

## Structure Determination of Nickel(II) Deoxophylloerythroetioporphyrin and a C<sub>30</sub> Homologue from an Oil Shale: Evidence that Petroporphyrins are derived from Chlorophyll

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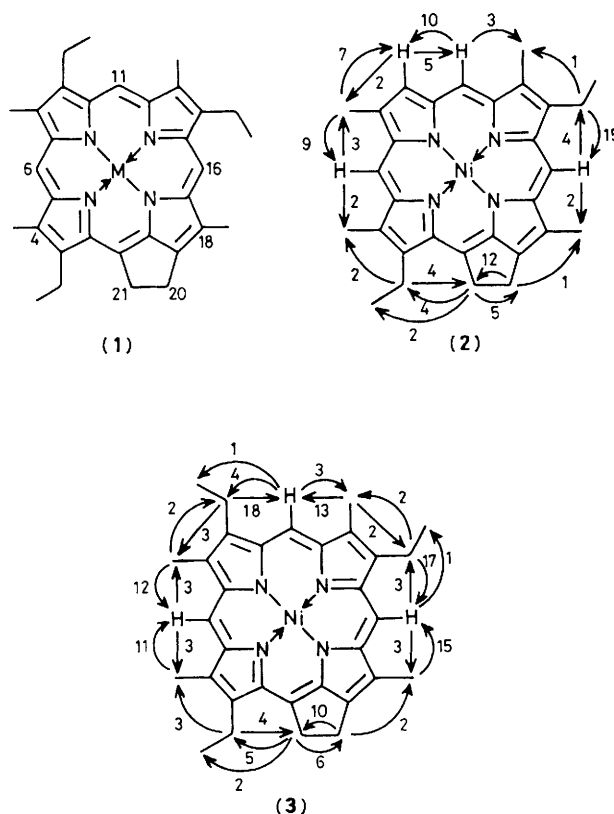
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Nuclear Overhauser effect difference spectroscopy has been used to define the structures of two porphyrins isolated from Julia Creek oil shale as nickel(II) 3,4-didehydro-3,9,14-triethyl-4,8,13,18-tetramethylphorbine (DPEP) and its 9-desethyl homologue, thereby providing support for the hypothesis that petroporphyrins originate from chlorophyll.

Verification of Treibs' hypothesis<sup>1</sup> that porphyrins of geological deposits (petroporphyrins) are derived from chlorophyll requires the isolation and unambiguous structure determination of deoxophylloerythroetioporphyrin,† DPEP [metalloDPEP is shown as (1)], or a related compound, from a geological source. Such structural proof has until now been lacking.<sup>2</sup>

In this laboratory we have examined the metalloporphyrins of the Julia Creek oil shale (Cretaceous, Toolebuc Formation, Queensland, Australia), avoiding the usual approach of strong acid-catalysed demetallation and possible artefact formation. The nickel porphyrins (11  $\mu\text{g g}^{-1}$  of shale) were separated by t.l.c. (silica, CCl<sub>4</sub>) and reverse-phase h.p.l.c. (C-18, MeOH) into 30 fractions (full details will be reported elsewhere). Two of the largest fractions (A 22 and B 9%), had single molecular ions corresponding to nickel DPEP (1; M = Ni) and its C<sub>30</sub>-homologue respectively. <sup>1</sup>H N.m.r. (300 MHz) indicated that each was essentially a single compound, with three *meso* protons and four  $\beta$ -methyls. The porphyrin in fraction A also had three  $\beta$ -ethyl substituents, while the other porphyrin had two  $\beta$ -ethyls, plus a  $\beta$ -H shown by decoupling experiments to be next to a  $\beta$ -methyl (allylic *J* 1.1 Hz, as expected<sup>3</sup>). In addition, a -CH<sub>2</sub>CH<sub>2</sub>- fragment, also adjacent to a  $\beta$ -methyl (homoallylic *J* 1.2 Hz), was identified in both porphyrins (Figure 1). Nuclear Overhauser effect (n.o.e.) studies, to determine spatial relationships of these substituents, were then required.

N.O.e. difference spectroscopy has been used successfully to examine porphyrins<sup>4</sup> and related macrocycles.<sup>5</sup> Application of this technique to the porphyrin in fraction B was straightforward, leading to its unequivocal identification as nickel(II) 3,4-didehydro-3,14-diethyl-4,8,13,18-tetramethylphorbine (2) (see Table 1 for signal assignments). Arrow heads on (2) show enhanced signals with percentage n.o.e., calculated by comparing the size ratio of positive (enhanced) and negative



(irradiated) signals in each difference spectrum with their corresponding ratio in the normal (blank irradiation) spectrum.

Initial n.o.e. difference results for A (in CDCl<sub>3</sub>) were consistent with (1; M = Ni), but overlap of signals from Me-4 and Me-18 precluded their unambiguous association with H-6 and H-16. However, this uncertainty was removed by changing the solvent to CDCl<sub>3</sub>-C<sub>6</sub>D<sub>6</sub> (2 : 3). Full n.o.e. data are given on (3),

† Systematic name: 3,4-didehydro-3,9,14-triethyl-4,8,13,18-tetramethylphorbine.

Table 1. <sup>1</sup>H N.m.r. signal assignments for (2) and (3).

	(2) <sup>a</sup>	(3) <sup>b</sup>	(3) <sup>c</sup>
CH <sub>3</sub> -CH <sub>2</sub> -3	1.67(t)	1.54(t)	1.47(t)
CH <sub>3</sub> -CH <sub>2</sub> -9	—	1.77(t)	1.72(t)
CH <sub>3</sub> -CH <sub>2</sub> -14	1.78(t)	1.78(t)	1.72(t)
CH <sub>3</sub> -CH <sub>2</sub> -3	3.92(q)	3.60(q)	3.49(q)
CH <sub>3</sub> -CH <sub>2</sub> -9	—	3.89(q)	3.80(q)
CH <sub>3</sub> -CH <sub>2</sub> -14	3.94(q)	3.90(q)	3.81(q)
CH <sub>3</sub> -4	3.51	3.35	3.23
CH <sub>3</sub> -8	3.61(d, <i>J</i> 1.1 Hz)	3.44	3.30
CH <sub>3</sub> -13	3.48	3.48	3.32
CH <sub>3</sub> -18	3.49(t, <i>J</i> 1.2 Hz)	3.35(t, <i>J</i> 1.2 Hz) <sup>d</sup>	3.24(t, <i>J</i> 1.2 Hz)
H <sub>β</sub> -20	4.02(m)	3.71(m)	3.46(m)
H <sub>β</sub> -21	5.24(m)	4.84(m)	4.59(m)
H-9	8.92(q, <i>J</i> 1.1 Hz)	—	—
H-6	9.87	9.63	9.65
H-11	9.74	9.71	9.74
H-16	9.80	9.64	9.70

<sup>a</sup> 3 mm in CDCl<sub>3</sub>. <sup>b</sup> 20 mm in CDCl<sub>3</sub>. <sup>c</sup> 20 mm in CDCl<sub>3</sub>-C<sub>6</sub>D<sub>6</sub> (2:3). <sup>d</sup> Partly obscured by CH<sub>3</sub>-4 signal.

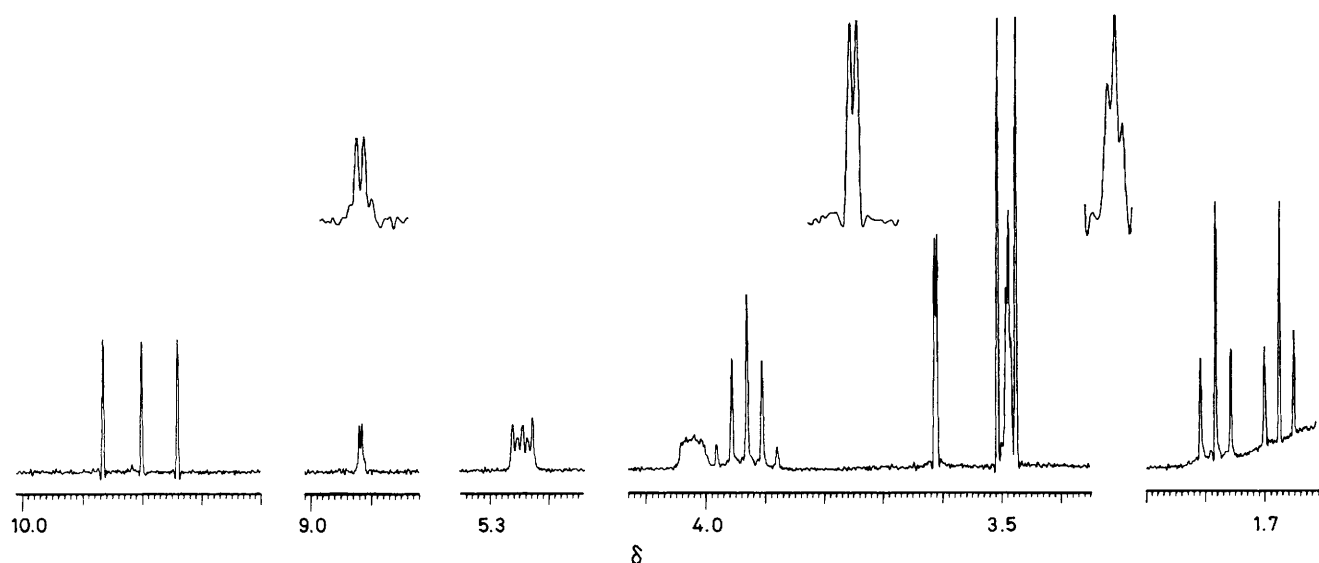


Figure 1. 300 MHz <sup>1</sup>H N.m.r. spectrum of (2) in CDCl<sub>3</sub> (3 mm). The free induction decay was Gaussian multiplied and zero filled to give 0.09 Hz digital resolution after Fourier transformation. Insets (left to right), expansion of signals at δ 8.92, 3.61, and 3.49.

in which enhancements from irradiation of H-6 and H-16 refer to CDCl<sub>3</sub>-C<sub>6</sub>D<sub>6</sub> solution results; signal assignments are reported in Table 1.

<sup>1</sup>H N.m.r. examination of a third fraction (C 12%), with molecular weight corresponding to nickel C<sub>31</sub>-DPEP, revealed five β-methyls, two β-ethyls, three *meso* protons, and a five-membered ring. Although this compound is clearly related to (2) and (3), very poor chemical shift dispersion in the methyl and *meso* proton regions prevented full characterisation by n.O.e. difference spectroscopy.

Determination of structures (2) and (3) establishes for the first time<sup>‡</sup> a definite link between petroporphyrins and chlorophyll. Generation of (2) and (3) would involve either removal or reduction of the chlorophyll vinyl substituent, reactions which vinyl porphyrins are known to undergo in the human intestine.<sup>7,8</sup> For this reason, it is suggested that bacteria play a significant role in the formation of petroporphyrins.

*Added in proof:* Recent n.O.e. difference results for C (in C<sub>6</sub>D<sub>6</sub>, 65 °C) have defined its structure as nickel(II) 3,4-dihydro-3,14-diethyl-4,8,9,13,18-pentamethylphorbine.

<sup>‡</sup> Parallel work in this laboratory (ref. 6) has resulted in the isolation and crystallisation of the major vanadyl porphyrin from Julia Creek oil shale. X-Ray crystallography established its structure as vanadyl DPEP (1; M = VO).

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