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A NOVEL FOSSIL PORPHYRIN WITH A FUSED RING SYSTEM: EVIDENCE FOR WATER COLUMN TRANSFORMATION OF CHLOROPHYLL?

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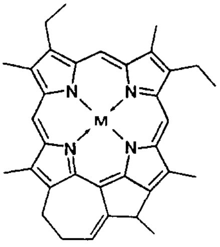
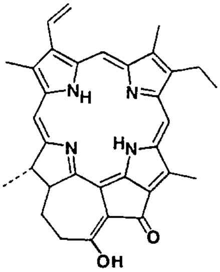
Abstract: *The occurrence of a* C_{34} *(*13^1*-methyl)-13,15-ethano-*13^2*,17-prop-*13^2*(*15^2*)-eno-porphyrin (1a) in the marine Serpiano oil shale suggests that metabolic transformation of chlorophyll in the fossil water column may have occurred prior to sediment incorporation.*

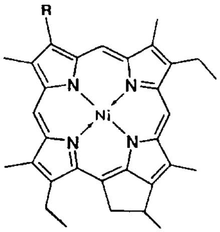
Recently, the assignment of the chlorin 2 was reported, and its presence in a sponge ascribed to metabolism of dietary chlorophyll[1]. These findings prompt us to report the occurrence of the alkyl porphyrin 1a in the marine Serpiano oil shale (Triassic, Switzerland), in which it occurs as a minor component of the vanadyl porphyrins. The fossil compound was isolated from a complex porphyrin fraction after demetallation as described previously[2,3]. The formula of the free base, $C_{34}H_{36}N_4$ (HRMS: 500.2952; required 500.2944) corresponds to a "rhodo-type" component, but the electronic spectrum (λ_{max} in CH_2Cl_2: 512, 548, 582, 639nm; rel. int. 100:17:33:13; Soret 416nm) is markedly different[4]. The ^1H NMR spectrum of the zinc(II) complex (1b), and appropriate decoupling and nuclear Overhauser effect experiments allowed assignment of the free base as (13^1-methyl)-13,15-ethano-3,8-diethyl-2,7,12,18-tetramethyl-13^2,17-prop-13^2(15^2)-enoporphyrin (Table).



1a: M = V=O
1b: M = Zn



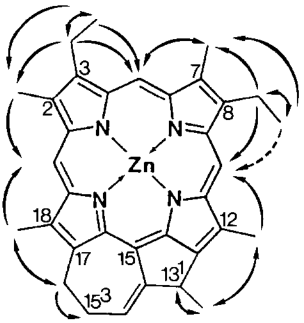
2



3: R = CH_3
4: R = CH_2CH_3

To our knowledge, chlorin 2 is the only reported biological tetrapyrrole with a fused ring moiety. It has been synthesised[5], however, from methylpyrophaeophorbide a, and was suggested[6] as an intermediate on the pathway to fossil porphyrins with a seven-membered exocyclic ring[6,7]. The only difference in the carbon skeletons of 2 and 1a lies in the presence of the methyl substituent at C-13^1 in the latter. Such a feature has not been reported in a biological tetrapyrrole pigment, although it has been observed in two fossil porphyrins (3,4) present in Gilsonite bitumen[8]. Despite this complexity, the similarity in the carbon skeletons of 1a and 2, taken with the proposed origin of 2 from ingested chlorophyll[1], suggests that an exocyclic fused ring moiety might have been present in an intermediate on the pathway to 1a prior to incorporation into the accumulating sediment.

Table. ^1H NMR data (200 MHz) for 1b in $CDCl_3$.

n.O.e. observed (shown by arrows)	δ ppm (Mult.)	Assignment
	9.46 (s)	H-20
	9.43 (s)	H-10
	9.31 (s)	H-5
	6.73 (dd)	CH-15^2
	4.93 (bq)	CH-13^1
	3.96 (m)	CH_2-15^4
	3.90 (m)	$CH_3\underline{CH_2}$-8,3
	3.54 (d)	CH_3-12
	3.43 (s)	CH_3-18
	3.39 (s)	CH_3-2,7
	3.27 (m)	CH_2-15^3
	2.06 (d)	$\underline{CH_3}CH$-13^1
	1.70 (t)	$\underline{CH_3}CH_2$-8
	1.68 (t)	$\underline{CH_3}CH_2$-3

Indeed, structural features in other fossil porphyrins with highly modified carbon skeletons, suggesting condensation of substituents on rings C and D of their precursor chlorophylls[6,7,9], may also have arisen from metabolic transformations of precursors in the water column rather than from post-depositional diagenetic transformations.

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