temperature and failed to catalyze the addition reaction. The latter case is particularily surprising because the perfluorophenyl group is reported to be about as electron attracting as the bromine atom.[3] Our previous work[5] suggests, however, that there is an equilibrium between the free TMT and bis(perfluorophenyl)zinc in solution, which may not be very favorable for the complex at higher temperatures. The reaction was not carried out with an excess of the diarylzinc and consequently the reactions actually observed were those of essentially uncomplexed TMT.

Appendix

Product Labeling Pattern in the Reaction of Indene with Deuterated and Undeuterated TMT, Assuming Random Redistribution. The equation used for the calculation of the theoretical values for the isotopic distribution in 1,2-bis(dimethylamino)indane is based on a binomial distribution. Thus, the value for the fraction of a given isotopic peak, $P(M)$, in the molecular ion of the diaminoindane is given by:

$$P(M) = 0.859D_n{}^2 + 2D_xD_y + 0.131D_{n-1}{}^2 + 2D_kD_l + 0.008D_{n-2}{}^2 + 2D_iD_j$$

D = relative isotopic abundances in the dimethylamino groups, assuming randomization. The subscripts, are integers, which range from 0 to 6

$$x + y = n; l + k = n - 1; i + j = n - 2$$

The coefficients were evaluated from the known isotopic composition of carbon and nitrogen and the fact that the molecule being examined has 13C and 2N, 85.9% of the ions in a given isotopic peak of the parent cluster have 13^{12}C and 2^{14}N, 13.1% have either one ^{13}C or one ^{15}N, and 0.8% have two mass units contributed by the heavier isotopes.

A given D is evaluated independently from the isotopic distribution of the parent dimethylnitrosamine-d_6, using the equation

$$D_z = (N_z - 0.028N_{z-1}) + 0.028N_z$$

Where N's are the intensities of a given peak in the parent ion of the nitrosamine, and 0.028 is the correction factor for ^{13}C and ^{15}N.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 76-24095). We are grateful to Mr. Joseph Mahaffy for pointing out how to do the statistical analysis of the deuterium label randomization.

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Petroporphyrins. 1. Preliminary Characterization of the Porphyrins of Gilsonite

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Abstract: Eight predominantly single carbon number porphyrin fractions were isolated chromatographically from a bitumen, gilsonite (Eocene, Uinta Basin, Utah). Each alkyl porphyrin fraction was analyzed by ^{1}H NMR, mass spectrometry, and LC. The seven etioporphyrins isolated ranged from C_{29} to C_{32} and contained only methyl, ethyl, and hydrogen substituents, but no meso (bridge) alkyl groups. One of the two C_{29} etioporphyrin fractions was unambiguously assigned as 2-ethyl-3,7,8,12,13,17,18-heptamethylporphine. The presence of an isocyclic ring was confirmed in the C_{31} DPEP porphyrin fraction. One of the two C_{32} DPEP porphyrins isolated cochromatographed on LC with standard deoxophylloerythroetioporphyrin. The combined spectrometric and chromatographic data indicate that the porphyrins are derived from chlorophyll *a*.

Introduction

Alkyl porphyrins in geological samples (petroporphyrins) occur as complex mixtures of two major series: the deoxophylloerythroetio (DPEP) and etio types (**1** and **2**, respectively).[1-4] It has been suggested that they are derived from defunctionalization of naturally occurring chlorophylls,[5-7] with additional carbon atoms in the higher members (>C_{32}) arising from either diagenetic transalkylation or chlorobium chlorophylls.[8] Evidence for these hypotheses was provided only by visible absorption and mass spectrometric data from total petroporphyrin mixtures. It is essential to isolate single carbon number species and elucidate their structures to investigate

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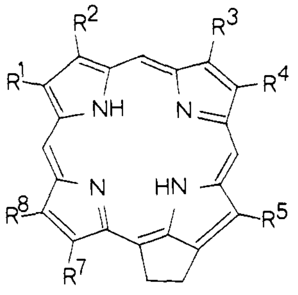
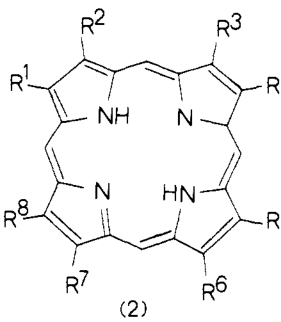


(1)



(2)

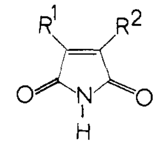
(1) $R^1,R^2,R^3,R^4,R^5,R^7,R^8$ = H or Alkyl

(1a) $R^1=R^3=R^5=R^8=CH_3$; $R^2=R^4=R^7=C_2H_5$

(2) $R^1,R^2,R^3,R^4,R^5,R^6,R^7,R^8$ = H or Alkyl

(2a) $R^1=R^3=R^5=R^8=CH_3$; $R^2=R^4=R^6=R^7=C_2H_5$

(2b) $R^1=C_2H_5$; $R^2=R^3=R^4=R^5=R^6=R^7=R^8=CH_3$



(3)

(3a) $R^1=R^2=CH_3$

(3b) $R^1=C_2H_5$; $R^2=CH_3$

further the origin of the petroporphyrins.

Gilsonite, a bitumen from the Uinta Basin, Utah, was selected as it has a simple distribution of nickel petroporphyrins in high concentration (ca. 100 ppm).[8-11] It was believed that isolation of single carbon number members would be facilitated by initial separation on thin layer chromatography (TLC) before demetalation, and by further chromatographic separation after demetalation. We report the chromatographic and spectrometric data for the isolated fractions and discuss their importance with respect to possible origins.

Results

The distributions of total nickel petroporphyrins, and of the fractions separated initially by TLC, were obtained by electron impact mass spectrometry (EIMS) (Table I). All three fractions contain both DPEP and etioporphyrins, and the carbon number maximum of each series increases with decreasing polarity (Table I). Certain of the fractions are not completely resolved (see below) because of small differences in R_f values (Table I). Fraction A was demetalated and rechromatographed (TLC) to yield eight products, designated A1, the most polar, to A8, the least polar; fractions B and C were treated similarly. Fraction B4 was separated by preparative high-performance liquid chromatography (LC) to give two fractions: fraction B4.1, mainly C_{30} etioporphyrin, and B4.2, predominantly C_{29} etioporphyrin.

EIMS. The spectra showed eight of the demetalated fractions to consist predominantly (>85%) of single carbon number species (Table II). Using MS only it is impossible to determine whether the porphyrins are single compounds or isomeric mixtures. Thus, B1 (C_{32} DPEP) gave two peaks on LC analysis, although the fraction has only one significant molecular ion. All fractions showed $(M - 15)^+$ as the major fragment ion, indicating benzylic cleavage of an ethyl substituent.[12-14] The low carbon number ($\leq C_{28}$) fractions (A5, A7, A8) showed this fragmentation, which gives evidence for one or more unsubstituted β positions. High-resolution MS data were obtained for A3 and C3 (C_{29} and C_{32} etioporphyrins, respectively), which confirmed the presence of the alkyl substituents (Table II).

Table I. Mass Spectrometric Data for Nickel Petroporphyrins of Gilsonite

	total Ni petroporphyrins	chromatographed fractions[a]		
		A	B	C
abundance, ppm	100	50	30	20
R_f		0.40-0.45	0.46-0.49	0.51-0.53
DPEP distribution[b]	C_{27}-C_{33}	C_{28}-C_{33}	C_{28}-C_{33}	C_{27}-C_{33}
DPEP maximum	C_{31}	C_{31}	C_{32}	C_{33}
etio distribution[c]	C_{27}-C_{32}	C_{27}-C_{32}	C_{27}-C_{32}	C_{27}-C_{32}
etio maximum	C_{30}	C_{29}	C_{30}	C_{31}
DPEP/etio ratio	1.6:1	3:1	3:2	1:3

[a] TLC on silica gel G (toluene-hexane, 1:1, v:v). [b] Corrected for ^{13}C contributions. [c] Corrected for ^{13}C and ^{60}Ni contributions.

Fourier Transform ^1H Nuclear Magnetic Resonance Spectrometry (^1H NMR). Spectra were obtained for A1, A3, A4, A6, B3, B4.1, C2, and C3 (Table III). The spectrum of A1 (C_{31} DPEP) was run in deuteriotrifluoroacetic acid to compare the chemical shifts with those of deoxophylloerythroetioporphyrin synthesized by Flaugh and Rapoport.[15] ^1H NMR showed that all the fractions contain methyl and ethyl substituents. The absence of absorptions at ca. 2.25 indicates that the porphyrins do not contain propyl groups.[16] Similarly, meso (bridge) methyl substituents were absent because absorptions at δ 4.6 were not observed.[17]

Fraction C3, a C_{32} etioporphyrin, has a very similar spectrum to that of etioporphyrin III (**2a**). However, it is also possible that this fraction is an isomeric mixture as all the positional isomers have very similar spectra.[18] The spectra of fractions A3 and A6 are particularly interesting; both compounds are C_{29} etiopetroporphyrins with the former totally substituted and the latter with an unsubstituted β position. This confirms the presence of porphyrin isomers in oils and bitumens, indicated in previous mass spectrometric studies.[3,10] The combined mass spectrometric and ^1H NMR data show that A3 is 2-ethyl-3,7,8,12,13,17,18-heptamethylporphine (**2b**), which was confirmed by oxidation to the maleimides (see below). The isocyclic ring in the DPEP fraction A1 is confirmed by the multiplet at δ 5.7.[15]

Oxidative Degradation. Fraction A3 was degraded to maleimides using a modification of the method of Ellsworth and Aronoff[19] to give 3,4-dimethylmaleimide (**3a**) and 3-ethyl-4-methylmaleimide (**3b**) in the ratio 2.6:1, confirming its structure as 2-ethyl-3,7,8,12,13,17,18-heptamethylporphine (**2b**).

TLC and LC. The LC retention times of the single carbon number porphyrins on 5μ Partisil are listed in Table II. There was good correlation between the combined TLC and MS data, and those of LC, with the exception of fractions A2 and B1, in which the C_{32} DPEP porphyrins were resolved into two components by LC. All the other species, which are mainly single components by TLC and MS information, produced only one major peak on LC.

The DPEP porphyrins are more polar than the etioporphyrins, although there is overlap in R_f between the etio fraction and the DPEP fractions A3, B2, and C1 (Table IV). The TLC data indicate that the polarity of the etioporphyrins relates directly to both carbon number and the number of unsubstituted β positions. Hence, A3 which is a fully alkyl-substituted C_{29} petroporphyrin, is more polar than A4, a fully alkyl-substituted C_{30} etioporphyrin, and A6, a monounsubstituted C_{29} etioporphyrin. There are insufficient data to determine the mode of separation of the DPEP porphyrins. The strongest evidence to date for the presence of deoxophylloerythroetioporphyrin (**1a**) in petroporphyrin distributions was obtained when the synthetic standard[20] cochromatographed

Table II. LC and Mass Spectrometric Data from Petroporphyrin Fractions of Gilsonite and Etioporphyrin III

fraction	significant ions *m/e* (%)	LC		major component	other components and comments
		min t_R,	% purity[a]		
A1	476 (3), 464 (7), 463 (35), 462 (100), 448 (6), 449 (18), 432 (5)	12.8	86	C_{31} DPEP	trace C_{32} DPEP
A2	490 (6), 477 (35), 476 (100), 462 (28), 448 (18), 447 (7)	12.8	27	C_{32} DPEP	C_{31} DPEP and trace C_{33} DPEP
		12.1	30		
		11.6	36		
A3[b]	462 (8), 448 (6), 438 (7), 437 (35), 436 (100), 422 (10), 421 (44), 420 (8)	10.2	92	C_{29} etio	trace C_{31} DPEP, C_{30} DPEP
A4	452 (6), 451 (33), 450 (100), 435 (36), 423 (8), 422 (12), 421 (11)	9.0	89	C_{30} etio	trace C_{28} etio
A5	450 (15), 424 (6), 423 (28), 422 (100), 408 (16), 407 (25)	8.7	74	C_{28} etio	trace C_{30} etio
A6	450 (5), 438 (10), 437 (30), 436 (100), 422 (20), 421 (45), 409 (10), 408 (18), 407 (13)	8.0	96	C_{29} etio	trace C_{27} etio, C_{30} etio
A7	478 (4), 464 (6), 450 (21), 436 (10), 435 (12), 422 (11), 408 (100), 393 (47)	7.0	20		
		7.5 7.6	80	C_{27} etio	probably two C_{27} etio + C_{30} etio
A8	478 (20), 464 (30), 450 (19). 436 (15), 422 (100), 408 (54), 407 (52)		c	C_{28} etio	complex mixture of C_{27}–C_{32} etio
B1	490 (5), 478 (8), 477 (36), 476 (100), 461 (26), 447 (4), 431 (6)	12.0	42	C_{32} DPEP	trace C_{33} DPEP; C_{32} DPEP components cochromatograph with C_{32} DPEP components in A2
		11.5[d]	56[d]		
B2	476 (20), 462 (100), 448 (55), 446 (38), 436 (20)		c	C_{31} DPEP	complex mixture of DPEP with etio
B3	452 (10), 451 (36), 450 (100), 436 (10), 435 (35), 422 (2)	9.1	100	C_{30} etio	cochromatographs with A4
B4	464 (10), 452 (14), 451 (37), 450 (100), 436 (80), 422 (42), 421 (46)	8.0	40	C_{29} + C_{30} etio	C_{28} etio + trace C_{31} etio; C_{29} cochromatographs with A6
		6.8	50		
C1	504 (18), 492 (10), 491 (35), 490 (100), 476 (15), 475 (25), 461 (12)	10.9	73	C_{33} DPEP	trace C_{34} DPEP, C_{32} DPEP
C2	478 (8), 464 (100), 450 (13), 449 (33), 436 (7), 435 (10)	8.1	98	C_{31} etio	trace C_{32} etio
C3[b]	480 (10), 479 (35), 478 (100), 463 (35), 450 (6)	7.2	96	C_{32} etio	trace C_{30} etio
etio-III	480 (10), 479 (38), 478 (100), 464 (12), 463 (39), 448 (14)	7.2			
B4.1	452 (12), 451 (30), 450 (100), 435 (30), 423 (10), 422 (12), 421 (6)	6.8	93	C_{30} etio	trace C_{28} etio

[a] From LC peak areas, assuming similar extinction coefficients. [b] Accurate mass: $C_{29}H_{32}N_4$ requires 436.262, found 436.263; $C_{32}H_{38}N_4$ requires 478.309, found 478.310. [c] Complex mixture. [d] Cochromatographs with authentic deoxophylloerythroetioporphyrin.

Table III. ^{1}H NMR Data for Isolated Petroporphyrin Fractions and Standard Etioporphyrin III

fraction	principal component	solvent	chemical shift, δ ppm, and peak multiplicity (no. of substituents)[a]					
			ring CH_3	ring CH_2CH_3[b]	ring CH_2CH_3[b]	H	meso H	isocyclic ring
A1	C_{31} DPEP	CF_3CO_2D	3.66 s (5)	4.10 m (2)[c]	1.78 m (2)		10.56 s 10.50 s (3)	5.71 m 4.34 m[c] (1)
A3	C_{29} etio	$CDCl_3$	3.61 s (7)	4.19 m (1)[d]	1.87 t (1)[d]		10.06 s (4)	
A4	C_{30} etio	$CDCl_3$	3.61 s 3.64 s (6)	4.10 q (2)	1.87 t (2)		10.07 s (4)	
A6	C_{29} etio	$CDCl_3$	3.60 3.63 m (5) 3.75	4.11 m (2)	1.88 m (2)	9.08 s (1)	10.03 10.07 m (4) 10.11	
B3	C_{30} etio	$CDCl_3$	3.60 s 3.63 s (6)	4.10 q (2)	1.86 t (2)		10.07 s (4)	
B4.1	C_{30} etio	$CDCl_3$	3.66 3.65 m (4) 3.74	4.16 m (3)	1.88 m (3)	9.11 s (1)	10.08 m (4)	
C2	C_{31} etio	$CDCl_3$	3.64 s (5)	4.10 q (3)	1.87 t (3)		10.08 s (4)	
C3	C_{32} etio	$CDCl_3$	3.64 s (4)	4.10 q (4)	1.87 t (4)		10.09 s (4)	
etio-III	standard	$CDCl_3$	3.64 s (4)	4.10 q (4)	1.88 t (4)		10.08 s (4)	

[a] Hydrocarbon impurities with chemical shifts (ca. δ 1.25 and 0.88) present in varying amounts in all the isolated petroporphyrins. [b] Chemical shifts at center of quartet or triplet. [c] Ring CH_2CH_3 + 2 protons from isocyclic ring overlap. [d] Weak spectrum, and integration data only approximate for CH_2 and CH_3 groups. s = singlet, t = triplet, q = quartet, m = multiplet.

Table IV. R_f Values and Absorption Spectra of the Demetalated Porphyrin Fractions of Gilsonite

fraction	principal component	visible spectrum, nm[a]					R_f
		Soret	band IV	band III	band II	band I	
A1	C_{31} DPEP	399	500	534	565	619	0.05-0.11
A2[c]	C_{32} DPEP	399	500	534	566	619	0.14-0.18
A3	C_{29} etio	400	498	531	566	618	0.23-0.26
A4	C_{30} etio	399	498	532	566	619	0.34-0.36
A5	C_{28} etio	398	498	533	567	621	0.39-0.41
A6	C_{29} etio	399	499	532	567	621	0.44-0.46
A7	C_{27} etio	399	498	532	566	621	0.60-0.61
A8[b]	C_{28} etio	399	500	534	565	618	0.64-0.65
B1[c]	C_{32} DPEP	399	500	533	566	619	0.15-0.18
B2[b]	C_{31} DPEP	399	498	531	564	617	0.22-0.24
B3	C_{30} etio	399	498	532	566	619	0.33-0.35
B4	C_{29} C_{30} etio	399	498	533	566	620	0.43-0.45
C1	C_{33} DPEP	399	496	531	564	621	0.25-0.27
C2	C_{31} etio	398	499	531	565	618	0.38-0.40
C3	C_{32} etio	399	500	533	567	620	0.48-0.50

[a] Accuracy of wavelength ±2 nm. [b] Complex mixture. [c] There are two C_{32} DPEP components.

on LC with the less polar of the two C_{32} DPEP porphyrins (B1) on 5μ Partisil. It is not possible at present to distinguish positional isomers in the DPEP series using either TLC or LC, and so it is not certain whether the single carbon number fractions are isomeric mixtures or single compounds.

Discussion

Gilsonite is associated with the Green River formation[21] and has a mild thermal history;[22] therefore, the petroporphyrins are unlikely to have undergone severe thermal alteration. Previous investigations of the distributions by MS have shown considerable variations,[8-11] which is not surprising because the properties of the substances vary significantly even within the same deposit.[23]

Separation of the Nickel Petroporphyrins. Fractionation of the nickel porphyrins before demetalation and further separation facilitates isolation of single carbon number porphyrins as it permits separation of some components, e.g., A3 and B2, which would cochromatograph on TLC as free-base porphyrins under the conditions used (Table IV). The complete resolution of the three metalloporphyrin fractions is difficult owing to the small differences in R_f values (Table I). Thus, fractions B3 and A4 probably contain the same major components because they have similar chromatographic and spectrometric properties. Similarly, fractions B1 and A2, and B4 and A6, have some components in common. Nevertheless, the advantages gained from decreasing the complexity of the total mixture before demetalation outweigh any problems from incomplete separation of the fraction.

Origin of the Petroporphyrins of Gilsonite. The results of this study indicate that the current hypotheses on the origins of the petroporphyrins require modification and extension.[5-8] Random alkylation processes, such as transalkylation, should lead to a more complex petroporphyrin distribution with a greater variety of substituents than that observed in this sample. The absence of meso (bridge) alkyl substituents also provides evidence against transalkylation[8] since the in vitro studies of Bonnett et al.[24] suggest that vanadyl octaethylporphyrin undergoes meso alkylation on heating with montmorillonite. The absence of propyl or isobutyl substituents in the fractions examined by ^1H NMR provides evidence that the chlorobium chlorophylls[8] are not major precursors of the porphyrins of gilsonite. The NMR data provide proof of the isocyclic ring of the only DPEP fraction (A1) isolated as essentially a single component, and LC information indicates the presence of deoxophylloerythroetioporphyrin in fraction B1. This information gives weight to the proposal that chlorophyll *a* is the major precursor; however, the degradation pathway proposed by Treibs[5] does not account for the presence of the two C_{32} DPEP porphyrins. Deoxophylloerythroetioporphyrin (**1a**) would be the only C_{32} DPEP predicted by the Treibs scheme. The NMR data also confirm the presence of porphyrin isomers in gilsonite; this was first indicated in the mass spectrometric studies of Alturki et al.[10]

The presence of at least one ethyl substituent even in low carbon number ($\leq C_{28}$) fractions provides evidence that the ethyl substituent in chlorophyll *a* remains intact throughout the degradation pathway, and implies that the four methyl substituents in chlorophyll *a* also remain intact. Thus, only the vinyl, isocyclic ring, and propionic substituents appear to undergo dealkylation and/or defunctionalization reactions, producing a limited number of isomers for each carbon number petroporphyrin. Therefore, the presence of 2-ethyl-3,7,8,12,13,17,18-heptamethylporphine can be rationalized on this basis. The data obtained here support the hypothesis that chlorophyll *a* is the major precursor of the gilsonite porphyrins.

Conclusions

The major petroporphyrins of gilsonite may be isolated as essentially single carbon number fractions via initial TLC separation of their nickel complexes followed by demetalation and further chromatography. The major DPEP porphyrin contains an isocyclic ring, and one of the two C_{32} DPEP isomers coinjects with synthetic deoxophylloerythroetioporphyrin on LC. All the etioporphyrins examined by ^1H NMR contain methyl and ethyl substituents, but no meso (bridge) alkyl substituents. One fraction, A3, was unambiguously assigned as 2-ethyl-3,7,8,12,13,17,18-heptamethylporphine.

The study indicates the porphyrins may derive from defunctionalization of chlorophyll *a*; however, the pathway is more complex than that predicted by Treibs,[5] as is shown by the presence of two C_{32} DPEP porphyrins. The evidence does not support the operation of random alkylation of the porphyrins.

Experimental Section

General. ^1H NMR spectra were obtained using a JEOL PFT-100 spectrometer in the Fourier transform mode, and chemical shifts are listed in parts per million on the δ scale from internal Me_4Si. Mass spectra were recorded using the direct insertion probe of a Varian MAT CH-7 mass spectrometer linked via a Carrick interface (Instem Ltd.) to a PDP 8e computer. High-resolution mass spectra were recorded on an A.E.I. MS902 mass spectrometer, using the peak matching technique with perfluorokerosene as internal standard. The samples were introduced by direct insertion probe, and elemental compositions from accurate mass measurements were obtained on a Digital Equipment Corp. LINC-8 computer. UV-visible absorption spectra were obtained on a Unicam SP 800 spectrophotometer. LC analyses were carried out on stainless steel columns (25 cm × 4.6 mm) packed with 5μ Partisil. The equipment comprised two Waters M6000D pumps, a Waters M660 solvent programmer, and a Varian Variscan 2635M detector, fitted with 8-μL flow cells. The solvents used were toluene-hexane (1:9, v:v) as solvent A and toluene-chloroform (1:1, v:v) as solvent B, programmed (10 min) from 25% B to 75% B using a linear program and a flow rate of 1.5 mL min^{-1} [25] GLC analysis of maleimides was performed on a Carlo Erba 2150 gas chromatograph using a glass column (20 m × 0.30 mm i.d. capillary coated with OV-1) using helium as carrier gas with a flow rate of 1 mL min^{-1}, programming from 60 to 260 °C at 4 °C min^{-1}.

TLC separations were carried out on Kieselgel G Type 60 (0.5 mm), preeluted with $CH_3CO_2C_2H_5$ and reactivated at 100 °C (2 h). All solvents were distilled before use.

Isolation and Chromatography of Nickel Petroporphyrins. Typically, powdered gilsonite (60 g) was extracted with toluene and methanol (1:1, v:v, 125 mL) by sonication (5 × 20 min) and centrifugation (2500 rpm, 20 min). The eluant was decanted and evaporated under reduced pressure, leaving a black tar (12.7 g, 21%) which was purified by column chromatography on alumina (300 g, BDH Ltd., grade II) using gradient elution of CH_2Cl_2 in hexane. The eluates were monitored by absorption spectrometry, and the petroporphyrin-containing fractions were combined and evaporated to dryness to produce an orange-red oil (1.5 g). This was purified further by column chromatography on silica gel (60 g, Hopkin and Williams Ltd., M.F.C. 100-200 mesh) by gradient elution using the same solvent system and monitoring as above. The crude metalloporphyrin mixture (60 mg) was separated into three fractions labeled A, R_f 0.40-0.45 (3 mg), B with R_f 0.46-0.49 (2 mg), and C, R_f 0.51-0.54 (1 mg), by TLC on Kieselgel G, eluting with toluene-hexane (1:1, v:v).

Isolation of Demetalated Petroporphyrin Fractions. Each fraction was demetalated with methanesulfonic acid[26] (0.5 mL) at 110 °C (2 h). The cooled solution was neutralized by saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was washed with water (2 × 10 mL), dried over Na_2SO_4, and evaporated to dryness. The demetalated porphyrins were purified by TLC, eluting twice with toluene-CH_2Cl_2 (1:1, v:v). Fraction A yielded eight components, A1-A8; fraction B yielded four components, B1-B4; fraction C yielded three components, C1-C3. The R_f values and visible absorption data are listed in Table IV.

Isolation of Fraction B4.1. Fraction B4 was a mixture of C_{29} and C_{30} etioporphyrins; the C_{30} etio component was isolated by preparative LC on 5μ Partisil. The mixture (30 × 10 μg) was eluted under isocratic conditions with hexane-toluene-methylene chloride (27:5:2, v:v:v) at 1.5 mL min^{-1} and the C_{30} etio fraction (t_R 8.8 min) was collected.

Degradation of Fraction A3. Fraction A3, C_{29} etioporphyrin (100 μg), was dissolved in trifluoroacetic acid (2 drops), and a solution of chromic oxide (0.33 g) in dilute H_2SO_4 (2.5 mL, 25%, w/v) preextracted with CH_2Cl_2 (3 × 10 mL). The yellow solution was maintained at 0 °C for 2 h and then left to stand at room temperature for 2 h. The solution was extracted with CH_2Cl_2 (4 × 2 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$ (2 mL) preextracted with CH_2Cl_2, then water (2 mL). The organic phase was evaporated to dryness. The products were analyzed on GLC and the structures of the products were confirmed by coinjection with standards. The ratio of 3,4-dimethylmaleimide and 3-ethyl-4-methylmaleimide was 2.6:1.

Acknowledgments. We thank the late Professor G. W. Kenner and Professor K. M. Smith for providing a sample of etioporphyrin III. We thank Professor E. W. Baker for a sample of deoxophylloerythroetioporphyrin and 3-ethyl-4-methylmaleimide. We are grateful to Morris Ashby Ltd. and the American Gilsonite Co. for the gifts of gilsonite. We wish to thank the National Aeronautics and Space Administration (Subcontract from NGL 05-003-003) for financial support. The computing and mass spectrometric facilities were provided by the Natural Environment Research Council (GR3/2951) and the Nuffield Foundation. We are most grateful to Mrs. A. P. Gowar and Dr. M. Murray for obtaining mass spectra and NMR spectra, respectively, and to Dr. S. K. HajIbrahim for valuable discussions. This paper is dedicated to the memory of Professor G. W. Kenner, with thanks from a grateful student (J.M.E.Q.).

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