

PETROPORPHYRINS IV¹. NUCLEAR OVERHAUSER ENHANCEMENT ¹H NMR STUDIES OF DEOXO-PHYLLOERYTHROETIO PORPHYRINS FROM GILSONITE.

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Abstract - Nuclear Overhauser enhancement ¹H NMR analysis of a C₃₁ and a C₃₂ DPEP alkyl porphyrin from the bitumen Gilsonite (Eocene, Uinta Basin, Utah, U.S.A.) and oxidative degradation studies indicate an origin from chlorophyll a.

The reported isolation of deoxophylloerythroetioporphyrin 1a and aetioporphyrin-III from a Triassic sediment², and proposals that these compounds were derived from chlorophyll a laid the foundation of molecular geochemistry^{3,4}. Subsequent mass spectrometric studies showed that alkyl porphyrins in geological samples occur as complex mixtures of two major polyalkylated series: the deoxophylloerythroetio-(DPEP) and the aetio-types, with a maximum carbon number range of C₂₆-C₃₉⁵⁻⁷. The demetallated alkyl porphyrins of the bitumen Gilsonite (Eocene, Uinta Basin, Utah, U.S.A.) have been separated into single carbon number species⁸, providing the opportunity to test the above proposals. Unambiguous assignment¹ of the C₃₂ aetio porphyrin as aetioporphyrin-III provides support for the above hypothesis; it remained essential, however, to assign at least one of the DPEP porphyrins. Previous studies showed that the less polar of the two C₃₂ DPEP isomers⁸ coelutes with synthetic deoxophylloerythroetioporphyrin 1a on high performance liquid chromatography (HPLC). We describe here the isolation and analysis using nuclear Overhauser enhancement (NOE) ¹H NMR of the less polar C₃₂ DPEP isomer, and a similar study of the C₃₁ DPEP porphyrin, the most abundant of the Gilsonite porphyrins.

The demetallated C₃₁ DPEP porphyrin, and an isomeric mixture of the demetallated C₃₂ DPEP porphyrins were isolated by TLC, as described previously⁸. The isomers were separated by preparative HPLC on 5 μ Partisil (25cm x 4.6mm i.d., stainless steel) by isocratic elution with hexane-toluene-chloroform (65:20:15, vol:vol:vol) at a flow rate of 1.5 ml min⁻¹. The peaks were monitored spectrophotometrically at 499nm, and the less polar fraction (t_R 5.9 min) was isolated > 90% pure by HPLC.

Metal-free porphyrins often give poorly resolved NMR spectra owing to aggregation⁹; thus, both the C₃₁ and C₃₂ compounds were converted to the Zn complexes⁹ which were examined by ¹H NMR (Table 1).

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Table 1. ^1H NMR of Gilsonite C_{31} DPEP and less polar C_{32} DPEP (as Zn complexes)

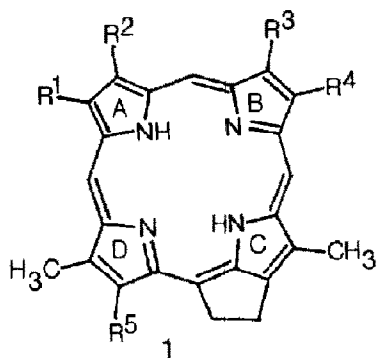
Compound	Shift (δ ppm), multiplicity (no. of substituents) ^a					HRMS (M^+)	
	Ring CH_3	Ring CH_2CH_3	Ring CH_2CH_3	Meso H	Isocyclic Ring	Requires	Found
C_{31} DPEP ^b	3.62s } 3.58s } (5)	4.15m(2) ^d	1.84t } 1.74t } (2)	10.11s } 10.08s } (3) 10.02s }	5.34m } 4.15m ^d } (1)	462.278	462.27
C_{32} DPEP ^c	3.65s } 3.60s } (4)	4.09m(3) ^d	1.86t } 1.74t } (3)	10.16s } 10.10s } (3) 10.07s }	5.38m } 4.09m ^d } (1)	476.294	476.29

^a In acetone- d_6 and ca. 10% pyridine- d_5 ; both spectra showed ca. 10% impurity.

^b Varian XL-100A-12.

^c JEOL PFT-100.

^d The ring $\text{CH}_2\text{-CH}_3$ and the β -attached CH_2 of the isocyclic ring overlap.



(a) $\text{R}^1=\text{R}^3=\text{CH}_3$; $\text{R}^2=\text{R}^4=\text{R}^5=\text{C}_2\text{H}_5$

(b) $\text{R}^2=\text{R}^3=\text{CH}_3$; $\text{R}^1=\text{R}^4=\text{R}^5=\text{C}_2\text{H}_5$

(c) $\text{R}^2=\text{R}^4=\text{CH}_3$; $\text{R}^1=\text{R}^3=\text{C}_2\text{H}_5$

(d) $\text{R}^1=\text{R}^2=\text{R}^3=\text{CH}_3$; $\text{R}^4=\text{R}^5=\text{C}_2\text{H}_5$

(e) $\text{R}^1=\text{R}^2=\text{R}^4=\text{CH}_3$; $\text{R}^3=\text{R}^5=\text{C}_2\text{H}_5$

(f) $\text{R}^2=\text{R}^3=\text{R}^4=\text{CH}_3$; $\text{R}^1=\text{R}^5=\text{C}_2\text{H}_5$

(g) $\text{R}^1=\text{R}^3=\text{R}^4=\text{CH}_3$; $\text{R}^2=\text{R}^5=\text{C}_2\text{H}_5$

Previous work has shown that $n\text{Oe}$ studies can be used to determine the position of substituents on the porphyrin macrocycle¹⁰: irradiation of a ring CH_3 or CH_2 - group provides a ca. 15% increase in intensity of the adjacent meso (bridge) protons. The information obtained from the $n\text{Oe}$ experiments is summarised in Table 2. The results show that both the C_{31} DPEP and C_{32} DPEP porphyrins have an ethyl group on the D ring, flanking the isocyclic ring on the C ring (1)

Oxidation of the C_{32} DPEP with chromic acid^{1,8,11} revealed only 3-ethyl-4-methyl-pyrrole-1H-2,5-dione, the C ring being degraded during the reaction¹². Thus, the combined spectrometric and degradative data prove that the substitution pattern of the C and D rings is identical to deoxyphylloerythroetioporphyrin 1a. The compound could still be one or a mixture of three possible isomers 1a, 1b, or 1c but it is most probable that it is 1a because it coelutes (HPLC) with the synthetic¹³ compound. Similarly, the C_{32} aetio porphyrin from Gilsonite is aetio-porphyrin-III¹, believed to be derived from the C_{32} DPEP skeleton¹⁴.

A similar degradative study of the C_{31} DPEP afforded 3,4-dimethyl-pyrrole-1H-2,5-dione and 3-ethyl-4-methyl-pyrrole-1H-2,5-dione in the ratio 1:2.2. The combined spectrometric and degradative data show that it also has the same substitution pattern in the C and D rings as deoxyphylloerythroetioporphyrin 1a. The C_{31} DPEP porphyrin is one, or a mixture of four

isomers Id-Ig. If the compound is derived directly from chlorophyll a, the only likely structure is Id, formed by cleavage of the vinyl group, the only functional group present originally in the A and B rings.

Table 2. nOe (% increases)^a for meso protons of Gilsonite C₃₁ DPEP and C₃₂ DPEP porphyrins (as Zn complexes).

δ (Irradiated Group)	Zinc C ₃₁ DPEP ^b			Comment	δ (Irradiated Group)	Zinc C ₃₂ DPEP ^c			Comment
	Meso protons (1)	Meso protons (2)	Meso protons (3)			Meso protons (1)	Meso protons (2)	Meso protons (3)	
	(10.11)	(10.08)	(10.02)			(10.16)	(10.10)	(10.07)	
4.75 (blank) ^d	0	0	0		1.80 (blank) ^d	0	0	0	
3.61 (CH ₃)	27	14	20 ^e	1,3 flanked by 2CH ₃	3.63 (CH ₃)	28	14	12 ^e	1 flanked by 2CH ₃
4.07 (CH ₂ CH ₃)	0	14	0	2 flanked by 1CH ₃ , 1C ₂ H ₅	4.09 (CH ₂ CH ₃)	0	14	15	2,3 flanked by 1CH ₃ , 1C ₂ H ₅

^a Absolute nOe values have an uncertainty $\pm 3\%$ (i.e. 27% is 24-30%); relative values are reliable.

^b Varian XL-100A-12.

^c JEOL PFT-100.

^d By definition, nOe = 0.

^e nOe low due to incomplete saturation of CH₃.

It seems unlikely that either DPEP compound would be formed in the sediment via the conversion of at least one methyl on the A or B ring to an ethyl substituent whilst the methyl groups in both the C and D rings remain intact. An alternative possibility, that the two porphyrins are derived from other, unknown precursor chlorins cannot be discounted. However, the identification of aetioporphylin-III as a major aetio porphyrin in Gilsonite does not support the latter hypothesis. All of the major porphyrins in Gilsonite contain methyl, ethyl and hydrogen β -substituents only⁸. This indicates that chlorophylls with extended (> C₂) β -alkyl substituents, e.g. Chlorobium chlorophylls, are not major precursors of the Gilsonite porphyrins⁷. The origin of the porphyrins of Gilsonite cannot be fully understood until the structure of the second (more polar) C₃₂ DPEP isomer is elucidated. The presence of this compound cannot be readily accounted for by the Treibs hypothesis³. Preliminary evidence suggests that it may not be derived from chlorophyll a, and may not contain a 5-membered isocyclic ring.

Although the structural data are incomplete for both the C₃₁ and the less polar C₃₂ DPEP porphyrins, the substitution pattern of the C and D rings is the same as in deoxyphylloerythroetioporphylin, the proposed^{3,4} product of defunctionalisation of chlorophyll a with the alkyl substituents in the latter remaining intact. The results provide direct evidence that the sedimentary DPEP alkyl porphyrins are derived mainly from chlorophyll a

Acknowledgements - We thank the American Gilsonite Company and Morris Ashby Ltd. for the gifts of Gilsonite. We are grateful to Professor E.W. Baker for the sample of synthetic deoxophylloerythroetioporphyrin. We also wish to thank the National Aeronautics and Space Administration (subcontract from NGL 05-003-003) for financial support. The HPLC facilities were provided by the Natural Environment Research Council (GR3/2420). We are most grateful to Dr. M. Murray and Mr. J.R. Burton for obtaining NMR and mass spectra respectively.

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(Received in UK 13 May 1980)