3,8,17-Triethyl-2,7,12,18-tetramethylporphyrin: a Widely-occurring Pigment of Chlorophyll Origin

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The structure of the title compound (1c), a major aetioporphyrin in Serpiano shale, has been assigned by nuclear Overhauser enhancement (n.O.e.) difference studies of the acetyl derivative.

Recent studies of the complex mixtures of alkyl metalloporphyrins in sedimentary organic matter have demonstrated the presence of a number of components with an exocyclic ring. Their structures are consistent with an origin *via* degradative pathways which have altered naturally-occurring chlorophylls.[1,2] Less attention has been paid to the other major type of fossil porphyrins, the aetioporphyrins, with the exception of the occurrence of (**1a**) and (**1b**) in an Eocene bitumen,[3,4] and (**1b**) in a Permian shale.[5]

We report here the structure of a C_{30}-component, a major aetioporphyrin of Serpiano oil shale (Triassic, Monte San Giorgio, Switzerland), in which it occurs mainly as the vanadyl complex. There is circumstantial evidence to indicate that the compound occurs widely in both sedimentary rocks and oils of different ages as the nickel and/or vanadyl complex.[4,6—8]

Components (**1c**) and (**2**) were isolated from a monoacetylated fraction as described previously.[9] Both compounds have mass spectra (high resolution, $C_{32}H_{36}N_4O$ and $C_{30}H_{34}N_4$) and electronic spectra consistent with aetioporphyrins, one showing an extended chromophore [(**2**) $\lambda_{max.}$ 506, 546, 571, 630 nm; relative intensities 64 : 100 : 62 : 10, Soret 405 nm; (**1c**) $\lambda_{max.}$ 493, 527, 562, 616, 620 nm; relative intensities 100 : 55 : 45 : 25 : 10, Soret 395 nm].

In the 200 MHz ^1H n.m.r. spectrum of the Zn^{II} complex of (**1c**) the chemical shifts of three of the *meso*-protons were not resolved sufficiently for nuclear Overhauser enhancement (n.O.e.) difference studies, but at 400 MHz the shifts of the acetylated derivative [(**2**) Zn^{II} complex] allowed n.O.e. difference experiments which established connections between β-substituents and the *meso*-protons [summarised in Table 1 and on (**2**) where arrows indicate enhancements observed]. No connection between the CH_3CO group and *meso*-H at δ 10.882 was observed, and the two methyl groups at C-2 and C-18 and the two overlapping methylene groups at C-3 and C-17 could not be distinguished. These features do not affect the structure assignment.

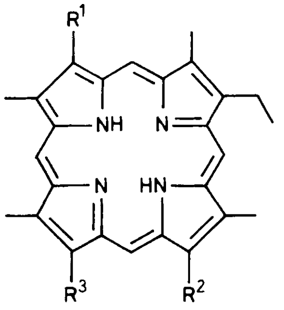
Table 1. ^1H N.m.r. data (400 MHz) for (**2**) (Zn^{II} complex) in $(CD_3)_2CO–C_5D_5N$.

δ	Multiplicity[a]	N.O.e.[b]	Assignment
10.882	s	4.085	H-15
10.309	s	4.122, 3.989	H-10
10.084	s	4.085, 3.618	H-5
10.049	s	3.604, 3.595	H-20
4.122	q (7.0, 1.891)	10.309, 3.618[c]	CH_3CH_2-8
ca. 4.085[d]	2q (7.0, 1.859)	10.882, 10.084, 3.604, 3.595	CH_3CH_2-3 CH_3CH_2-17
3.989	s	10.309, 3.324	CH_3-12
3.618	s	10.084, 4.122[c]	CH_3-7
3.604	s	10.049	CH_3-2 or 18
3.595	s	10.049	CH_3-2 or 18
3.324	s	3.989	CH_3CO-13
1.891	t (7.0, 4.122)	—[e]	CH_3CH_2-8
ca. 1.859[d]	2t (7.0, 4.085)	—[e]	CH_3CH_2-3 CH_3CH_2-17

[a] *J* Hz, δ coupled nuclei. [b] Chemical shifts where enhancements seen when δ signal irradiated. [c] Weak enhancement observed. [d] Average shift of overlapping signals. [e] Not determined.

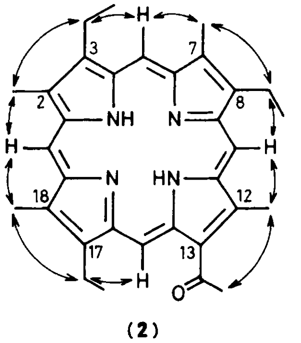
The results confirm that the parent alkyl porphyrin is (**1c**). Furthermore, (**1c**) afforded (**2**) on Cu^{II} insertion and acetylation,[9] and (**2**) was converted into (**1c**) by methanesulphonic acid. In addition, (**1c**) coeluted on analytical-scale h.p.l.c. with a significant component of the demetallated Ni^{II} porphyrin fraction from the shale, and with the synthesised compound under reverse phase conditions which separate it from structural isomers, as described in the accompanying paper.[10] The mass spectrum of the isolated compound, under H_2 chemical ionisation conditions was also compatible with (**1c**).[11]

We propose that this widely-occurring C_{30}-aetioporphyrin, with a β-H at C-13, has originated from chlorophylls *a* and/or *c*. It is noteworthy that the porphyrin acid (**1d**) has been found recently as the Ni^{II} complex in Messel oil shale,[2] which has experienced a milder thermal history than the Serpiano shale; decarboxylation of (**1d**) under sedimentary conditions could afford (**1c**). In turn, (**1d**) can be formed by degradation of chlorophyll *a* under basic conditions,[12] and has been proposed



(**1**)

a; $R^1 = R^2 = R^3 = CH_3$
b; $R^1 = R^2 = R^3 = C_2H_5$
c; $R^1 = R^3 = C_2H_5, R^2 = H$
d; $R^1 = C_2H_5, R^2 = H, R^3 = CH_2CH_2CO_2H$



(**2**)

to originate, in the Messel shale, from chlorophyll *via* cleavage of the exocyclic ring during early diagenesis.[2]

M. I. C. and G. A. W. thank the Brazilian Nation Research Council (CNPq) and the S.E.R.C. respectively for Studentships. We are grateful to British Petroleum p.l.c. and N.E.R.C. for h.p.l.c. and low resolution mass spectrometric facilities, respectively. Dr. D. Games (University College of Cardiff) is thanked for high resolution mass spectrometric measurements as are Drs. O. Howarth and E. Curzon (University of Warwick) for 400 MHz ^{1}H n.m.r. experiments.

Received, 10th January 1985; Com. 050

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