

A NOVEL CHLOROPHYLL c RELATED PETROPORPHYRIN IN OIL SHALE

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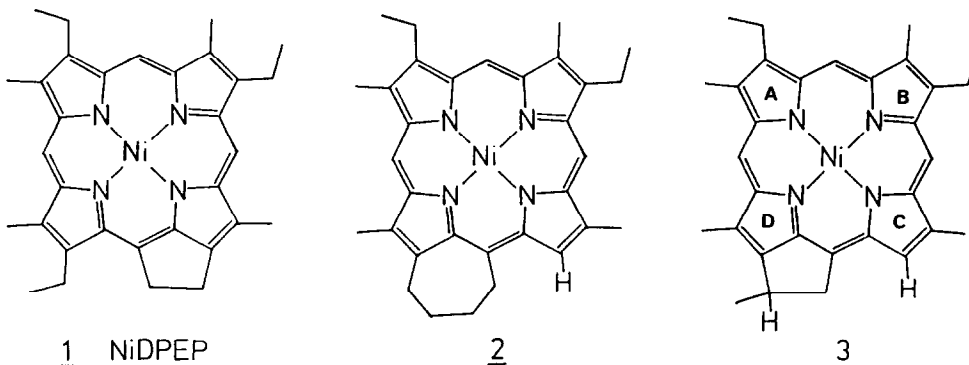
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Summary : A novel C₃₁ nickel petroporphyrin skeleton, 15,17-(15²-methyl)ethano-3,8-diethyl-2,7,12,18-tetramethylporphyrin 3, related to chlorophyll c, has been isolated from the Messel oil shale, and its structure determined by selective decoupling and nuclear Overhauser effect studies.

Although metalloporphyrins have been discovered in geological sources a long time ago², precise structural data on individual compounds have only been obtained recently due to the development of suitable analytical techniques able to deal with the complexity of geoporphyryns³. Separation of pure compounds by HPLC combined with n.m.r.⁴, nuclear Overhauser effect studies in n.m.r.⁵⁻⁹, and, in one case, X-ray diffraction¹⁰, have indeed led to the determination of several structures related to the Aetio and DPEP series, as well as to the discovery of an unsuspected porphyrin series bearing a seven membered ring^{6,8}, yet unknown in living organisms. Most of these results were compatible with an origin of the petroporphyrins from chlorophylls, thus confirming the early hypothesis of Treibs.

We report here the isolation and identification of a novel C₃₁ geoporphyryn skeleton, 15,17-(15²-methyl)ethano-3,8-diethyl-2,7,12,18-tetramethylporphyrin 3, the major porphyrin, occurring as a nickel complex, in the Eocene Messel oil shale (near Darmstadt, Germany)¹¹.

Extraction (toluene-MeOH 3:1 at 60°C) of the powdered shale (600 g) gave a residue which was successively chromatographed on silica gel (eluent CHCl₃) and alumina (gradient from hexane to CHCl₃ via CH₂Cl₂) while following the presence of the porphyrin chromophore. The resulting non polar porphyrin fraction (ca 5 mg), essentially composed of Ni complexes (as shown by X-ray fluorescence), was separated (HPLC, RP 18, EtOH then MeOH; detection: 405 nm) into three major pure components (and some minor)¹².



Two compounds were identified as known structures 1 (Ni(II) DPEP)⁷ and 2⁸ using n.m.r. and mass spectrometry.

We propose structure 3 for the third and major component on the basis of the visible, mass and n.m.r spectra. The chromophore of 3 ($\lambda_{\max} = 395, 513, 551 \text{ nm}$; rel.int. 100:6:11) was typical of a Ni-porphyrin. The molecular peak (15 eV) indicated a C_{31} skeleton ($M^+ = 518$) with the same degree of unsaturation as DPEP.

The n.m.r. spectrum of 3 (see table) displayed the signals for 2 Et, 4 CH_3 and 1 H, all attached to β -pyrrolic positions and 3 meso-H. Furthermore the presence of a $-CH_2-CH(CH_3)-$ fragment was confirmed by a decoupling experiment. Decoupling also showed that CH_3-12 and CH_3-18 were coupled with H-13 ($J=1.1 \text{ Hz}$) and H_C ($J=1.1 \text{ Hz}$) respectively. Similar allylic and homoallylic couplings - and identical J values - are present in 2 and 1 respectively^{7,8}.

N.O.e. difference spectroscopy¹³ (in C_6D_6) allowed us to precise the relative positions of all substituents (see figure) :

a) irradiation of CH_3-18 caused enhancement of the meso H-20 signal b) irradiation of the ethyl CH_2 groups enhanced the meso protons H-5, H-10 and the uncoupled CH_3 signals c) the signal of the pyrrolic H (H-13), as well as the signals of H_B and H_C increased on irradiation of H_A . The above data fixed the relative position of the substituents along the "west" and "south" sides of the molecule (positions 1,2 and 13 to 20). Since irradiation of the ethyl CH_2 groups gave a n.O.e. to one (or two) of the uncoupled CH_3 signals, there must be on ring A or B a $CH_3-C\beta-C\beta-Et$ arrangement. The fact that of the two remaining meso-H (5 and 10) each is next to an Et group (see above) leaves only one possibility for structure 3. A 2D n.O.e. experiment¹⁴ showed the expected correlations : H-5 \leftrightarrow CH_3-2 or 7 ; H-10 \leftrightarrow CH_3-12 ; H-20 \leftrightarrow CH_3-2 or 7 and CH_3-18 .

	C_6D_6	$CDCl_3$
CH_3-CH_2-3 or 8	1.82 (t)	} 1.79 (t)
CH_3-CH_2-3 or 8	1.83 (t)	
CH_3-CH_2-3 and 8	3.92 (q)	3.95 (q)
CH_3-2 or 7	3.38	} 3.50
CH_3-2 or 7	3.39	
CH_3-18	3.44(d, $J_{HC}=1.1 \text{ Hz}$)	3.51 (broad)
CH_3-12	3.57(d, $J_{H-13}=1.1 \text{ Hz}$)	3.63 (broad)
$H_A - 15^1$	5.14(dd, $J_{AB}=17.0 \text{ Hz}$, $J_{AC}=7.0 \text{ Hz}$)	5.40(dd, $J_{AB}=17.0 \text{ Hz}$, $J_{AC}=6.8 \text{ Hz}$)
$H_B - 15^1$	4.46(dd, $J_{AB}=17.0 \text{ Hz}$, $J_{BC}=2.5 \text{ Hz}$)	4.64(dd, $J_{AB}=17.0 \text{ Hz}$, $J_{BC}=2.5 \text{ Hz}$)
$H_C - 15^2$	4.29 (m)	4.56 (m)
CH_3-15^2	1.83(d, $J_{HC}=7.0 \text{ Hz}$)	1.97(d, $J_{HC}=7.0 \text{ Hz}$)
H - 13	8.93(q, $J_{CH_3-12}=1.1 \text{ Hz}$)	8.93 (broad)
H - 5	10.01	} 9.80 (2H) and 9.85 (1H)
H - 10	10.09	
H - 20	9.95	

Table : 1H NMR assignments for 3 (200 MHz)

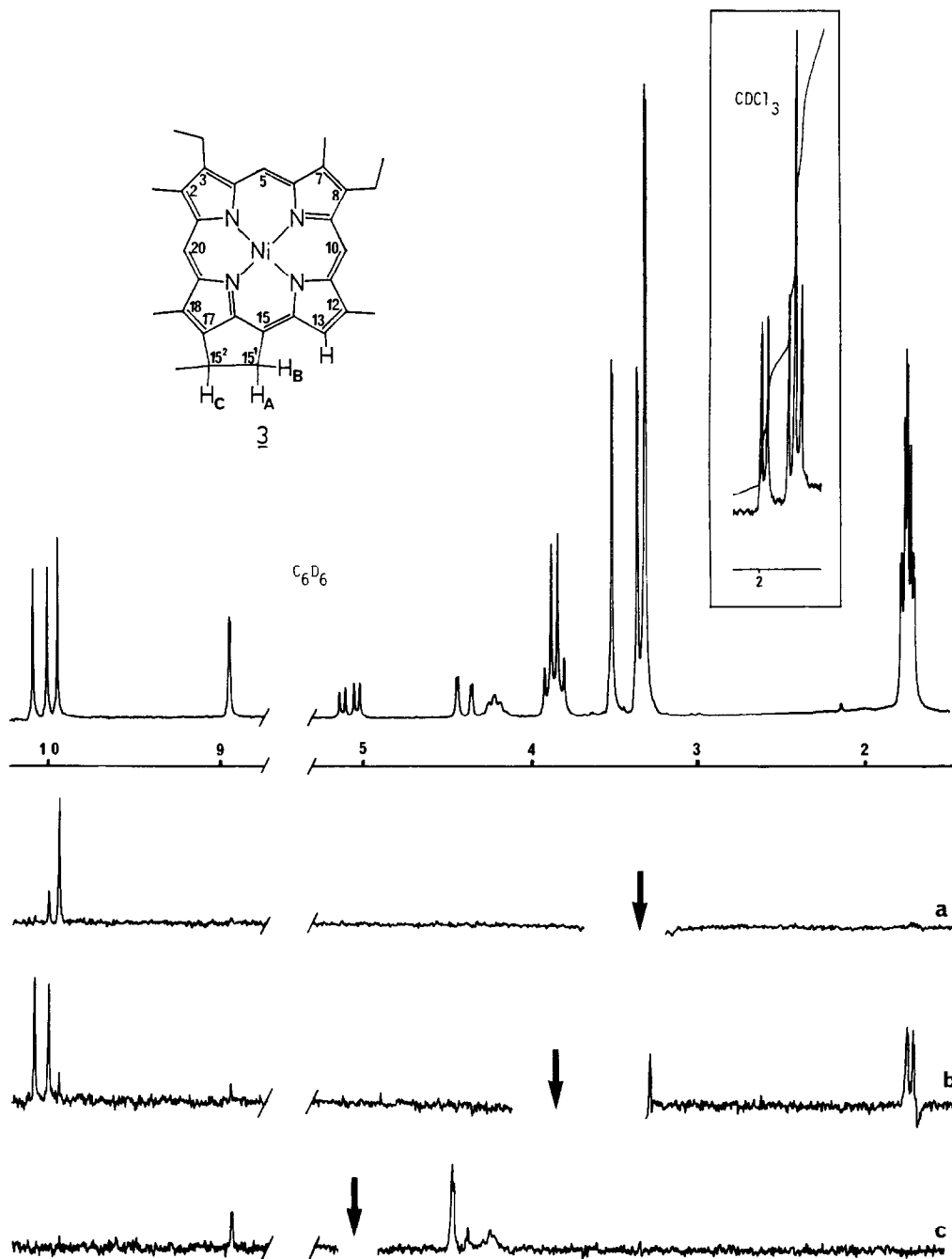
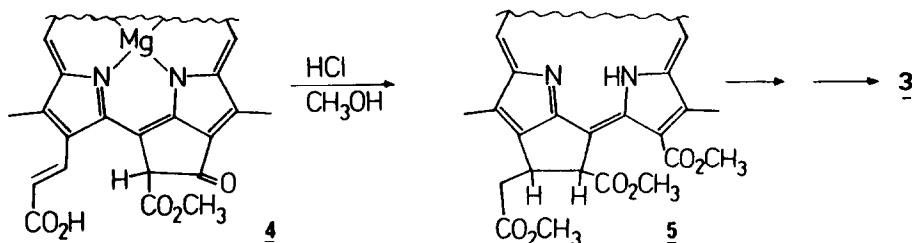


Fig. 200 MHz ^1H n.m.r. spectra (Bruker WP 200 SY).

Top : Reference spectrum (ca 1 mg in 0.5 ml C_6D_6). Insert : high field signals in CDCl_3 .

Bottom : Difference n.o.e. spectra : a) saturation of CH_3 -18 (40 db below 0.2 W) ; due to close proximity, CH_2 -2 and -7 are partly saturated ; b) saturation of CH_2 -3 and -8 (40 db below 0.2 W) ; c) saturation of H_A (45 db below 0.2 W).

To our knowledge the porphyrin skeleton 3 has not been observed in living organisms so far. However an acid-catalysed rearrangement of chlorophyll *c*, 4, has been shown to produce 5¹⁵, which could give 3 by decarboxylation and vinyl reduction under geochemical conditions³. It is very likely therefore that petroporphyrin 3 is a molecular fossil of chlorophyll *c*¹⁶, which is a universal constituent of algae and dinoflagellates¹⁷.



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