

Isolation of a Series of Vanadyl-tetrahydrobenzoporphyrins from Timahdit Oil Shale. Structure Determination and Total Synthesis of the Major Constituent

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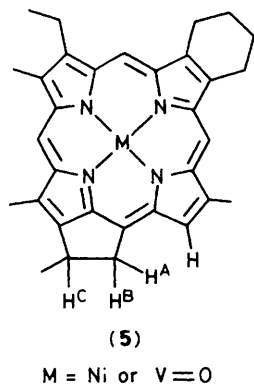
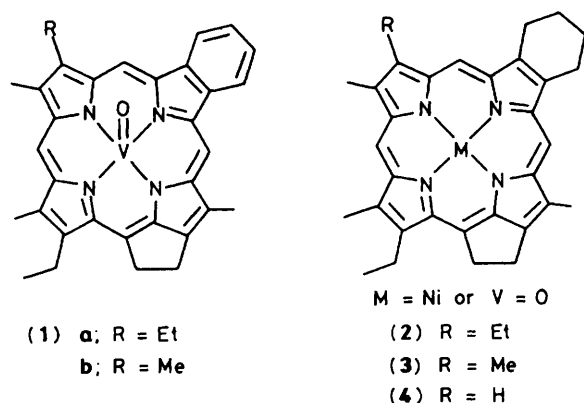
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A series of vanadyl-tetrahydrobenzoporphyrins was isolated from an oil shale and the structure of the major constituent demonstrated by n.m.r. studies and total synthesis; hypotheses concerning the origin of these petroporphyrins from biological precursors are discussed.

The occurrence of 'rhodo'-type petroporphyrins was first observed in geological samples in 1934 by Treibs,¹ but only in 1986 were the first pure compounds isolated from Boscan oil, and their structures, unequivocally assigned² as benzoporphyrins (**1a,b**). Although no natural chlorophyll known at present could be identified as a precursor of such a structure, the

occurrence in a less mature sediment of a component, tentatively described as having a tetrahydrobenzo ring, suggested the possibility of a 'geological' precursor for the benzo ring of 'rhodo'-type petroporphyrins.³

In this communication we report (i) the isolation of a series of tetrahydrobenzoporphyrins from the Moroccan Timahdit

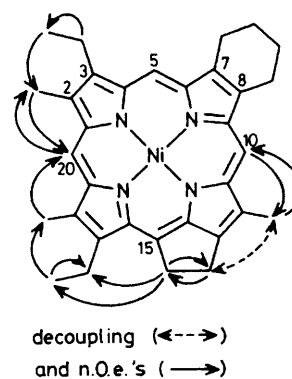


carbonate oil shale (15% organic carbon; Maastrichtian; -65 Myr); (ii) the full structural assignment by nuclear Overhauser enhancement (n.O.e.) experiments of the major compound, as well as likely structures for three other members of the series as deduced from n.m.r. data; and (iii) the total synthesis of the major compound.

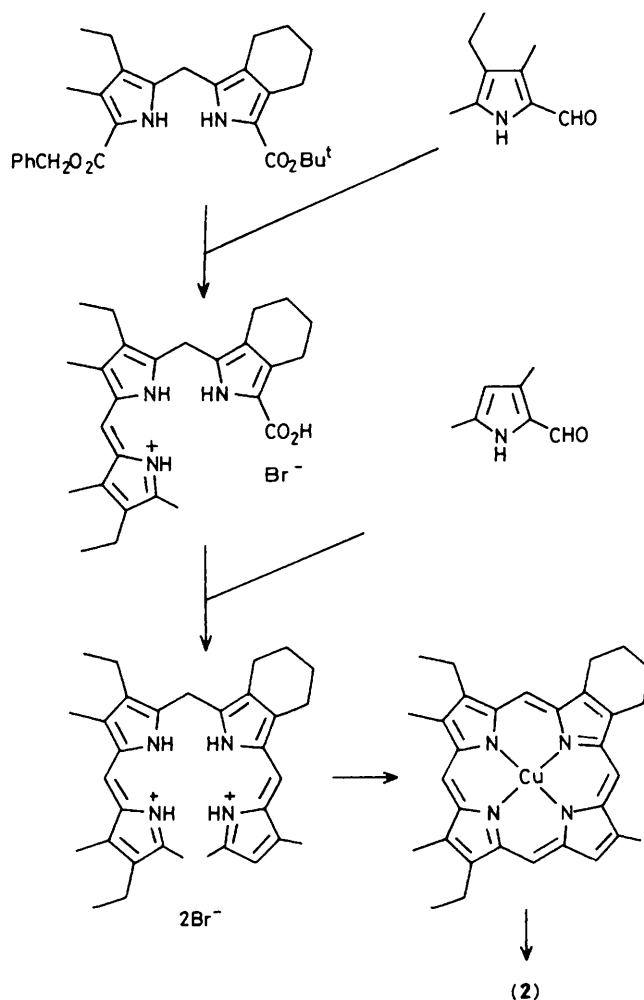
From the mixture of vanadyl-porphyrins extracted from the shale⁴ (the composition of the minor nickel fraction will be discussed elsewhere) *ca.* 20 pure vanadyl-petroporphyrins could be isolated after t.l.c. separation (silica gel) into four bands and isolation of individual components by reverse phase h.p.l.c. (RP18; MeOH). At this stage the vanadyl complexes were demetallated (MeSO₃H, 110°C, 1.5 h) and remetallated [excess Ni(MeCOCHCOMe)₂ in refluxing C₆H₆, 5-6 h]. From each of the two major bands we isolated two tetrahydrozobenzoporphyrins: (2) and (5) (less polar), and (3) and (4) (more polar) belonging to the DPEP [(2), (3) and, (4)] (DPEP = deoxyphyloerythroetioporphyrin) and 'chlorophyll-*c*'⁵ (5) series (the remaining structures will be described elsewhere).

Mass spectral data indicated the presence of two unsaturations (in addition to the porphyrin macrocycle) which were identified as five- and six-membered rings by n.m.r. spectroscopy. Except for the substituents of the modified ring B and the vicinal positions, all chemical shifts were found to be similar to those of the corresponding 'normal' nickel complexes^{5,6} (Me and Et attached to ring B) [see Scheme 1 for the n.m.r. data of the major component (2)]. N.O.e. experiments allowed us to follow the substitution pattern of (2) (M = Ni) from position 3 to position 10 (anticlockwise) leaving no alternative for the remaining assignments (see Scheme 1).

Additional structural evidence for (2) (M = Ni) was provided by comparison with a sample obtained by total synthesis. This synthesis (see Scheme 2) followed the classical *a,c*-biladiene route.⁷⁻⁹ The modified ring B was introduced as *t*-butyl cyclohexeno-3,4-pyrrole-2-carboxylate, obtained using Barton's isonitrile method.¹⁰ The subsequent dipyrromethane formation, aldehyde condensations, *a,c*-biladiene cyclisation



Scheme 1. N.m.r. chemical shifts for compound (2) (nickel complex) δ 9.96 (2H) and 10.04 (1H) (5-, 10-, 20-H), 3.44 (2-Me), 3.48 (12-Me), 3.46 (18-Me), 3.95 (q, 3-Et) and 1.86 (t, 3-Et), 3.85 (q, 17-Et) and 1.70 (t, 17-Et), 4.91 and 3.70 (both m, 5-membered ring), and 3.93 and 2.30 (both m, 6-membered ring).



Scheme 2. Reagents and conditions according to ref. 7-10.

to porphyrin, and building of the five-membered ring paralleled Smith's synthesis of DPEP.⁸ The nickel complex of the product was found to be identical with (2) (M = Ni) (coelution on reverse phase h.p.l.c., n.m.r. and mass spectral data).

Although it is clear from the presence of the five-membered ring that these new porphyrins are degradation products of chlorophyll-like precursors, the occurrence of tetrahy-

drobenzo- and benzo-petroporphyrins in marine oil shales, and crude oils² raises several questions with regard to their origin. In particular, it is crucial to understand² whether they are primary (*viz.* retaining the carbon framework of a precursor) or secondary diagenetic products (*viz.* does the six-membered ring result from the cyclisation of some Chlorobium bacteriochlorophyll extended chain). Since the known substituents of ring *b* in Chlorobium bacteriochlorophylls (Me and alkyl chains) do not suggest an easy cyclisation, it is tempting to follow Clezy's suggestion¹¹ of an acetic + propionic chain condensation at an early stage of the biosynthesis (intact or only partially decarboxylated uroporphyrinogen or uroporphyrin stages). This obviously suggests the occurrence in the past, but possibly also at present, of chlorophylls (bacteriochlorophylls?) possessing a six-membered ring fused to porphyrin ring *b*, this six-membered ring possibly retaining a functional group. Other features of the series of postulated precursors must be: (i) a 3-vinyl group (or one of its precursors, *e.g.* a hydroxyethyl group) as strongly suggested by the variations observed (Et, Me, H) in the major petroporphyrin series,^{2,6,12} (ii) a propionic-acrylic alternative for the C-17 side chain, only an acrylic side-chain being able to rearrange to eventually give (5) (as in the diagenetic product of chlorophyll-*c*⁵) if, in addition, a β -ketoester is present in the five-membered ring.

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