The Etioporphyrins of Oil Shale: Structural Evidence for their Derivation from Chlorophyll

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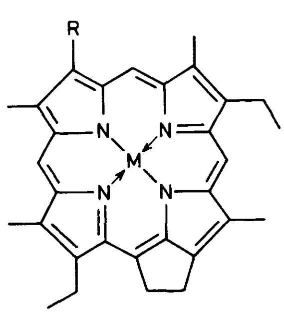
The structures of several nickel etioporphyrin homologues isolated from Julia Creek (Queensland) oil shale indicate derivation from chlorophyll.

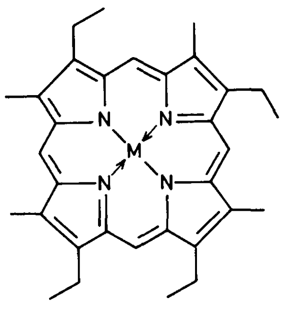
Recent reports from this laboratory[1] have supported Treibs' hypothesis[2] that the major metalloporphyrins of geological deposits [the deoxyphylloerythroetioporphyrin (DPEP) series; metallo-DPEP is shown as (**1**)] are derived from chlorophyll. However, the origin of the accompanying etiotype petroporphyrins has been the subject of some debate. In the belief that etioporphyrin-III (**2**) was the predominant member of this group and that iron was the chelated metal, Treibs proposed that protoheme (**3**) was their progenitor.[2] This proposal was apparently refuted by Glebovskaia and Volkenshtein[3] who reassigned to nickel porphyrins the visible absorption of geological extracts which Treibs had attributed to hemes; reinforcement came later with Corwin's observation[4] that chlorophyll is overwhelmingly more abundant than protoheme in the biosphere. As a consequence, the etio series of petroporphyrins was thought more likely to be derived from chlorophyll, *via* cleavage of the exocyclic ring of DPEP. This situation changed dramatically with Bonnett's recent identification of iron etiotype porphyrins, one of which was almost certainly mesoheme-IX (**4**), in two brown coals.[5] Cytochromes were suggested as possible precursors. I now

Table 1. ^{1}H N.m.r. signal assignments for (**6**), 2 mM in $CDCl_3$–C_6D_6 (1:1).

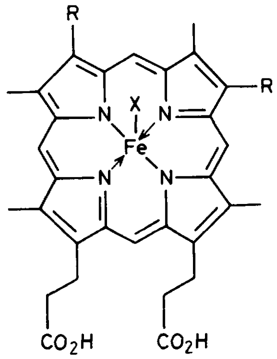
CH_3CH_2-8	1.67 (t)	CH_3-18	3.29
CH_3CH_2-17	1.65 (t)	H-3	8.87 (q, *J* 1.1 Hz)
CH_3CH_2-8	3.78 (q)	H-13	8.89 (q, *J* 1.1 Hz)
CH_3CH_2-17	3.75 (q)	H-5	9.63
CH_3-2	3.42 (d, *J* 1.1 Hz)	H-10	9.76
CH_3-7	3.26	H-15	9.66
CH_3-12	3.43 (d, *J* 1.1 Hz)	H-20	9.73



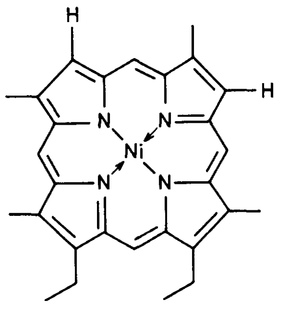
(1) R = Et, Me, H



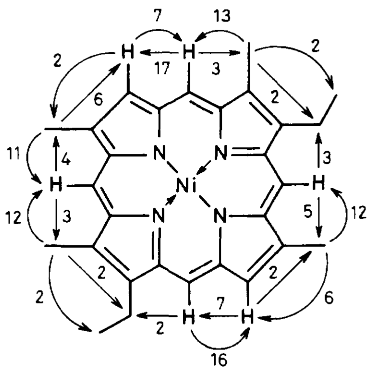
(2)



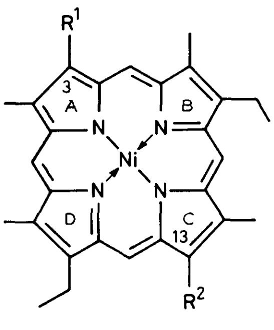
(3) R = CH=CH$_2$
(4) R = Et



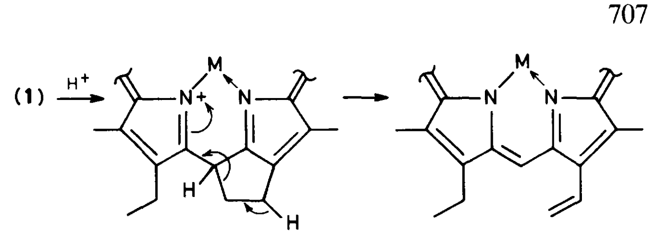
(5)



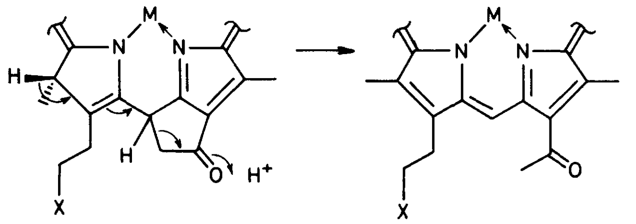
(6)



(7) $R^1 = R^2 =$ Me
(8) $R^1 = R^2 =$ Et
(10) $R^1 =$ Et, $R^2 =$ Me
(11) $R^1 =$ Me, $R^2 =$ Et
(12) $R^1 =$ Et, $R^2 =$ H
(13) $R^1 =$ H, $R^2 =$ Et
(14) $R^1 =$ Me, $R^2 =$ H
(15) $R^1 =$ H, $R^2 =$ Me



Scheme 1



(9)

X = H or CO$_2$R

Scheme 2

report that the structures of several nickel etioporphyrins isolated from Julia Creek oil shale[1a,c] strongly suggest that they are derived from chlorophyll.

Fraction G (3% of total nickel porphyrins; fractions A—F have been described elsewhere[1c,6]) had a single molecular ion corresponding to a C_{28} etioporphyrin nickel complex, and examination by ^{1}H n.m.r. spectroscopy at 300 MHz revealed that it had four *meso* protons, as expected. Signals from two β-ethyl and four β-methyl groups, plus two β-hydrogen atoms which were shown by appropriate decoupling experiments to be adjacent to β-methyl groups (^4J 1.1 Hz), were also identified. Derivation from heme would require fraction G to have structure (**5**), but this was shown not to be so by nuclear Overhauser effect (n.O.e) difference spectroscopy.[7] Thus, irradiation of the two β-protons and their adjacent β-methyl groups caused enhancement of all four *meso* proton signals. These and other irradiations made full connections around the macrocycle and led unambiguously to its identification as nickel(II) 8,17-diethyl-2,7,12,18-tetramethylporphyrin (**6**). Signal assignments are given in Table 1 and n.O.e. results [1c] appear on structure (**6**) (% enhancements).

The n.m.r. spectrum of fraction H (2%), which was shown by mass spectrometry to be a C_{30} homologue of G, revealed four *meso* protons, two β-ethyl and six β-methyl groups which were arranged to produce two-fold symmetry. N.O.e. experiments proved that the ethyl groups were adjacent to methyl groups but two structures, nickel(II) 8,17-diethyl-2,3,7,12,13,18-hexamethylporphyrin (**7**), and the isomer with reversed ring D substituents, were possible. The compound readily formed single crystals (m.p. > 300 °C) from dichloromethane–hexane, suitable for study by *X*-ray crystallography. Preliminary *X*-ray data favour structure (**7**); the *X*-ray analysis is continuing.

A third fraction (I, 4%) was identified as nickel(II) etioporphyrin-III (**8**)† since (i) its principal molecular ion occurred at *m/z* 534 (C_{32} etio), (ii) oxidative degradation[8] gave almost exclusively ethylmethylmaleimide (identified by g.c.–mass spectral comparison with an authentic sample), and (iii) its 300 MHz ^{1}H n.m.r. spectrum revealed four non-equivalent β-methyl and β-ethyl groups (Figure 1).

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† This porphyrin has also been found in the bitumen gilsonite.[8]

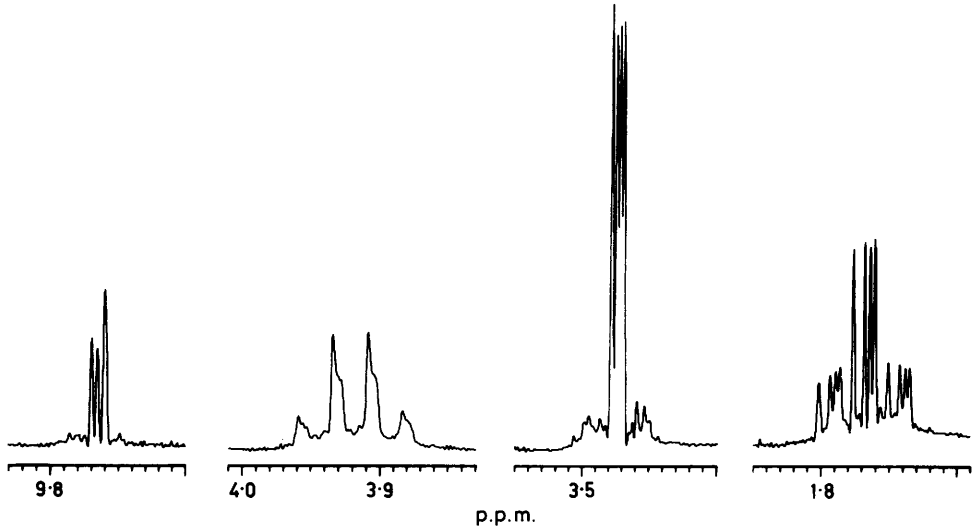

Figure 1. 300 MHz n.m.r. spectrum of (**8**) in $CDCl_3$ (3 mM). The free induction decay was Gaussian multiplied and zero filled to give 0.09. Hz digital resolution after Fourier transformation.

It is generally believed that thermal dealkylation of etioporphyrin-II as (**2**) is responsible for the formation of the lower etiotype petroporphyrin homologues. Clearly, the specificity of structures (**6**) and (**7**), with the absence of identifiable quantities of positional isomers, proves that they could not have been generated in this way from (**8**). Instead, it is likely that all three were formed from a common precursor with functional groups convertible into hydrogen, methyl, or ethyl at C-3 and C-13. Chlorophyll is the obvious candidate; its vinyl substituent is altered in exactly this manner during formation of the three DPEP homologues (**1**, M = Ni) also found in Julia Creek shale.[1c] Cleavage of the exocyclic ring in (**1**) could then produce a second vinyl group (Scheme 1) for transformation like the first. However, it is possible that generation of a 13-vinyl group (or its equivalent) could occur at a much earlier stage of chlorophyll degradation. Thus, protonation of the chlorin tautomer (**9**) could produce an acetylporphyrin (Scheme 2), while similar fragmentation of the secondary alcohol corresponding to (**9**) would give a 13-vinylporphyrin directly.

If processes such as these were responsible for the formation of (**6**), (**7**), and (**8**), then six more compounds, (**10**)—(**15**), with differential substitution at C-3 and C-13, would be expected in the shale. Indeed, three fractions (J, 4%, K, 3%, and L, 5%) with principal molecular ions corresponding to nickel C_{31}-, C_{30}-, and C_{29}-etioporphyrins, respectively, were shown by n.m.r. spectroscopy to be mixtures of at least two compounds. Although it has not yet been possible to determine the exact structures of any of these, the β-substituents of the major components were identified as: J, three ethyls and five methyls; K, three ethyls, four methyls plus a hydrogen; and L, two ethyls, five methyls, and one hydrogen. It is therefore probable that these last fractions contain the three isomeric pairs of etioporphyrin homologues (**10**)—(**15**).

The apparently different origins of the etioporphyrins from Julia Creek oil shale and brown coal[5] deserve comment. In anaerobic depositional environments, like that which is believed to have produced the Julia Creek shale,[9] the readily oxidized chlorophyll macrocycle would be preserved for transformation into petroporphyrins, including the etioporphyrins reported here. However, the more oxidizing conditions associated with brown coal formation would favour survival of the more robust, but far less abundant, protoheme-related structures. As a consequence of the different source material, the lower etioporphyrin homologues of coal would be expected to have structures different from those found in oil shale.

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