

Molecular Fossils of Chlorophyll *c* of the 17-nor-DPEP Series. Structure Determination, Synthesis, Geochemical Significance.

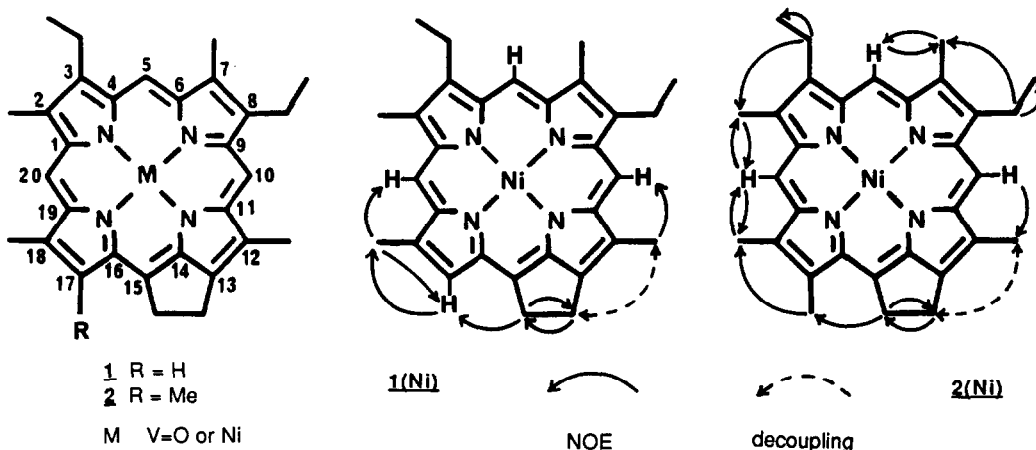
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Abstract: Two porphyrins **1** and **2**, having totally (**1**) or partially (**2**) lost the C-17 substituent, have been isolated from two Moroccan oil shales of Cretaceous age. An origin from chlorophyll *c*, which possesses a 17-acrylic side-chain, can explain this transformation. A synthesis of **1** from chlorophyll (*a* + *b*) is described. Porphyrin **1** is widely distributed in sediments and its relative abundance with regard to other molecular fossils of chlorophyll *c* is discussed briefly.

Porphyrins are widespread pigments present in sedimentary organic matter. The early hypothesis that sedimentary porphyrins (petroporphyrins) are the fossils of chlorophylls, has been confirmed in recent years¹. However the identification of a given chlorophyll as the specific precursor of a porphyrin was only obtained in some cases²⁻⁶. In this article we describe the isolation from two oil shales and the unequivocal structure determination of two specific biological markers derived from chlorophyll *c*, both belonging to the 17-nor-deoxophylloerythroetioporphyrin series (17-nor-DPEP), as well as the synthesis, from chlorophyll (*a* + *b*), of the major component, following a route inspired by the diagenetic hypothesis.

Porphyrins **1** and **2** were isolated from the Timahdit and Oulad Abdoun oil shales (Maastrichtian, Morocco)⁷. Compound **1** (M: V=O) is one of the major components of the Timahdit vanadyl-porphyrin fraction, while the less abundant **2** was obtained from the same fraction and from the Oulad-Abdoun nickel-porphyrin fraction⁸. When necessary the vanadyl group was replaced by nickel [demetallation in CH₃SO₃H (100°C) followed by treatment with Ni(acac)₂ in refluxing benzene]. The isolation and HPLC purification of the individual porphyrins followed published procedures⁶⁻⁸.

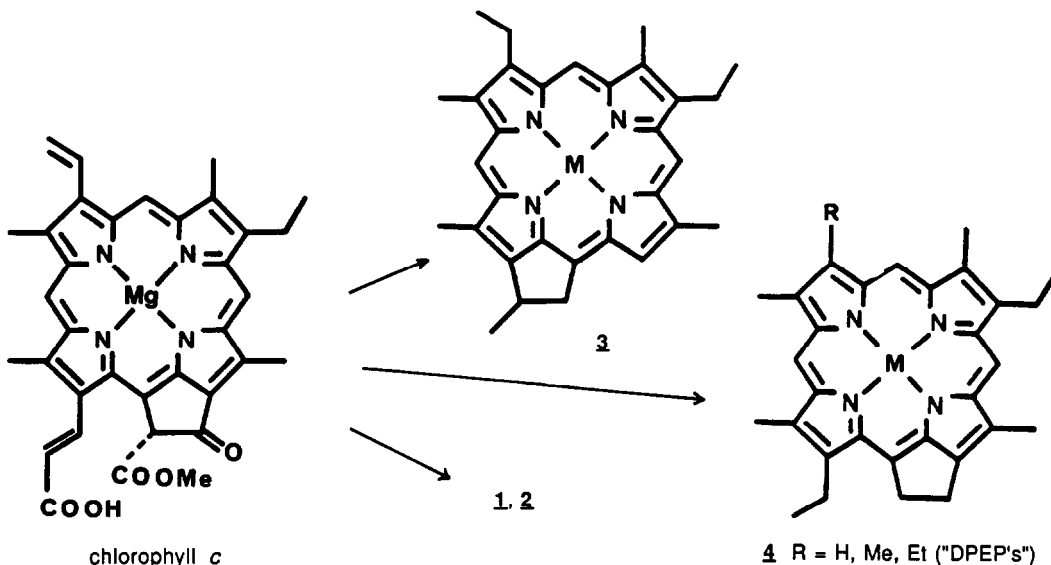


NMR data for **1** and **2** (400MHz, C₆D₆, <10⁻³M)

	1 (N1)	2 (N1)
5-H		10.06
10-H	10.02(3H)	10.07
20-H		9.99
2-Me		3.44
	3.40(2Me)	
7-Me		3.43
12-Me	3.41(t, J = 1.3Hz)	3.46(t, J = 1.3Hz)
18-Me	3.57(d, J = 1.0Hz)	3.41
3-Et CH ₂	3.93(q, 2CH ₂)	3.96 or 3.97(q)
8-Et CH ₃	1.84 or 1.85(t)	1.86(t, 2CH ₃)
17	H 8.90(q)	CH ₃ 3.19
5-membered ring	4.81 (m) 3.70 (m)	4.66 (m) 3.62 (m)

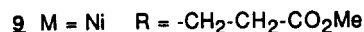
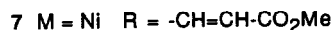
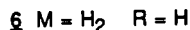
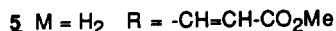
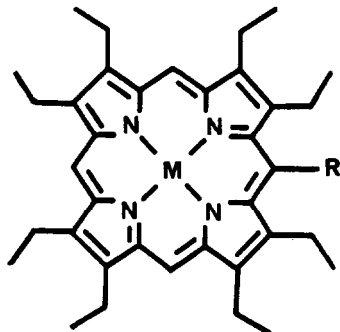
The structure assignments were deduced from an NMR study (decoupling + NOE, see figure above). For **2**, only one structure was compatible with the NMR data, while, for **1**, identical NMR chemical shifts (ring A and B Me and Et, NOE indicated a Me + Et substitution *per* ring) left several possibilities, the "natural" one being later confirmed by synthesis (see below). Structure **1** (vanadyl complex) has been proposed previously by Shul'ga and coworkers⁹ for a porphyrin isolated from a Siberian oil. This was done only on the basis of NMR chemical shifts of the free base, which left the possibility of different isomers.

It is difficult to account for the loss of the very stable 17-propionic chain of most chlorophylls; however the 17-acrylic side chain of chlorophyll *c* is a likely precursor of 17-H or 17-Me. It would parallel, as earlier suggested by Shul'ga *et al.*⁹, the degradation of the 3-vinyl group. The presence, in the same Moroccan oil shales, of the DPEP's **4** and of **3**¹⁰, the latter being a typical fossil of chlorophyll *c*², strengthens this hypothesis.

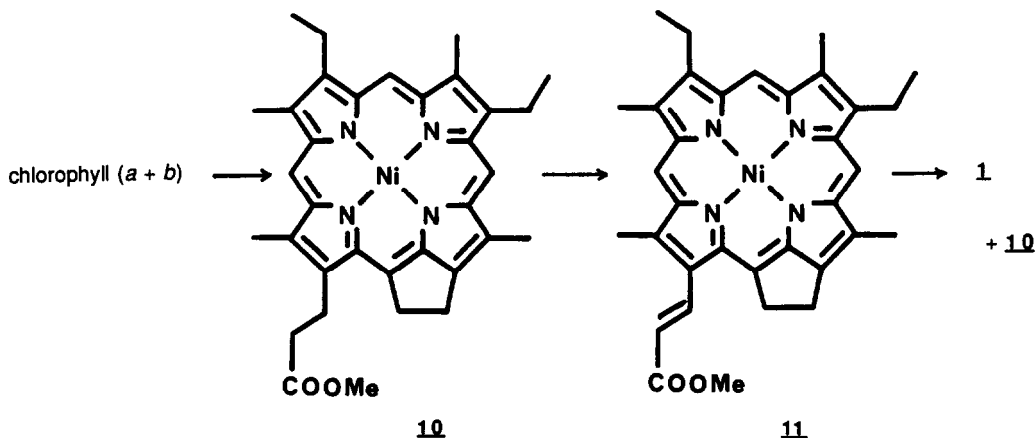


Selected diagenetic routes from chlorophyll *c* to petroporphyrins

In the laboratory, the quantitative cleavage of a vinyl group attached to a porphyrin nucleus has been carried out by heating the free base in a large excess of resorcinol¹¹. We first checked that under similar conditions (sealed tube, 160°C, 1hr) the acrylic derivative **5**¹² furnished H₂OEP **6** in high yield (>90%). Under the same conditions the corresponding nickel complex **7** was found to be quite stable (< 5% transformed), only traces of NiOEP **8** and a reduction product **9** being detectable.



These results suggested a synthetic route from chlorophyll *a* to **1** (scheme below). A chlorophyll (*a* + *b*) mixture was transformed¹³ into ester **10** (DPEP series) which was dehydrogenated *via* a phenylselenoxide according to Reich *et al.*^{14,15}. Demetallation of **11** (H₂SO₄), followed by heating in resorcinol (200°C, 6hr) gave a crude free base which was immediately metallated [Ni(acac)₂ in refluxing benzene]. Purification of the product (TLC) gave **1** (30%) which proved to be identical to the natural porphyrin (HPLC RP-18, NMR, MS). In addition to **1** an equivalent amount of **10**, resulting, as above, from reduction, was isolated.



This study demonstrates once again that the precise structure of sedimentary porphyrins should be unequivocally assigned (minimal requirements: NMR + NOE and/or synthesis and/or X-ray structural determination), if they are to be used as biological markers. A simple NMR spectrum would distinguish the true DPEP's (13,15-ethanoporphyrins) from several isomers (15,17-butanoporphyrins, **3**, etc) which are often classified as "DPEP's" according to the composition obtained from mass spectrometry. However, even within the "true" DPEP series, isomers of **1** and **2** exist, and which have the same substituents, but attached to different positions. For example **1** is an isomer of 3-devinylDPEP, which may originate from almost any chlorophyll, and **2** an isomer of 7-norDPEP which was earlier postulated as a fossil of chlorophyll *b*. Three of us (RO, HJC, PA)¹⁷ provided the best illustration of these remarks by erroneously assigning structure **4** (M = Ni, R = H) to a minor product isolated from the Eocene Messel oil shale⁶, a product which eventually proved to be **1** (M = Ni)...!

Compound **1** (M: V=O or Ni) seems to be a biomarker of wide geochemical significance:(i) it is specific for a given precursor (chlorophyll *c* from various groups of algae); (ii) it is widely distributed: Moroccan shales (this work), Messel oil shale (Eocene, West Germany, see above), Julia Creek oil shale (Cretaceous, Australia)¹⁰, Siberian oil⁹, Monterey oil (Miocene, California, USA)¹⁰. The relative abundance of **1** (cleavage of the side-chain) and **3** (rearrangement of the five-membered ring²), both from chlorophyll *c*, shows large variations which could be correlated with the sedimentary environment. For example, the rearrangement pathway is by far the major one in the carbonate-poor Messel shale (**3** being the most abundant of the alkylporphyrins), while the cleavage pathway is major in the carbonate-rich Moroccan shales and the Monterey oil.

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