Identification of Polar Porphyrins in Oil Shale

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Several porphyrin acids [(**1**)—(**6**); C_{30}—C_{33}] have been isolated from the Messel oil shale and identified by nuclear Overhauser effect studies and synthesis; they imply the existence of several diagenetic pathways leading from the chlorophylls to the alkylpetroporphyrins.

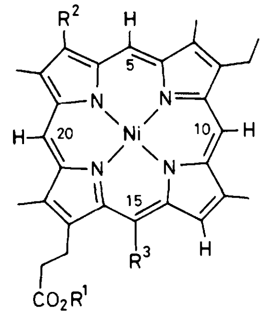
Although the structures of alkylpetroporphyrins have been increasingly studied in recent years[1] very few data are available on their polar counterparts. The occurrence of petroporphyrins bearing carboxylic acid groups has been mentioned occasionally in sediments and crude oils[2] but, with one recent exception,[3] none of these compounds has been isolated and fully characterised. Carboxylated petroporphyrins are obligatory intermediates in the Treibs[4] scheme of transformation of chlorophylls into polyalkylporphyrins; it had been suggested that their preservation would exclude high temperatures.[2] In this communication we report the occurrence of such compounds as major porphyrins in the thermally immature Messel oil shale (near Darmstadt, West Germany).[5]

Extraction of the powdered shale gave two major nickel porphyrin fractions: alkylporphyrins[5] and acids (as methyl esters after treatment with CH_2N_2) (yield 7 and 12 mg/kg shale). The methyl esters were separated (reverse phase h.p.l.c.) and characterised by mass and n.m.r. spectra (see

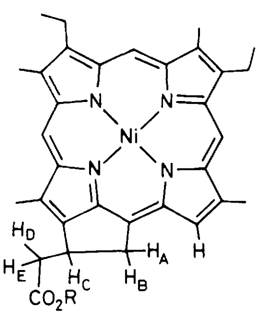
Table 1. ^1H N.m.r. data[a] of porphyrin monocarboxylic acids, as methyl esters.

	δ					
Position[b]	(**1**) ($CDCl_3$)	(**3**) ($CDCl_3$)	(**2**) (C_6D_6)	(**4**) (C_6D_6)	(**5**) ($CDCl_3$)	(**6**) ($CDCl_3$)
5-H	9.57	9.52	10.00	10.01	9.89	9.81(1H)
10-H	9.54	9.48	9.98	10.06	9.83	
20-H	9.45	9.50	9.87	9.92	9.76	9.80(2H)
15-(H or Me)	Me 4.17	Me 4.15	9.89	—	—	—
2-Me	3.51(d)	3.41	3.36(2Me)	3.38	3.63(d)	3.51(2Me)
7-Me	3.43	3.40		3.40	3.55	
18-Me	3.37	3.39	3.34(1Me)	3.38	3.49	
12-Me[c]	3.51(d)	3.51(d)	3.48(d)	3.55(d)	3.51(t)	3.49(2Me)
3-(H or Et)	8.80(q)	2×CH_2 3.84(q)	2×CH_2 3.90(q)	CH_2 3.91(q)	8.94(q)	CH_2 3.94(q)
				3.92(q)		3.96(q)
8-Et	CH_2 3.84(q)		Me 1.80(t)	Me 1.82(t)	3.96(q)	Me 1.78(t)
	Me 1.73(t)	2×Me 1.72(t)	1.81(t)	1.84(t)	1.80(t)	1.79(t)
13-H[c]	9.17(q)	9.14(q)	8.84(q)	8.82(q)	—	—
propionic	4.26(t)	4.24(t)	4.25(t)	—	4.28(t)	4.24(t)
side-chain	3.05(t)	3.03(t)	3.10(t)		3.06(t)	3.03(t)
ester Me	3.82	3.83	3.44	3.63	3.82	3.81
ethano bridge				H_A 5.30(dd)		
				H_B 4.67(dd)	5.24(m)	5.20(m)
	—	—	—	H_C 4.82(m)	4.06(m)	4.01(m)
				H_D 3.30(dd)		
				H_E 2.80(dd)[d]		

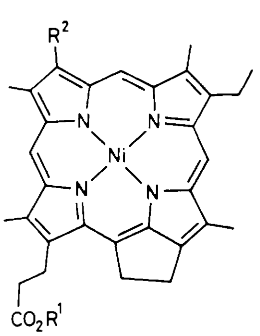
[a] All spectra run at concentration $<10^{-3}$ M; J values vicinal 7 Hz, allylic and homoallylic 1—1.2 Hz, unless indicated; (**2**) and (**4**) in C_6D_6 for better resolution; brace indicates signals not specifically attributed. [b] The numbering shown on (**1**) was used throughout the series. [c] J 1 Hz. [d] J_{AB} 17; J_{AC} 6.5; J_{BC} 2.0; J_{CD} 9.5; J_{CE} 5.5; J_{DE} 16 Hz.



(**1**); R^1=Me, H, R^2=H, R^3=Me
(**2**); R^1=Me, H, R^2=Et, R^3=H
(**3**); R^1=Me, H, R^2=Et, R^3=Me



(**4**); R = Me, H



(**5**); R^1 = Me, H, R^2 = H
(**6**); R^1 = Me, H, R^2 = Et

Table 1). Structural assignments were supported by the synthesis of (**2**), (**3**),[6]† and (**6**),[7] [(**6**) has already been characterised in Messel shale[3]], comparison of the data‡ for (**1**) and (**3**), (**5**) and (**6**), and (**4**) and its decarboxylated counterpart,[5] and several nuclear Overhauser effect (n.O.e.) experiments.

The major component of the acid fraction, (**6**) (R^1 = H) belongs to the DPEP (deoxophylloerythroetioporphyrin) series. In addition compounds (**1**) and (**2**), which are classical degradation products of chlorophyll a or b under basic conditions, are present in significant amounts. The simultaneous occurrence of carboxylic groups and a degraded cyclopentane ring indicates the possibility of several parallel diagenetic routes leading from the chlorophylls to the polyalkylporphyrins (aetio- and phyllo- series). Compound (**4**) (R = H) obviously derives from chlorophyll c, but its relative abundance is low compared with the corresponding decarboxylated porphyrin which is the most abundant component of the polyalkylporphyrin mixture of the same shale.[5] Finally the loss of the 3-vinyl group seems to be a minor process, porphyrins (**1**) and (**5**) (R^1 = H) being at least ten times less abundant than (**3**) and (**6**) (R^1 = H).

The isolation and characterisation of a series of petroporphyrinic acids from the polar fraction of the Messel oil

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† The acids were first methylated (CH_2N_2) and then treated with $Ni(acac)_2$ in benzene to give (**2**) and (**3**). (Hacac = $MeCOCH_2COMe$.)

‡ See also ref. 1(d) and 1(e). All spectra of new and reference compounds were measured at concentration $< 10^{-3}$ M to avoid aggregation effects on chemical shifts.

shale fills a gap in the classical Treibs scheme. It also confirms the chlorophyllic (a + b, c) origin of these porphyrins and the survival of carboxylic functions in this class of compounds under mild diagenetic conditions.

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