyl-13(17)-(2-methoxycarbonylethyl)-17-(2-N,N-dimethylaminocarbonylethyl)porphyrins (VIIIb and IXb) were obtained as for the zinc complex (IIb), from a mixture of isomeric porphyrins (VIIIa) and (IXa). Yield 97%, R_f 0.65. λ_{max} ($\varepsilon \cdot 10^{-3}$): 405 (202), 538 (11.6), 572 nm (14.3). IR spectrum: 1595, 1645 (amide C=O), 1732 cm^{-1} (ester C=O). The isomeric zinc complexes (VIIIb) and (IXb) were obtained in quantitative yields on heating porphyrins (VIIIa) and (IXa) with zinc acetate in chloroform.

2,8,12,18-Tetramethyl-3,7-diethyl-13-(2-methoxycarbonylethyl)-17-(2-N,N-dimethylaminocarbonylethyl)porphyrin zinc complex (XIb), was obtained as for zinc complex (VIIIb) and (IXb), from (XIa). Yield 95%. R_f 0.68. λ_{max} ($\varepsilon \cdot 10^{-3}$): 404 (202), 537 (12.0), 573 nm (15.8). IR spectrum: 1600, 1645 (amide C=O), 1733 cm^{-1} (ester C=O).

3,7,12,18-Tetramethyl-2,8-diethyl-13-(2-N,N-dimethylaminocarbonylethyl)-17-(2-methoxycarbonylethyl)porphyrin zinc complex (XIIb) was obtained as for the zinc complexes (VIIIb) and (IXb), from (XIIa). Yield 95%, R_f 0.7. λ_{max} ($\varepsilon \cdot 10^{-3}$) 404 (126), 537 (8.7), 572 nm (10.0). IR spectrum: 1600, 1645 (amide C=O), 1735 cm^{-1} (ester C=O).

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