Occurrence of Bacteriopetroporphyrins in Oil Shale

Ruben Ocampo, Henry J. Callot,* and Pierre Albrecht*

Laboratoire de Chimie Organique des Substances Naturelles, UA 31 associée au CNRS, Département de Chimie, Université Louis Pasteur, 1, rue Blaise Pascal, 67008 Strasbourg, France

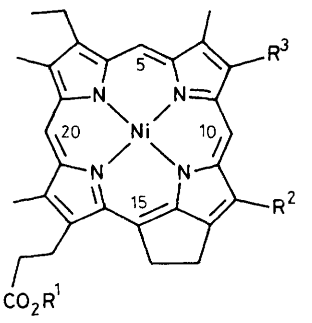
The structures of the higher homologues (C_{34}—C_{36}) of porphyrin acids of the Messel oil shale, elucidated by nuclear Overhauser effect studies in the case of the C_{35} compound, reflect their origin from photosynthetic bacteria.

The immature Messel oil shale contains a polar porphyrin fraction mainly composed of monocarboxylic acids.[1,2] The structures of several components (C_{30}—C_{33}) of this major porphyrin fraction have been elucidated and shown to derive probably from chlorophylls (a+b) or c.[1,3] Although the occurrence of higher homologues of alkylporphyrins has been

Table 1. ^1H N.m.r. data[a] of bacteriopetroporphyrins (as methyl esters).

			δ						
Positions			**(1)**		**(2)**		**(3)**		**(4)**
5-H			10.00		9.99		10.02		10.03
10-H			10.00		10.03		10.07		10.07
20-H			9.89		9.89		9.91		9.91
2-Me			3.38—3.40		3.39—3.40		3.40		3.40
7-Me							3.44		3.45
18-Me							3.40		3.40
3-Et	CH_2		3.92 or 3.93(q)		3.91 or 3.94(q)		3.93(q)		3.94(q)
	Me		1.84(t)		1.84(t)		1.84(t)		1.85(t)
propionic side-chain									
	CH_2		2.94(t)		2.96(t)		2.97(t)		2.97(t)
	CH_2		4.16(t)		4.18(t)		4.21(t)		4.21(t)
	Me		3.54		3.54		3.54		3.54
ethano bridge			3.58(m)		3.65(m)		3.66(m)		3.68(m)
			4.78(m)		4.82(m)		4.84(m)		4.85(m)
8		CH_2	3.92 or 3.93(q)		3.91 or 3.94(q)	CH_2	3.95(t)	CH_2	3.87(d)
		Me	1.84	Me	1.84	CH_2	2.34(6 lines)	CH	2.70(9 lines)
						Me	1.31(t)	2×Me	1.35(d)
12		Me	3.38—3.40	CH_2	4.00(q)	CH_2	4.02(q)	CH_2	4.03(q)
				Me	1.93(t)	Me	1.93(t)	Me	1.94(t)

[a] 200 MHz in C_6D_6, concentration $< 10^{-3}$ M; for compounds (**2**) and (**4**) the signals were assigned by comparison with (**1**) and (**3**).



(1); R^1 = Me, H, R^2 = Me, R^3 = Et
(2); R^1 = Me, H, R^2 = Et, R^3 = Et
(3); R^1 = Me, H, R^2 = Et, R^3 = Pr^n
(4); R^1 = Me, H, R^2 = Et, R^3 = Bu^i

noted in geological samples, no conclusive structural evidence has been obtained so far and several hypotheses have been proposed for the origin of these higher homologues.[4,5] We report here the occurrence and structural elucidation of higher homologues (C_{34}—C_{36}) of porphyrin acids typical of micro-organisms.

In the previous communication[1] we have shown that the major component (>50%) of the porphyrin acid fraction of the Messel oil shale, Ni-complex (**1**) [C_{33}, Ni deoxophylloerythroetioporphyrin (DPEP) series], was preceded (RP 18 h.p.l.c. on methyl esters) by a group of porphyrins containing a smaller number of carbon atoms (C_{30}—C_{32}). However careful investigation of the minor and more lipophilic components of the esterified acid fraction revealed the presence of three compounds in noticeable amounts (C_{34}, C_{35}, and C_{36} as indicated by mass spectrometry). These higher homologues of (**1**) were separated as pure compounds on RP 18 h.p.l.c. using methanol as an eluant.

The n.m.r. data (Table 1) established the following. (a) All three compounds, (**2**), (**3**), and (**4**), belonged to the DPEP series; (b) one methyl group of (**1**) was replaced by an ethyl group; (c) the only difference between (**2**), (**3**), and (**4**) was the successive replacement of an ethyl group in (**2**) [and (**1**)] by n-propyl, (**3**), and iso-butyl, (**4**), fragments, as shown by decoupling experiments, the remaining signals being nearly identical.

Assuming that these compounds are part of a homologous series of porphyrins we undertook a nuclear Overhauser effect difference study on the most abundant compound (**3**) to assign the relative positions of all the substituents. This study, summarised by arrows in Figure 1, fixed the substitution pattern for (**3**), and by analogy for (**2**) and (**4**). This substitution pattern is typical for Chlorobium chlorophylls d or e:[6,7] one carbon homologation on position 12 and permethylation of position 8.

The occurrence of acids (**2**), (**3**), and (**4**) in an immature shale represents clear evidence for photosynthetic bacterial input. Furthermore the substitution pattern and the absence of the higher homologues seems to eliminate an alkylation–dealkylation process in this case which may be operative in more mature sediments.[4,5]

Bacteriochlorophylls a+b should, under diagenetic conditions, lead to the same petroporphyrins as chlorophyll a+b from higher plants and algae. Furthermore given the recent identification[1,3] of chlorophyll c derived petroporphyrins typical of algae, it is possible that most of the characterised petroporphyrins in Messel shale originate from photosynthetic bacteria and algae.

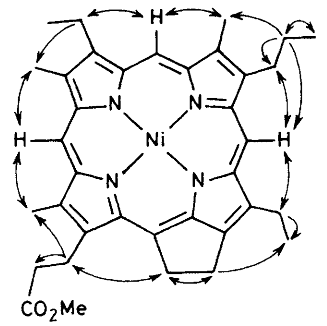


Figure 1. N.O.e's are indicated by the arrows.

The discovery of bacteriopetroporphyrins is one further example of the contribution of microbial constituents to sedimentary organic matter and fossil fuels,[8] largely illustrated by the ubiquitous occurrence of bacterial terpenes, in particular of hopanoids.[9]

We thank Dr J. P. Kintzinger for helpful discussions, Mrs E. Krempp for technical assistance in the n.m.r. spectroscopic studies, and the management of the Messel mine for shale samples. One of us (R. O.) thanks the Consejo Nacional de Ciencia y Tecnologia (CONACYT), Mexico for financial support.

Received, 17th September 1984; Com. 1316

References

1 R. Ocampo, H. J. Callot, and P. Albrecht, *J. Chem. Soc., Chem. Commun.*, preceding communication, and references cited therein.
2 G. G. Habermehl, G. Springer, and M. H. Frank, *Naturwissenschaften*, 1984, **71**, 261.
3 R. Ocampo, H. J. Callot, P. Albrecht, and J. P. Kintzinger, *Tetrahedron Lett.*, 1984, **25**, 2589.
4 E. W. Baker and J. W. Louda in 'Advances in Organic Geochemistry 1981,' eds. M. Bjørov, P. Albrecht, C. Cornford, K. De Groot, G. Eglinton, E. Galimov, D. Leythaeuser, R. Pelet, J. Rullkotter, and G. Speers, Wiley, London, 1983, p. 401.
5 J. M. E. Quirke, G. J. Shaw, P. D. Soper, and J. R. Maxwell, *Tetrahedron*, 1980, **36**, 3261.
6 A. H. Jackson in 'Chemistry and Biochemistry of Plant Pigments,' ed. T. W. Goodwin, 2nd Edition, Academic Press, 1976, vol. 1, p. 1.
7 K. M. Smith, D. A. Goff, J. Fajer, and K. M. Barkigia, *J. Am. Chem. Soc.*, 1982, **104**, 3747 and references cited therein; K. M. Smith, D. A. Goff, J. Fajer, and D. M. Barkigia, *J. Am. Chem. Soc.*, 1983, **105**, 1674.
8 G. Ourisson, P. Albrecht, and M. Rohmer, *Sc. Am.*, 1984, **251**, 44.
9 G. Ourisson, P. Albrecht, and M. Rohmer, *Trends Biochem. Sci.*, 1982, **7**, 236.