Identification of a Homologous Series of Nickel(II) 15,17-Butanoporphyrins from an Oil Shale

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Structure determination, by nuclear Overhauser effect difference spectroscopy, of three nickel porphyrins isolated from Julia Creek oil shale reveals that each contains a seven-membered exocyclic ring.

The preceding communication[1] presented evidence of the long-assumed link between petroporphyrins and chlorophyll.[2] While two DPEP[1] and two etio-type[3,4] petroporphyrins have now been characterised, structure elucidation of the many types of tetrapyrroles found in the geosphere[5] is needed before their origin and chemistry can be fully understood.

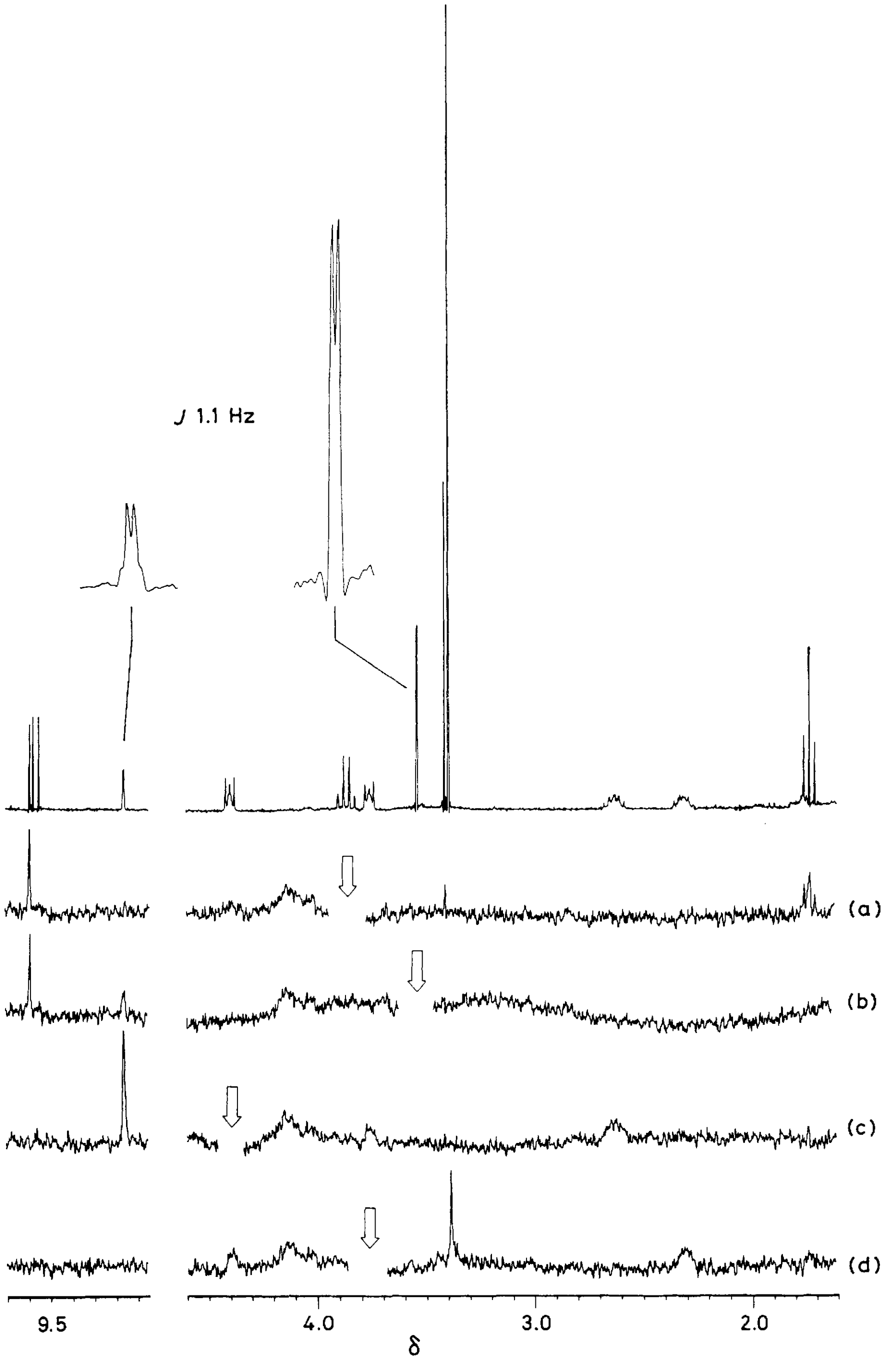
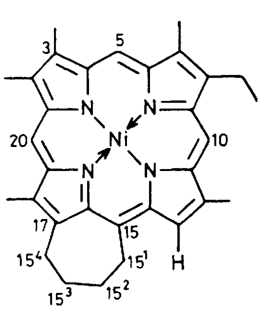


Figure 1. Resolution-enhanced 300 MHz ^{1}H n.m.r. spectrum of fraction E (1) with n.O.e. difference spectra (a)—(d) resulting from irradiation (0.2 W attenuated 45 dB) of the indicated resonances.

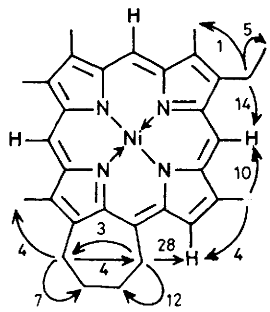
Table 1. ^1H N.m.r. signal assignments for (**1**), (**3**), and (**4**) in $CDCl_3$.

	(1)[a]	(3)[b]	(4)[c]
$C\mathit{H}_3$-CH_2-3	—	1.73(t)	—
$C\mathit{H}_3$-CH_2-8	1.73(t)	1.73(t)	1.73(t)
CH_3-$C\mathit{H}_2$-3	—	3.86(q)	—
CH_3-$C\mathit{H}_2$-8	3.87(q)	3.85(q)	3.86(q)
CH_3-2	3.39	3.40	3.54(d, *J* 1.1 Hz)
CH_3-3	3.39	—	—
CH_3-7	3.42	3.41	3.39
CH_3-12	3.54(d, *J* 1.1 Hz)	3.54(d, *J* 1.1 Hz)	3.55(d, *J* 1.1 Hz)
CH_3-18	3.39	3.38	3.41
-CH_2-15^1	4.39(m)	4.39(m)	4.40(m)
-CH_2-15^2	2.62(m)	2.61(m)	2.62(m)
-CH_2-15^3	2.31(m)	2.31(m)	2.31(m)
-CH_2-15^4	3.76(m)	3.75(m)	3.77(m)
H-3	—	—	8.84(q, *J* 1.1 Hz)
H-13	9.17(q, *J* 1.1 Hz)	9.15(q, *J* 1.1 Hz)	9.19(q, *J* 1.1 Hz)
H-5	9.55[d]	9.54	9.53
H-10	9.59	9.58	9.61
H-20	9.57[d]	9.57	9.66

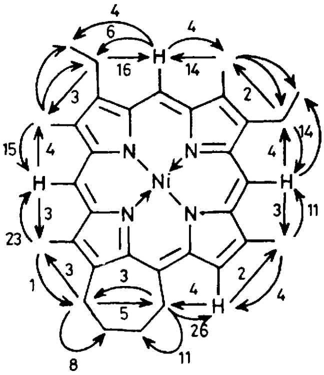
[a] 3 mM. [b] 5 mM. [c] 1 mM. [d] Assignments may be reversed.



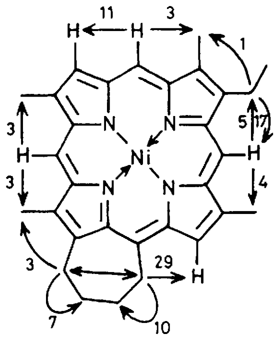
(1)



(2)

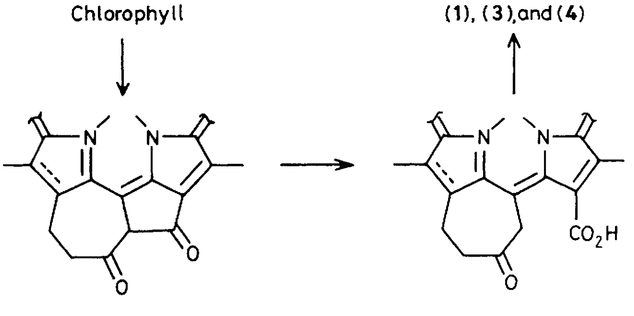


(3)



(4)

Separation of the nickel(II) porphyrins of Julia Creek oil shale[1] gave three fractions (D 4, E 2.5, and F 1.5%), which were isomeric with, but less polar than nickel C_{32}-, C_{31}- and C_{30}-DPEP respectively.† 300 MHz ^1H N.m.r., with appropriate decoupling, showed that all three porphyrins had a β-methyl group allylically coupled (*J* 1.1 Hz) to a β-H, plus three *meso* protons and a -$[CH_2]_4$- fragment attached at each end to the macrocycle. Additional β-substituents were as follows: D, two ethyls and three methyls; E, one ethyl and four methyls (Figure 1); F, one ethyl and three methyls, with one of the latter adjacent to a second β-H (allylic *J* 1.1 Hz). Structures incorporating a seven-membered exocyclic ring were therefore indicated but distinction between the many possible positional isomers required the use of nuclear Overhauser effect (n.O.e.) difference spectroscopy.[1,6] The following were key experiments in the structure determination of E (Figure 1): (a) irradiation of the ethyl methylene resulted in enhancement of the *meso* proton signal at lowest field, (b) irradiation of the methyl doublet caused enhancement of the same *meso* signal, as well as the β-H (as expected), (c) the β-H signal experienced a large increase (28%) when the low-field terminal methylene of the -$[CH_2]_4$- chain (δ 4.39) was irradiated, (d) irradiation at the other end of the chain (δ 3.76) caused enhancement of a β-methyl. These results define the structure of E as 15,17-butano-8-ethyl-2,3,7,12,18-pentamethylporphyrin (**1**); n.O.e. data are summarised on (**2**) and signal assignments appear in Table 1.



Scheme 1

Similar n.O.e. experiments showed that D and F have structures (**3**)‡ and (**4**) respectively, and so differ from (**1**) only in the nature of their C-3 substituent.

While a vinyl group could provide the three different C-3 substituents of (**1**), (**3**), and (**4**), the origin of the novel seven-membered ring is not readily apparent. An undiscovered or extinct tetrapyrrole may have been the progenitor, but it is also conceivable that the propionate side-chain of chlorophyll could, at some stage of its degradation, condense with the adjacent five-membered ring and lead to the β-diketone (**5**) (Scheme 1). Hydrolytic cleavage of the cyclopentanone ring, giving (**6**), followed by decarboxylation and deoxygenation would then provide the observed structures.

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† The occurrence of two C_{32}-DPEP isomers in the bitumen gilsonite has been reported, ref. 3.

‡ A very recent publication (ref. 7) reports the characterisation, by n.O.e. difference spectroscopy, of metal-free (**3**) derived from the vanadyl porphyrins of Serpiano oil shale.

I thank Mr. A. Muradian of CSR Limited for providing Julia Creek oil shale, and Dr. J. K. Saunders (University of New South Wales) for access to a Bruker CXP 300 n.m.r. spectrometer. Technical assistance by Miss J. Wymer is gratefully acknowledged.

Received, 8th August 1983; Com. 1067

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