ALKYLPYRROLES IN KEROGEN PYROLYSATES:
EVIDENCE FOR ABUNDANT MACROMOLECULARLY-BOUND
TETRAPYRROLE PIGMENTS

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INTRODUCTION

Porphyrins and related compounds are well known biological markers often applied in geochemistry.[1,2] These tetrapyrrole pigments also occur in kerogen since upon off-line pyrolysis of kerogen DPEP-and ETIO-porphyrins are released.[3] Recently, Barakat and Yen reported that major amounts of 3-ethyl-4-methyl-1*H*-pyrrole-2,5-dione and, to a lesser extent, 3,4-dimethyl-1*H*-pyrrole-2,5-dione were formed upon controlled stepwise oxidation of a Monterey kerogen from the Santa Maria basin and Green River shale kerogen.[4] These compounds are thought to be derived from oxidation of entrapped ETIO-porphyrins.

Here we report the identification of C_1-C_6 alkylpyrroles as major pyrolysis products of a Miocene kerogen from the Monterey Formation (CA, USA) and provide evidence that they are derived from macromolecularly-bound tetrapyrrole structures. A more detailed and expanded account of this work will be presented elsewhere.[5]

SAMPLE

The kerogen sample studied is from an immature outcrop in the Santa Barbara basin of the Miocene Monterey Formation (CA, USA). Kerogen isolation was performed by HCl/HF treatment of the solvent-extracted sediment and yielded a kerogen isolate with the elemental composition: C, 60.31%; H, 6.45%; N, 3.55%; $S_{tot.}$, 9.81%; ash, 4.62%; O (by difference), 15.26%.

EXPERIMENTAL

Flash pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS; 610°C, 10 s) was performed using a Curie point pyrolyser mounted on an Hewlett-Packard 5890 gas chromatograph equipped with a 25 m x 0.32 mm i.d. capillary column coated with CP Sil-5 (film thickness 0.45 μm). The gas chromatograph was connected with a VG-70s mass spectrometer operated at 70 eV with a cycle time of 1.8 s and a mass range m/z 50-800 at a resolution of 1000.

Flash pyrolysis-mass spectrometry (Py-MS) was performed using the FOM autoPYMS system. Pyrolysis (770°C) was performed *in vacuo* (180°C) and the products were transferred *via* an expansion chamber (200°C) to a Baltzers QMA 150/QMG 511 quadrupole mass spectrometer. The following MS conditions were employed: electron impact ionization, 15 eV; mass range, *m/z* 25-250; scan rate, 10 scans.s^{-1}.

RESULTS AND DISCUSSION

GC-MS of a flash pyrolysate of a kerogen isolated from an immature (R_o= *ca.* 0.30%) Monterey sediment revealed the abundance of a number pyrroles with alkyl side-chains containing 1-6 carbon atoms. Figure 1 shows a part of the total ion current and a summed mass chromatogram of *m/z* 80.07 + 81.08 +

94.08 + 95.09 + 108.10 + 109.11 + 122.11 + 123.12 + 136.13 + 137.13 + 150.14 + 151.14 of the flash pyrolysate, indicating the abundance of the C_1-C_6 alkylpyrroles. This was also evident from the Py-low voltage MS data (Figure 2) which show the abundance of *m/z* 81, 95, 109, 123 and 137, the molecular ions of the C_1-C_5 alkylpyrroles.

The alkylpyrrole composition in the flash pyrolysate is dominated by a small number of specific alkylpyrroles: 2,3,4-trimethylpyrrole, 3-ethyl-4-methylpyrrole, 2,3-dimethyl-4-ethylpyrrole, 2,4-dimethyl-3-ethylpyrrole and 3-ethyl-2,3,5-trimethylpyrrole (Table 1). Most of these compounds were identified by using authentic standards.

A similar alkylpyrrole composition was found to be present in the flash pyrolysate of the asphaltene fraction isolated from the bitumen of the same Monterey sediment sample. This lends further support to the hypothesis that asphaltenes can be thought of as small, "soluble" parts of kerogen.[6]

The very specific alkyl substitution pattern of the major alkylpyrroles (i.e. with an ethyl and a methyl group at position 3 and 4 and 0-2 methyl group(s) at the other positions) strongly suggest that they are derived from tetrapyrrole pigments (e.g. chlorophyll-*a*, bilirubin).

Therefore, the lininear tetrapyrrole bilirubin was flash pyrolysed under the same conditions as the kerogen sample. Indeed, C_1-C_6 alkylpyrroles were formed and their distribution is dominated by the same structural isomers as in case of the Monterey kerogen pyrolysate (Figure 3). Similar results were obtained for chlorophyll-*a* and protoporphyrin-IX dimethyl ester. These results are in good agreement with literature data.[7]

These results suggest that the Monterey kerogen contains significant amounts of macromolecularly-bound tetrapyrrole units. Quantitative pyrolysis of the kerogen and bilirubin using a polymer internal standard indicate that the kerogen on a weight for weight basis contains *ca.* 15% "bilirubin equivalents". This very high amount of tetrapyrrole pigments suggests either an abundant algal contribution to the sediment (probably related to upwelling conditions) or unique preservation characteristics associated with this deposit or a combination of both factors.

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TABLE 1. Alkylpyrroles identified in the pyrolysates.

peak number	compound(s)
1	C_1 alkylpyrroles
2	C_2 alkylpyrroles
3	C_3 alkylpyrroles
4	2,3,4-trimethylpyrrole
5	3-ethyl-4-methylpyrrole
6	2,3-dimethyl-4-ethylpyrrole
7	2,4-dimethyl-3-ethylpyrrole
8	3-ethyl-2,3,5-trimethylpyrrole

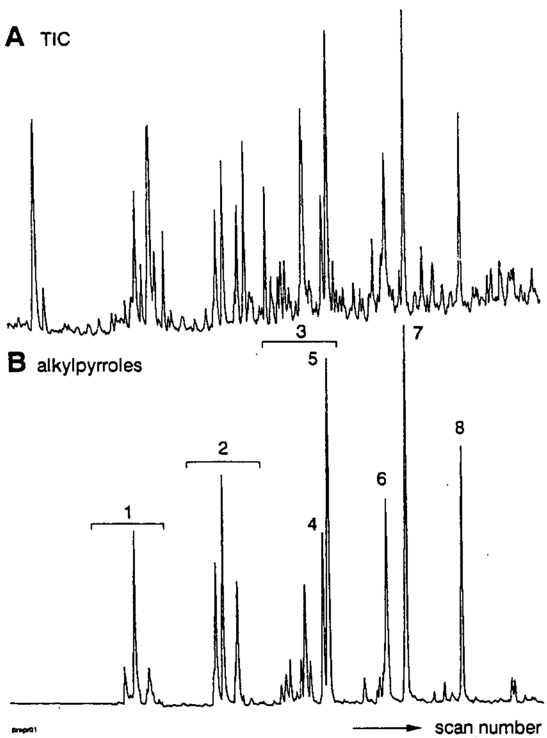

Figure 1. Partial Total Ion Current (TIC; A) of the flash pyrolysate (610°C) of the Monterey-25 kerogen and accurate mass chromatograms (mass window 0.01 amu) of m/z 80.07 + 81.08 + 94.08 + 95.09 + 108.10 + 109.11 + 122.11 + 123.12 + 136.13 + 137.13 + 150.14 + 151.14 showing the distributions of the C_1-C_6 alkylpyrroles (**B**). Peak numbers refer to alkylpyrroles listed in Table 1.

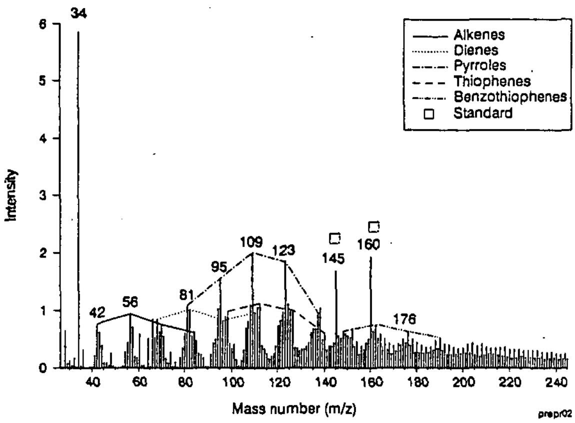

Figure 2. Py-MS spectra of Monterey-25 kerogen. For quantitation poly-4-*t*-butylstyrene was co-pyrolysed, which gives rise to its monomer, 4-*t*-butylstyrene (m/z 160, 145).

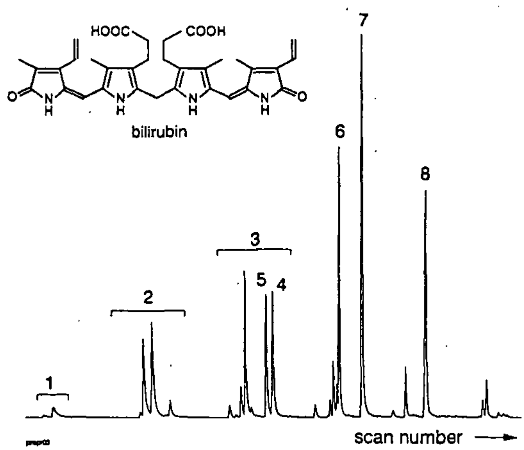

Figure 3. Accurate (mass window 0.01 amu) summed mass chromatograms of m/z 80.07 + 81.08 + 94.08 + 95.09 + 108.10 + 109.11 + 122.11 + 123.12 + 136.13 + 137.13 + 150.14 + 151.14 for the flash pyrolysate (610°C) of bilirubin. Peak numbers refer to alkylpyrroles listed in Table 1.