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IDENTIFICATION OF A NOVEL C_{33} DPEP PETROPORPHYRIN FROM BOSCAN CRUDE OIL : EVIDENCE FOR GEOCHEMICAL REDUCTION OF CARBOXYLIC ACIDS.

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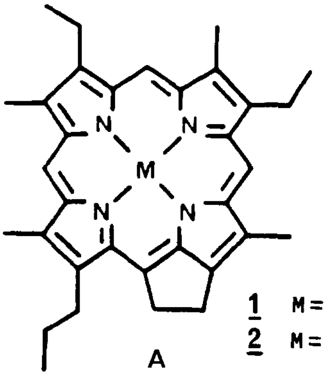
ABSTRACT : The isolation and structural determination (n.m.r., n.O.e., synthesis) of a C_{33} member of the DPEP series from Boscan crude oil indicates that total reduction of the propionic side-chain of a precursor chlorophyll may occur during the processes leading to oil formation.

Two major hypotheses have been put forward to explain the occurrence in *sediments and petroleums of petroporphyrins of carbon number higher than* C_{32} *which* were unexpected from "classical" chlorophylls (a, b, c, bacteriochlorophylls a, b) : trans-alkylation or homologated bacterial precursors such as the chlorophylls from photosynthetic bacteria of the Chlorobium group (bacteriochlorophylls c and d).

The structure of petroporphyrins derived from bacteriochlorophylls d was demonstrated recently[1]. They were extracted together from an immature oil shale (Messel oil shale, lacustrine, Eocene, West Germany); in order to extend these observations to a more general basis we looked for another geological sample of different origin and maturity.

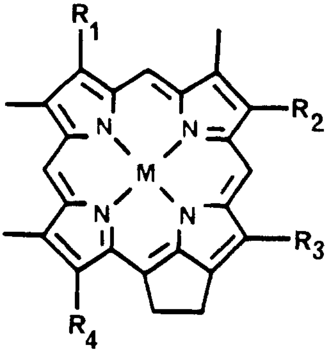
Boscan crude oil (Cretaceous, Venezuela) was a good candidate because, in *contrast to Messel, it is relatively mature and rich in homologated porphyrins with a carbon* skeleton reaching at least C_{40}[2].

In the search for high C-number porphyrins we separated successively the vanadyl-porphyrin fraction, demetallated these complexes, metallated the resulting bases into their diamagnetic nickel counterparts and isolated the fraction which showed a retention time greater than that of NiDPEP C_{32} on reverse phase HPLC (RP 18).



1 M = V=O
2 M = Ni

A



B1 , **B2** , **B3**

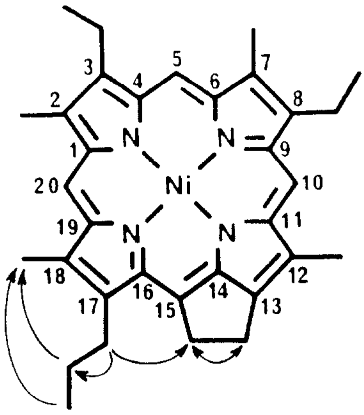
B1 $R_1=R_4=Et$, $R_2=nPr$, $R_3=Me$
B2 $R_1=Me$, $R_2=nPr$, $R_3=R_4=Et$
B3 $R_1=Me$, $R_2=R_3=Et$, $R_4=nPr$

The largest peak which followed NiDPEP C_{32} was collected ; the n.m.r. spectrum of the corresponding mixture of porphyrins showed a signal which could only be attributed to a propyl group in the major component. Further HPLC purifications gave compound 2 in a purity > 90 %[3].

The n.m.r. spectrum showed the presence of one five-membered ring, one propyl, two ethyl and four methyl groups in addition to three free meso positions, while the resulting molecular weight (M^+ = 546 corresponding to a C_{33} skeleton) was confirmed by MS. If one assumes the component to be in a natural series, several possibilities (A and B_1-B_3) could be considered based on known geochemical transformations. Structures B_1-B_3 could be eliminated on the basis of chemical shifts and nuclear Overhauser effect (n.O.e.) experiments :

N.m.r. data of 2 (200 MHz ; concentration < 10^{-3} M)

Positions		C_6D_6	$CDCl_3$
H-5		10.05	
H-10		10.02	9.83
H-20		9.99	9.81(2H)
isocyclic 5-membered ring		4.88(m) and 3.66(m)	5.21(m) and 4.01(m)
CH_3-2	CH_3-12	3.42($2CH_3$) and	
CH_3-7	CH_3-18	3.45($2CH_3$)	3.51
C_2H_5-3	CH_2	3.94(q) and 3.95(q)	3.95(q) and 3.96(q)
C_2H_5-8	CH_3	1.85(t) ($2CH_3$)	1.80(t) and 1.79(t)
nPr-17	CH_2	3.78(t)	3.86(t)
	CH_2	2.11(6^{et})	2.10(6^{et})
	CH_3	1.32(t)	1.30(t)

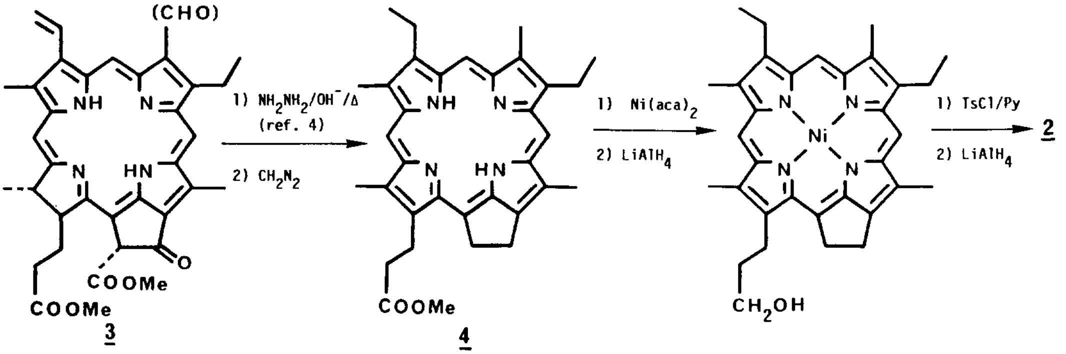


Observed n.O.e.

a) the two ethyl groups show almost identical chemical shifts which would be expected for A, but not B.

b) n.O.e. experiments allowed us to reconstruct the "southern" side of the molecule with the propyl group next to the isocyclic 5-membered ring (see arrows).

The superimposition of several signals (methyls, ethyls) made further assignments difficult. However compound 2 was synthesized from chlorophyll a+b via methylpheophorbide a+b 3. Baker's method[4], originally applied to pyropheophorbide a+b, gave DPEP ester 4 which was metallated with nickel. Its side-chain was reduced ($LiAlH_4$, tosylate, $LiAlH_4$) into a propyl group[5]. The n.m.r. spectra of the synthesized 2 and of the natural product were run in C_6D_6 and $CDCl_3$ under the same conditions (low concentration < 10^{-3} M to avoid aggregation) and the chemical shifts were found to be identical within 0.01 ppm. Furthermore, both products coeluted on analytical HPLC column (RP 18, 4μ, 250 x 4.6mm ; MeOH).



3

4

Although we have not yet identified petroporphyrins of bacterial origin such as B_1-B_3 in Boscan oil (see however ref. 2e), the identification of 1 is the first example of a petroporphyrin precursor whose acidic side-chain has apparently been fully reduced to a propyl group[6]. It illustrates once more the fact that full structural identification of petroporphyrins (either through n.O.e. experiments or synthesis) is clearly necessary for the interpretation of their geochemical significance. This presumed reduction process represents another possibility for explaining the occurrence of alkylpetroporphyrins with a higher (at least one more) carbon number than DPEP C_{32}, and may apply to any precursor chlorophyll.

Full geochemical reduction of carboxylic acids into alkanes has often been invoked in order to explain the predominance of even carbon numbered n-alkanes occurring in many anoxic sediments[7]. These conditions apply well to Boscan crude oil which originates from a source rock deposited in a reducing carbonate environment as indicated by a high phytane/pristane ratio and a slight predominance of even numbered n-alkanes[8]. Although hypotheses such as a direct origin of even numbered alkanes from marine bacteria have also been suggested[9], our results clearly indicate that a reduction pathway is very likely to operate in the geochemical processes leading to the formation of petroleum.

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3. Boscan crude oil was chromatographed twice on silicagel and once on alumina, the porphyrin fraction being eluted with $CHCl_3$. Demetallation (CH_3SO_3H, 110°C, 90 min) followed by remetallation (Ni(acac)$_2$, benzene, 80°C) gave the nickel complexes. HPLC purification of the major fraction following NiDPEP C_{32} was performed on reverse phase columns (RP 18, 250 x 21.2 mm, 8 µm ; MeOH-$CHCl_3$ 80:20, for preparation, MeOH for final purification ; RP 18, 250 x 4.6 mm, 4 µm, MeOH).
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5. Compound 4 was prepared from methylpheophorbide a+b according to ref. 4. and converted into its nickel complex (Ni(acac)$_2$, benzene, 80°C). $LiAlH_4$ reduction gave an alcohol which was tosylated (TsCl, Py). $LiAlH_4$ reduction of this ester gave 2.
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