

Partial Syntheses of Messel Oil Shale Bacteriopetroporphyrins from the Bacteriochlorophylls-d

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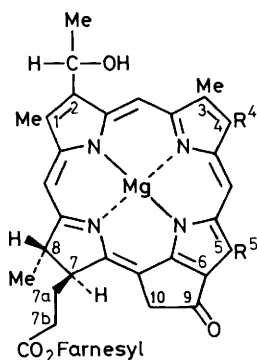
Chemical degradation of the natural bacteriochlorophyll-d homologous mixture to give the corresponding bacteriopetroporphyrin methyl esters is described; ^1H n.m.r. spectroscopy of the nickel(II) complexes is used to establish that the pigments are identical with those isolated from immature Messel oil shale.

Approximately 35 petroporphyrins have been isolated from petroleum deposits and characterized.¹ Almost all of these can be assigned to one of three major types, (1) the deoxophylloerythroetioporphyrin (DPEP) series, containing an exocyclic five-membered ring characteristic of the chlorophylls, or a six² or seven-membered³ exocyclic ring, (2) etioporphyrins⁴ which do not possess an exocyclic ring, and (3) 'rhodoporphyrins,' recently shown to be monobenzoporphyrins.⁵

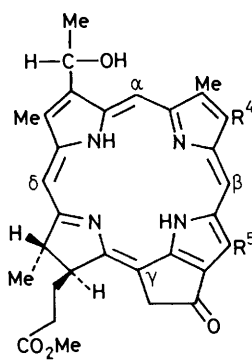
Treibs⁶ originally proposed that chlorophyll-a is the precursor of the C_{32} DPEP, and he outlined a diagenetic scheme to account for its formation. Others⁷ have pointed out that chlorophyll-a is not the only precursor for the C_{32} DPEP. Evidence has also been obtained which suggests^{8,9} that chlorophylls b, c_1 , c_2 , and bacteriochlorophylls a, and d may

also be precursors of petroporphyrins. Diagenetic pathways to petroporphyrins, similar to that of Treibs,⁶ can be proposed for all of these chlorophylls.

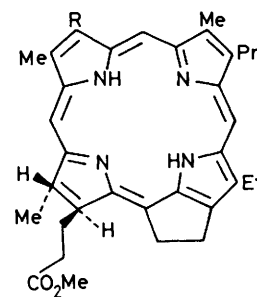
There has been some disagreement about the source of the extra methylene groups in the homologous series of petroporphyrins.¹⁰ In a particularly significant development,⁹ Ocampo *et al.* isolated a series of homologated petroporphyrins from immature Messel oil shale which were shown, mainly by ^1H n.m.r. techniques, to bear substituent patterns similar to those of the *Chlorobium* chlorophylls, thereby establishing their origin from photosynthetic bacteria. There are several homologous series of porphyrins which can be obtained from green and brown photosynthetic bacteria, and these have been shown for the bacteriochlorophylls c,¹¹ d (1),^{12,13} and e¹⁴ to



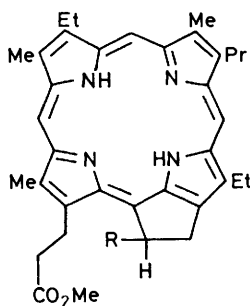
(1) $\text{R}^4 = \text{Et}, \text{Pr}, \text{Bu}^i, \text{neoPn}$
 $\text{R}^5 = \text{Me}, \text{Et}$



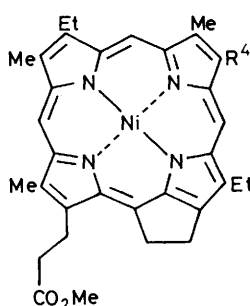
(2) $\text{R}^4 = \text{Et}, \text{Pr}, \text{Bu}^i, \text{neoPn}$
 $\text{R}^5 = \text{Me}, \text{Et}$
(3) $\text{R}^4 = \text{Pr}; \text{R}^5 = \text{Et}$
(10) $\text{R}^4 = \text{Et}, \text{Pr}, \text{Bu}^i, \text{neoPn};$
 $\text{R}^5 = \text{Et}$



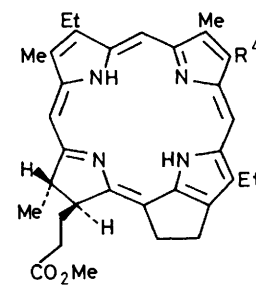
(4) $\text{R} = \text{CH}(\text{OH})\text{Me}$
(5) $\text{R} = \text{CH}=\text{CH}_2$
(6) $\text{R} = \text{Et}$



(7) $\text{R} = \text{H}$
(8) $\text{R} = \text{OH}$



(9) $\text{R}^4 = \text{Pr}$
(12) $\text{R}^4 = \text{Et}$
(13) $\text{R}^4 = \text{Bu}^i$



(11) $\text{R}^4 = \text{Et}, \text{Pr}, \text{Bu}^i, \text{neoPn}$

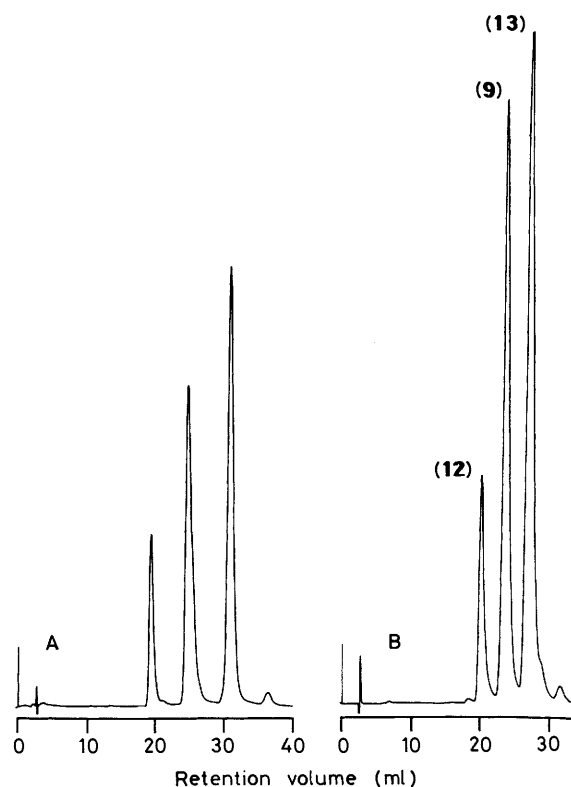


Figure. Reversed-phase h.p.l.c. traces, at flow rate of 1.0 ml/min using a Waters Associates Z-Module, a 4 μ C-18 cartridge, and with a variable wavelength detector set at 405 nm, of A, natural mixture of methyl 5-ethylbacteriopheophorbides-d (**10**) using 10% H₂O/90% methanol, and B, synthetic nickel(II) bacteriopetroporphyrin methyl esters (**9**), (**12**), and (**13**) using 45% H₂O–55% THF. Assignments of methyl bacteriopheophorbides-d (**10**) in trace A are, from left to right, 4-ethyl-5-ethyl-, 5-ethyl-4-propyl-, 5-ethyl-4-isobutyl-, and 5-ethyl-4-neopentyl-, respectively

possess combinations of ethyl, propyl, isobutyl, and neopentyl substituents at position 4, and methyl or ethyl at position 5. Thus, it is clear that isolation and characterization of homologous series of petroporphyrins bearing such unique homologation at the 4 and 5 positions is excellent evidence for their origin by way of bacteriochlorophylls. In this paper we show that natural bacteriochlorophylls d can be degraded to give 'synthetic' petroporphyrins which are, on the basis of ¹H n.m.r. evidence [for the monomethyl esters of the nickel(II) complexes], identical with those isolated by Ocampo *et al.*

The homologous mixture of bacteriochlorophylls-d (**1**) were isolated from *Chlorobium vibrioforme* forma *thiosulfatophilum*, and converted into the corresponding methyl bacteriopheophorbides (**2**) by treatment with 5% sulphuric acid in

* All products in the separated 4-propyl series were characterized by mass spectrometry, n.m.r. spectroscopy, spectrophotometry, and satisfactory elemental combustion analyses. In the unseparated series of homologous mixtures, only n.m.r. and spectrophotometry were used.

† M.p. 221–223 °C (Found: C, 70.0; H, 6.55; N, 9.15. C₃₆H₄₀N₄NiO₂ requires C, 69.8; H, 6.5; N, 9.05%); *m/z* (%) 618.2505 [100%, M⁺ (Calc. = 618.2509)], 603 (40) and 589 (68); λ_{max} , 394 (ϵ 217 000), 514 (12 600), and 552 nm (24 200); δ_{H} [C₆D₆], 300 MHz (GE QE300), 9.95, 9.91, and 9.78 (each s, 1 H, β , α , and δ *meso*-H), 4.69 (m, 2 H, 10-CH₂), 4.06 (t, 2 H, 7a-CH₂), 3.82–3.92 (m, 6 H, 2a-, 4a-, 5a-CH₂), 3.55 (m, 9-CH₂), 3.44 (s, 3 H, OMe), 3.34 (s, 3 H, 3-Me), 3.30 (s, 3 H, 1-Me), 3.27 (s, 3 H, 8-Me), 2.85 (t, 2 H, 7b-CH₂), 2.25 (m, 2 H, 4b-CH₂), 1.83 (t, 3 H, 5b-Me), 1.75 (t, 3 H, 2b-Me), and 1.22 (t, 3 H, 4c-Me).

methanol.¹² The pheophorbides were separated by preparative reversed phase high performance liquid chromatography (h.p.l.c.),¹² and the 5-ethyl-4-propyl homologue (**3**) was selected* for transformation into the corresponding bacteriopetroporphyrin. Thus, treatment with sodium borohydride in the presence of trifluoroacetic acid gave a mixture of the 2-(1-hydroxyethyl) (**4**) (10%) and 2-vinyl (**5**) (72%) pheophorbides. Treatment of the 2-(1-hydroxyethyl) compound (**4**) with toluene-*p*-sulphonic acid in hot *o*-dichlorobenzene gave a 93% yield of (**5**). Catalytic hydrogenation of (**5**) afforded a quantitative yield of the 2-ethyl pigment (**6**) which was treated with 2,3-dichloro-5,6-dicyanobenzoquinone to give 57–79% yields of the corresponding porphyrin (**7**); a by-product in this reaction (which could be suppressed by avoidance of silica gel chromatography) was the 10-hydroxy-9-deoxyphyloerythrin (**8**), the site of hydroxylation being established by ¹H n.m.r. nuclear Overhauser enhancement (n.O.e.) experiments. Complexation of (**7**) with nickel(II) gave a quantitative yield of the required porphyrin (**9**);† comparison of chemical shifts and establishment of the n.O.e. network showed our material to be identical with the 5-ethyl-4-propyl compound isolated by Ocampo *et al.*⁹

Having established the pathway to bacteriopetroporphyrin, the complete mixture of methyl 5-ethylbacteriopheophorbides-d [**10**], h.p.l.c. trace, Figure, A] was subjected to the same series of transformations. Results and yields were comparable throughout the series, except it was shown that treatment of the methyl bacteriopheophorbides (**10**) with a larger excess of sodium borohydride and trifluoroacetic acid for an extended period of time gave directly a high yield of the 2-ethyldeoxopheophorbides (**11**). Oxidation as before and nickel(II) chelation gave the homologous mixture of nickel(II) bacteriopetroporphyrin methyl esters (**9**), (**12**), and (**13**) (h.p.l.c., Figure, B). These compounds (with the exception of the very small amount of 4-neopentyl material) were separated using semi-preparative h.p.l.c., and ¹H n.m.r. spectra confirmed their identity with the same homologues isolated by Ocampo *et al.*⁹

Application of this chemistry to the bacteriopheophorbides c and e, and full characterization of those products (including n.O.e. connectivities) is in progress, and will be reported in a full paper.

Acknowledgements

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