15,17-Butano-3,8-diethyl-2,7,12,18-tetramethylporphyrin - a Novel Naturally Occurring Tetrapyrrole

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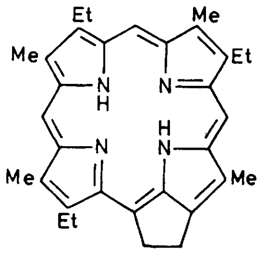
The title compound (**2**) has been isolated from a Triassic oil shale and its structure determined by nuclear Overhauser effect difference studies.

Since the original report of the occurrence of sedimentary metalloporphyrins,[1] only a limited number of structural studies have been carried out. The structures of two components related to 3,4-didehydro-3,9,14-triethyl-4,8,13,18-

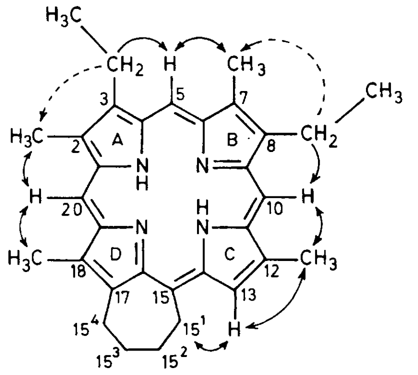
tetramethylphorbine (1), and of two aetioporphyrins from the bitumen gilsonite (Eocene, Uinta Basin, Utah, U.S.A.), have been partially or fully elucidated respectively.[2–4] It has been suggested that these components may have an origin in chlorophyll a.[2–4] Structural information on other sedimentary porphyrins is essential if their origins and pathways of formation are to be understood.

High concentrations (*ca.* 1000 p.p.m.) of oxovanadium(IV) porphyrins occur in the Serpiano oil shale (Triassic, Monte San Giorgio, Switzerland).[5–9] Approximately 2 mg of the title compound (2) (mass spectrum: $C_{32}H_{36}N_4$) which does not co-chromatograph with (1) on h.p.l.c. was isolated as the free base by t.l.c. and h.p.l.c. (>95% purity).[10] ^{1}H N.m.r. spectroscopy (200 MHz) indicated the presence of 4 β-Me, 2 β-Et, 1 β-H, a single $[CH_2]_4$ grouping, and three *meso*-protons. Chemical ionisation mass spectroscopy with hydrogen as the reagent gas[11] showed, at the appropriate m/z values, dipyrrolic fragment ions containing rings A and B, rings C and D and, at lower relative intensity, rings B and C. Among the expected monopyrrolic fragment ions, ions containing ring D were also present. These results led to a set of gross structures related to (2), differing only in the ring ordering.

Nuclear Overhauser effect (n.O.e) difference spectroscopy[12] has been used previously to make spatial connections between *meso*-protons and neighbouring β-substituents in porphyrins[12,13] and other macrocycles.[14] In (2) the lack of functionality led to very poor chemical shift dispersion in the *meso* and β-methyl regions (Table 1), giving severe frequency selectivity problems. Nevertheless, the use at 400 MHz of extremely low power (50 dB below a nominal 0.2 W) gave sufficient selectivity for specific n.O.e.s of *ca.* 1% to be observed (Figure 1).



(1)



(2)

Table 1. ^{1}H N.m.r. chemical shifts (400 MHz) for (2) as free base in $CDCl_3$.

Proton	Chemical shift	Proton	Chemical shift
$-CH_2-CH_3$	1.857(t) 1.862(t)	15^4-CH_2	3.91(m)
15^3-CH_2	2.31(m)	$3-CH_2-Me$	4.06(q)
15^2-CH_2	2.75(m)	$8-CH_2-Me$	4.08(q)
7-Me	3.60(s)	15^1-CH_2	4.92(m)
18-Me	3.61(s)	13-H	9.36(br. s)
2-Me	3.62(s)	5-H	9.92(s)
12-Me	3.76(br. s)	10-H	10.05(s)
		20-H	10.06(s)

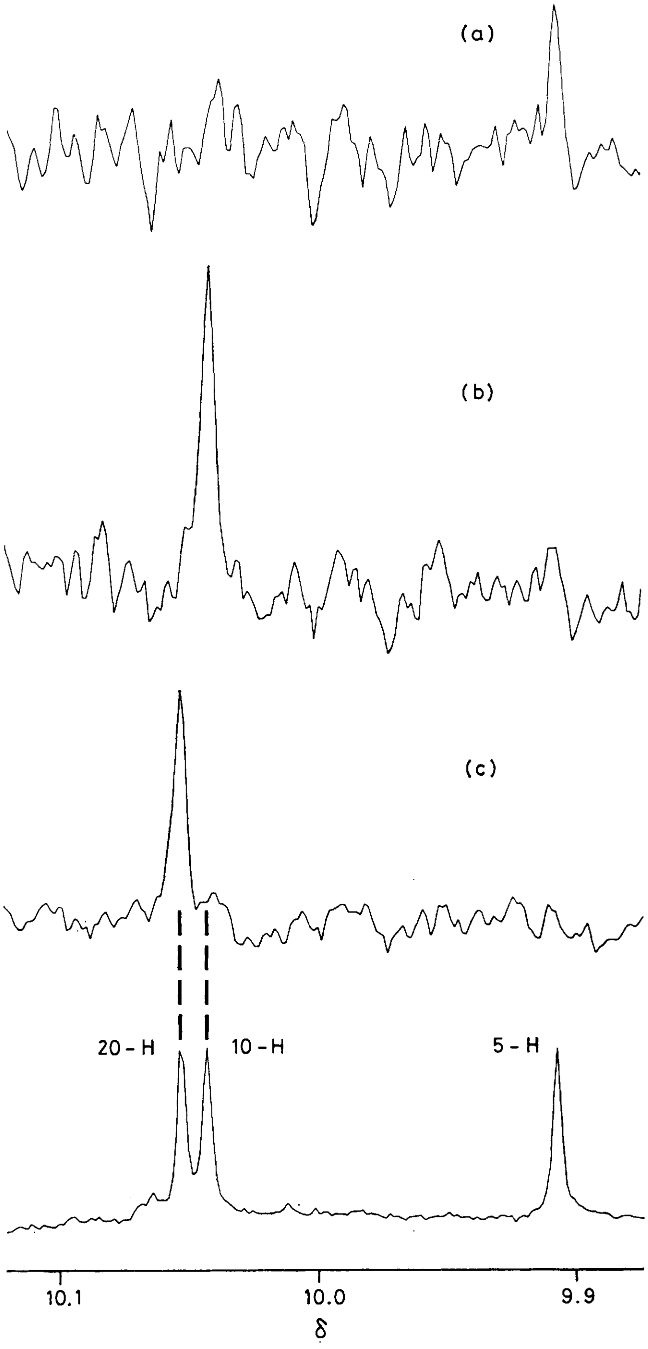


Figure 1. Partial 400 MHz ^{1}H n.m.r. spectra of the *meso*-region of (2). Lowest is the normal spectrum, above are n.O.e. difference spectra arising from the irradiation of (a) 3-CH_2, (b) 12-Me, and (c) 2-Me.

The small enhancements are in part due to slow molecular tumbling.[12] The resulting connections between substituents are summarised on (**2**),† which is the only structure consistent with the n.O.e. and decoupling observations. The connection between 2-Me and 3-CH_2 is weak, and so there remains a slight ambiguity between the assignments of 2-Me and 18-Me, but this does not affect the structure determination or the bulk of the assignments (Table 1). The exocyclic ring protons were assigned by n.O.e. to and from 13-H, and spin decoupling along the chain. The relative simplicity of these resonances, which is retained at −60 °C, is due to rapid conformational equilibration of the severely puckered seven membered ring.

The isolated component does not occur uniquely in the Serpiano oil shale, and has been identified by h.p.l.c. coinjection in several marine shales (Pliocene–Middle Miocene). In the absence of a known precursor natural product with the appropriate carbon skeleton, the origin of (**2**) is difficult to envisage in detail. There is, however, a precedent for the formation of a tetrapyrrole with a 7-membered exocyclic ring,[15] although it is not clear if such a reaction would operate in sediments.

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† Arrow head shows enhanced signal. Double-headed arrow denotes n.O.e. observed in both directions.