

LETTER

Alkylpyrroles in a kerogen pyrolysate: Evidence for abundant tetrapyrrole pigments*

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Abstract—C₁–C₆ alkylated pyrroles were identified as major constituents of the flash pyrolysate of a kerogen from the Miocene Monterey Formation (California, USA) using gas chromatography with an N-selective detector and gas chromatography-mass spectrometry. The major alkylpyrroles identified are 2,3,4-trimethylpyrrole; 3-ethyl-4-methylpyrrole; 2,3-dimethyl-4-ethylpyrrole; 2,4-dimethyl-3-ethylpyrrole; and 3-ethyl-2,4,5-trimethylpyrrole. The alkyl substitution patterns of the alkylpyrroles strongly suggest an origin from tetrapyrrole pigments. Evidence for this hypothesis was provided by flash pyrolysis of the tetrapyrrole pigments chlorophyll-*a*, protoporphyrin-IX dimethyl ester, and bilirubin, which yielded alkylpyrroles with a similar isomer distribution. Quantitative pyrolysis using a polymer internal standard of both the kerogen and the tetrapyrrole pigments revealed that ca. 5% of the kerogen consists of macromolecularly bound tetrapyrrole pigments or that this fraction contains ca. 5% insoluble tetrapyrrole salts. These results show that in specific cases tetrapyrrole pigments can contribute significantly to the sedimentary organic matter.

INTRODUCTION

KEROGEN, THE INSOLUBLE ORGANIC matter in the crust of the Earth, consists of complex macromolecules, whose structure and origin is still a matter of controversy. In the classical view of kerogen formation (e.g., TISSOT and WELTE, 1984), these macromolecules are proposed to be formed by abiogenic random repolymerisation and polycondensation reactions of a small fraction of the monomers of biopolymers (e.g., carbohydrates, proteins). Recently, however, it has been demonstrated that specific, insoluble and nonhydrolysable macromolecular structures present in organisms may become selectively preserved in the fossil record and thus may form a substantial part of kerogen (TEGELAAR et al., 1989). For example, the outer cell walls of algae and cuticular membranes of higher plants contain resistant, highly aliphatic biopolymers, which are mainly comprised of C and H. Selective preservation of these types of biopolymers are considered to be the origin for a major fraction of the C and H in kerogen (TEGELAAR et al., 1989). Similarly, selective preservation of the oxygen-containing biopolymers lignin and tannin has been proposed to explain the high amounts of oxygen in brown coals (e.g., VAN KREVELEN, 1961; NIP et al., 1988; WILSON and HATCHER, 1988). Organic sulphur (S_{org}) in geomacromolecules has a different origin; it is mainly formed during syndepositional reactions of inorganic sulphur species with organic matter leading to the synthesis of geomacromolecules (SINNINGHE DAMSTÉ et al., 1988b, 1990; KOHNEN et al., 1991).

The origin of C, H, O and S_{org} in geomacromolecules can thus be at least partially explained by the above. However, the origin of the fifth most abundant element in kerogen, N (typically 2–3% by weight), is much less clear. Ubiquitously occurring N-containing biopolymers (i.e., proteins, DNA/RNA and, to a lesser extent, chitin) do contain significant amounts of N but their preservation potential is generally low (DE LEEUW and LARGEAU, 1992). Therefore, they cannot act as a major precursor of N in kerogen. An alternative source for N in kerogen are the various cyclic tetrapyrroles (including (bacterio)chlorophylls) occurring in higher plants, algae and bacteria and phycocyanobilin (IV) and phycoerythrobilin (V) occurring in cyanobacteria and certain types of algae.

In this paper we report identification of C₁–C₆ alkylpyrroles as major pyrolysis products of a Miocene kerogen from the Monterey Formation (California, USA) and provide evidence to indicate that they are derived from tetrapyrrole structures.

EXPERIMENTAL

Samples

The sediment sample is from the Upper Miocene Monterey Formation (California, USA), a phosphatic-siliceous-carbonate rock sequence, and was collected from an outcrop near Vandenberg Air Force Base (Santa Barbara County). The sample is organic-rich (TOC = 17.3%) and contains immature organic matter (R₀ = ca. 0.30%). The sediment sample was powdered in a disc mill (TEMA) and Soxhlet extracted with CH₂Cl₂/MeOH (93/7, v/v) for 72 h. Asphaltenes were precipitated from the bitumen by adding a 40-fold excess of *n*-heptane and were purified by repeating the precipitation procedure a further three times. Kerogen isolation was performed by HCl/HF treatment of the solvent-extracted sediment and yielded

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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%. Full experimental details are given in EGLINTON (1988).

Bilirubin (Aldrich) and protoporphyrin-IX dimethyl ester (II; Aldrich) are commercially available. Chlorophyll-*a* (I) was extracted from spinach with acetone and purified on a silica column (acetone/hexane, 3/7) followed by reversed phase HPLC.

Flash Pyrolysis-Gas Chromatography (Py-GC)

Flash Py-GC was carried out using a pyrolysis reactor, previously described by VAN DE MEENT et al. (1980a), which was directly mounted on the injector block of a Varian 3700 gas chromatograph. The temperature of the injector block was 250°C. Samples were applied to ferromagnetic wires by pressing the sample (kerogen) on the wire or by adding a few droplets of a solution (other samples). The wires were heated within 0.15 s to their Curie temperatures (610°C) and were kept at this temperature for 10 s. Separation of the pyrolysis products was accomplished by a fused silica capillary column (25 m \times 0.32 mm) coated with CP-Sil 5 (film thickness 0.45 μ m) using helium as carrier gas. The temperature was programmed from 0°C (5 min), by using a cryogenic unit, to 300°C (20 min) at a rate of 3°C \cdot min⁻¹. The gas chromatograph was equipped with an FID. Quantitative flash pyrolysis was performed by copyrolysis of a mixture of the sample and the internal standard poly-4-*t*-butylstyrene, which yields upon pyrolysis the monomer 4-*t*-butylstyrene in high yield.

Flash Pyrolysis-Gas Chromatography-Atomic Emission Spectroscopy (Py-GC-AED)

Element-selective detection of the pyrolysate was performed using an HP 5890 gas chromatograph interfaced to an HP 5921A Atomic Emission Detector (AED). Flash pyrolysis (610°C, 1.5 s) was induced using a Horizon Curie-point pyrolyser. Separation of the pyrolysate was achieved on an HP-1 column (50 m \times 0.32 mm, film thickness 0.52 μ m) programmed from 30 to 300°C at 5°C \cdot min⁻¹ using helium as carrier gas. The atomic emission lines for C (193 nm) and N (174 nm) were simultaneously monitored with S (181 nm).

Flash Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

Flash pyrolysis-GC-MS analyses were performed on two instruments. A Hewlett-Packard 5480 gas chromatograph connected with a VG-70s mass spectrometer was used with pyrolysis and chromatographic conditions identical to those described above for Py-GC. Electron impact mass spectra were obtained at 70 eV with a cycle time of 1.8 s and a mass range m/z 50–800 at a resolution of 1000. Data acquisition was started 1 min after pyrolysis. Supplementary Py-GC-MS experiments were performed using a commercially available Curie-point pyrolyser (Horizon Instruments). In these experiments samples (ca. 10 μ g) were coated onto wires with a Curie temperature of 770°C. The pyrolyser was mounted on a Carlo Erba 4160 gas chromatograph, the latter being directly interfaced to a Finnigan 4500 quadrupole mass spectrometer. The temperature of the pyrolysis unit was held at 250°C. GC conditions: capillary column coated with DB-5 (30 m \times 0.32 mm, film thickness 0.25 μ m), temperature program: 35°C (5 min)–310°C at 4°C \cdot min⁻¹. MS conditions: ionization voltage, 50 eV; scan range, m/z 50–650; scan rate, 1 scan \cdot s⁻¹.

Flash Pyrolysis-Mass Spectrometry (Py-MS)

Curie-point pyrolysis-mass spectrometry was performed using the FOM autoPYMS system. The sample was coated onto a wire with a Curie temperature of 770°C and pyrolysed (1 s) in a high-frequency coil using a Fischer power source. Pyrolysis 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 spec-

trometer. The following MS conditions were employed: electron impact ionization, 15 eV; mass range, m/z 25–250; scan rate, 10 scans \cdot s⁻¹. Approximately 200 scans were summed to provide the averaged spectrum. The Py-MS analysis was conducted in triplicate, and the spectrum presented is the average of the three measured spectra.

Authentic Standards

3-Ethyl-2,4-dimethylpyrrole, 4-ethyl-2,3-dimethylpyrrole, and 3-ethyl-2,4,5-trimethylpyrrole were obtained by reduction of sodium copper chlorophyllin (WILLSTÄTTER and ASAHINA, 1911). In brief, sodium copper chlorophyllin (Sigma) in EtOAc was treated with tin powder and HCl at 80°C. The pH of the reaction mixture was adjusted to 8 and the alkylpyrroles formed were extracted with *n*-hexane. GC-MS of this mixture revealed the presence of the aforementioned alkylpyrroles.

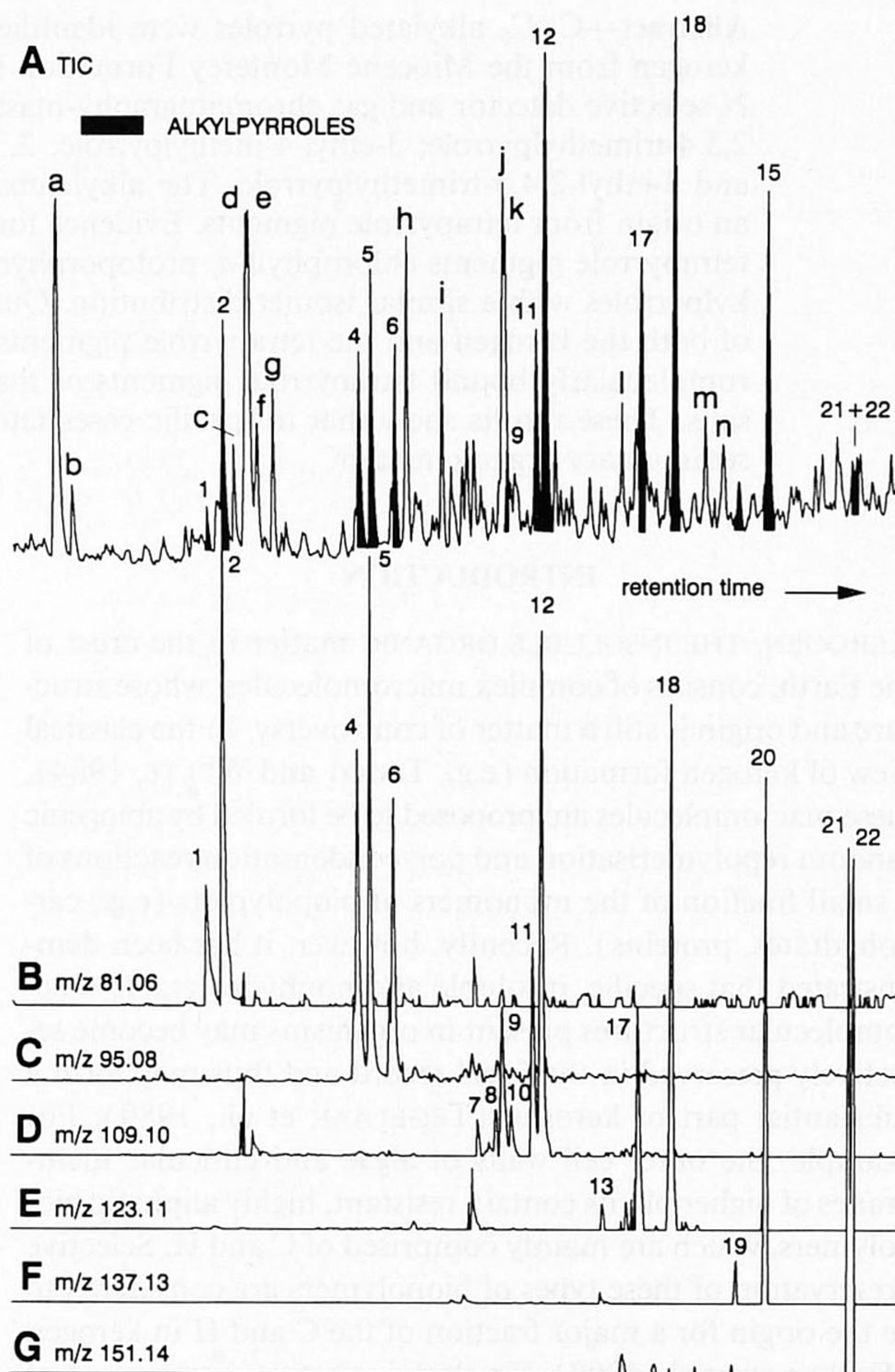


FIG. 1. Partial Total Ion Current (TIC; A) of the flash pyrolysate (610°C) of the Monterey kerogen and accurate mass chromatograms (mass window 0.01 amu) of m/z 81.06 (B), 95.08 (C), 109.10 (D), 123.11 (E), 137.13 (F) and 151.14 (G) showing the distributions of the C₁–C₆ alkylpyrroles. Peak numbers refer to alkylpyrroles listed in Table 1. Peaks labelled by letters indicate other components. Key: a = toluene + 2-methylthiophene; b = 3-methylthiophene; c = ethylbenzene + 2-ethylthiophene; d = 2,5-dimethylthiophene; e = *m*- and *p*-xylene; f = 2,4-dimethylthiophene; g = 2,3-dimethylthiophene; h = 2-ethyl-5-methylthiophene; i = 2,3,5-trimethylthiophene; j = 1,2,3-trimethylbenzene; k = 3-isopropyl-2-methylthiophene; l = C_{4,1}-thiophene; m = 1,2,3,4-tetramethylbenzene; n = 2-pentyl-thiophene + 2,3-dimethyl-5-propylthiophene.

RESULTS AND DISCUSSION

Identification of Alkylpyrroles

The flash pyrolysate (610°C) of the isolated kerogen of an immature sediment sample from the Monterey Formation contained a number of abundant, initially unknown, low-molecular-weight compounds. It was shown by using a N-selective detector (AED) that this suite of components contains N. By means of flash pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), these components were identified as pyrroles containing alkyl substituents with up to six carbon atoms (in total). Figure 1 shows a part of the total ion current of the flash pyrolysate (trace A) and the mass chromatograms of the molecular ions of the alkylpyrroles (traces B–G). Peak numbers refer to compounds listed in Table 1. The C₁–C₆ alkylpyrroles were identified by comparison of mass spectral and relative retention time data with data from the literature (BALTES and BOCHMANN, 1987; MCLAFFERTY and STAUFFER, 1988) and in some cases with data obtained for authentic standards as indicated in Table 1.

Figure 1 shows that the C₁–C₆ alkylpyrroles are the major pyrolysis products of the particular Monterey kerogen examined. Py-low voltage (15 eV) MS data (Fig. 2a) also reveal the abundance of the alkylpyrroles in the Monterey kerogen pyrolysate by the high intensity of the molecular ions at *m/z* 81, 95, 109, 123, and 137. The Py-GC-MS data (Fig. 1) reveal a strong dominance of specific alkylpyrrole isomers.

The C₃- and C₄-alkylpyrroles are dominated by 2,3,4-trimethyl-pyrrole and 3-ethyl-4-methylpyrrole and by 2,3-methyl-4-ethylpyrrole and 2,4-dimethyl-3-ethylpyrrole, respectively. Furthermore, only two of all the seventy-two theoretically possible C₅-alkylpyrrole isomers are present with 3-ethyl-2,4,5-trimethylpyrrole dominating. The alkyl substitution patterns of the pyrroles bear a strong similarity to those of alkylpyrroles moieties present in naturally occurring tetrapyrrole pigments (e.g., chlorophyll-*a* (I), protoporphyrin-IX (II), bilirubin (III), phycocyanobilin (IV), phycoerythrobilin (V), and DPEP (VI) and ETIO (VII) porphyrins). Therefore, it is proposed that these alkylpyrroles were formed by flash pyrolysis from tetrapyrrole pigments present in the kerogen.

The same suite of C₁–C₆ alkylpyrroles was found to be present (albeit in somewhat lower relative abundance) in the flash pyrolysate (610°C) of the asphaltene fraction isolated from the bitumen of the same Monterey sediment sample.

Model Compounds

To test whether alkylpyrroles can be generated from tetrapyrrole pigments, a number of tetrapyrrole pigments [chlorophyll-*a* (I), protoporphyrin-IX (II) dimethyl ester, bilirubin (III), octaethylporphyrin (VII, R₁–R₈ = ethyl), vanadyl octaethylporphyrin, nickel octaethylporphyrin, and nickel ETIO-porphyrin-III] were subjected to flash pyrolysis

Table 1: Compound identification and pyrolysis yields of selected alkylpyrroles.

compound	I ^a	MS characteristics	CL ^b	concentration (mg/g) ^c	
				Mont. ker.	bilirubin
1 2-methylpyrrole	824	81(63),80(100),53(25)	C ^d		
2 3-methylpyrrole	832	81(63),80(100),53(25)	C ^d	0.6	1.0
3 2,5-dimethylpyrrole	907	95(67),94(100),80(25)	C ^e		
4 2,4-dimethylpyrrole	909	95(64),94(100),80(19)	C ^e	0.6	2.9
5 2,3-dimethylpyrrole	916	95(68),94(100),80(28)	C ^e	0.9	2.9
6 3,4-dimethylpyrrole	931	95(65),94(100),80(25)	C ^e	0.7	0.8
7 ethylmethylpyrrole	983	109(42),108(8),94(100)	T		
8 ethylmethylpyrrole	993	109(43),108(10),94(100)	T		
9 2,3,5-trimethylpyrrole	997	109(62),108(100),94(32)	C ^e	n.d. ^f	6.4
10 4-ethyl-2-methylpyrrole	1003	109(52),108(14),94(100)	C ^e		
11 2,3,4-trimethylpyrrole	1016	109(63),108(100),94(38)	C ^e	0.6	4.3
12 3-ethyl-4-methylpyrrole	1021	109(46),108(11),94(100)	C ^{e,g}	1.9	6.5
13 ethyldimethylpyrrole	1061	123(40),108(100),94(20)	T		
14 ethyldimethylpyrrole	1076	123(42),108(100),94(10)	T		
15 ethyldimethylpyrrole	1079	123(39),108(100),93(6)	T		
16 ethyldimethylpyrrole	1082	123(38),108(100),93(10)	T		
17 2,3-dimethyl-4-ethylpyrrole	1083	123(38),108(100),93(6)	SC	0.9	8.0
18 2,4-dimethyl-3-ethylpyrrole	1105	123(51),122(41),108(100)	SC	1.7	13.2
19 2,3-diethyl-4-methylpyrrole	1149	137(35),122(100),107(25)	T ^h		
20 3-ethyl-2,4,5-trimethylpyrrole	1168	137(37),122(100),107(7)	SC	1.0	10.1
21 2,3-diethyl-4,5-dimethylpyrrole	1224	151(30),136(100),121(18)	T ^h		
22 2,4-diethyl-3,5-dimethylpyrrole	1231	151(32),136(100),121(22)	T ^h	8.9 ⁺	56.1 ⁺

^a pseudo Kovats retention index as determined by linear interpolation with the homologous series of *n*-alkanes as a reference, with *n*-decane = 1000.

^b CL = Confidence Level of structural assignment; T = tentative; C = confident, mass spectrum is identical with a mass spectrum from the literature; SC = standard confirmed, retention time and mass spectral data agree with those of an authentic standard.

^c as determined by integration of peaks of appropriate alkylpyrroles and 4-*t*-butylstyrene in the FID traces of the pyrograms of mixtures of known amounts of sample and poly-4-*t*-butylstyrene.

^d relative retention data are in agreement with those published by BALTES and BOCHMANN (1987).

^e assignment of positions of substituents is in analogy with that reported for alkylthiophenes (SINNINGHE DAMSTE et al., 1988b).

^f n.d. = not determined.

^g shows a characteristic abundant *m/z* 67 (25%) in its mass spectrum.

^h assignment of positions of substituents is based on the likelihood that this pyrrole can be formed from the studied model compounds.

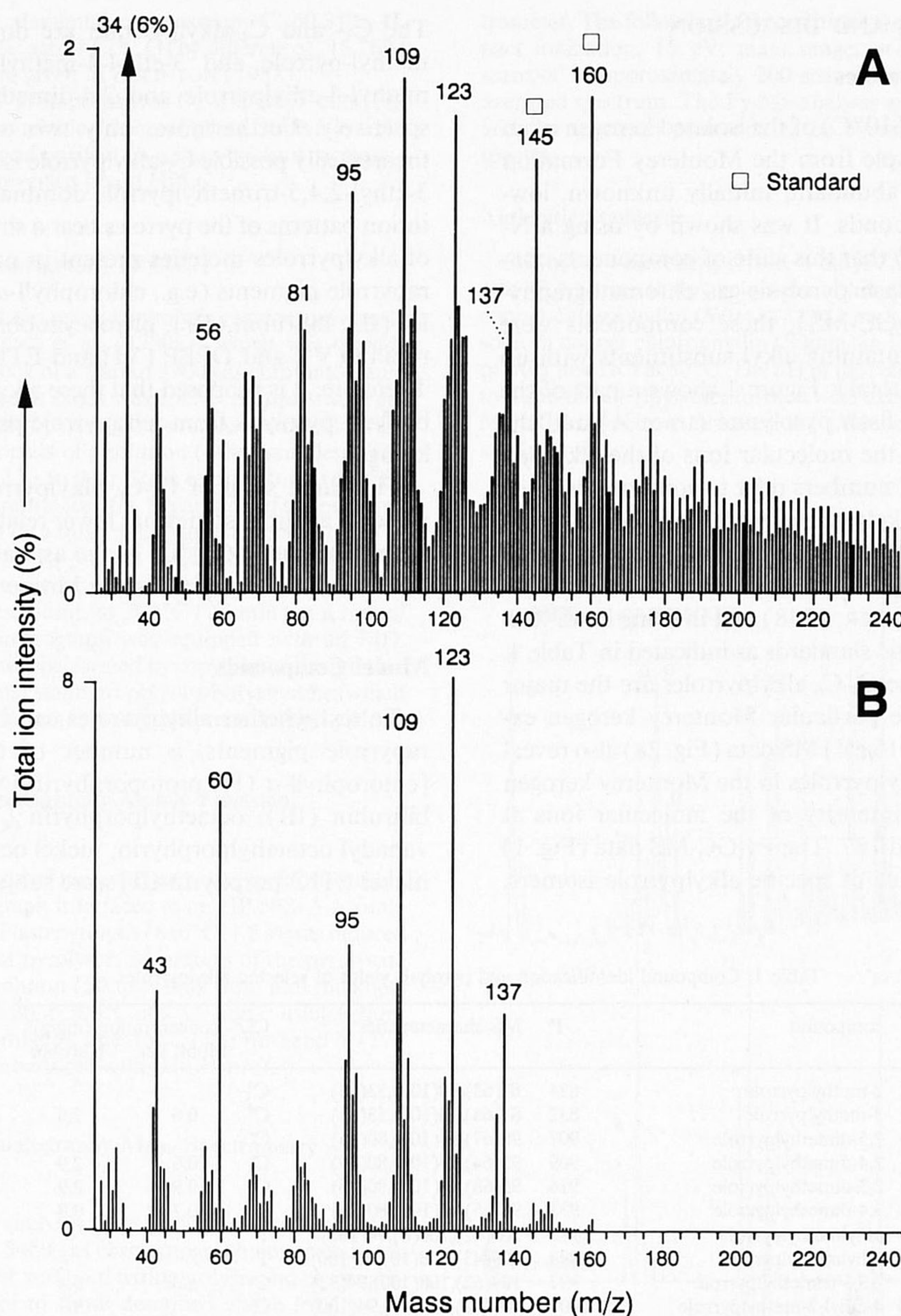


FIG. 2. Partial Py-MS spectra of (A) Monterey kerogen (modified from EGLINTON et al., 1991) and (B) bilirubin. The latter spectrum is taken from literature data (MEUZELAAR et al., 1982). For quantitation poly-4-*t*-butylstyrene was co-pyrolysed with the Monterey kerogen, which gives rise to its monomer, 4-*t*-butylstyrene (m/z 160, 145).

and the composition of their pyrolysates was examined with GC-MS. Flash pyrolysis using a ferromagnetic wire with a Curie temperature of 610°C of the linear tetrapyrrole bilirubin (III) generated a mixture of compounds with abundant alkylpyrroles (Fig. 3). In addition, the pyrolysate also contains 3,4-dehydro-2-pyrrolidone and (2'-carboxyethyl)pyrrole derivatives as expected from the structure of bilirubin. The abundance of alkylpyrroles in the bilirubin pyrolysate indicates that the 2'-carboxyethyl moieties are easily decarboxylated during flash pyrolysis. However, the characteristic substitution pattern of the 3-(2'-carboxyethyl)-4-methylpyrrole moieties in bilirubin is strongly retained in the most abundant alkylpyrroles in the flash pyrolysate. Comparison of the alkylpyrrole distribution in the bilirubin flash pyrolysate

with that of the Monterey kerogen pyrolysate (Fig. 4) reveals that (1) the same positional isomers are present and (2) the relative abundance of these isomers is comparable. Similar alkylpyrrole components were generated by flash pyrolysis of the cyclic tetrapyrrole chlorophyll-*a* (I) and protoporphyrin-IX (II) dimethyl ester (Fig. 5). In the former case substantial amounts of phytadienes were also formed as previously described by VAN DE MEENT et al. (1980b). These results are in accordance with a Py-MS spectrum recorded for protoporphyrin-IX (II) dimethyl ester (BRACEWELL et al., 1987), also indicating a facile degradation into alkylated pyrroles. This was also reported by WHITTEN et al. (1966) for the controlled thermal degradation of mesoporphyrin (II, with two ethyl groups instead of the ethenyl groups). Pyrroles

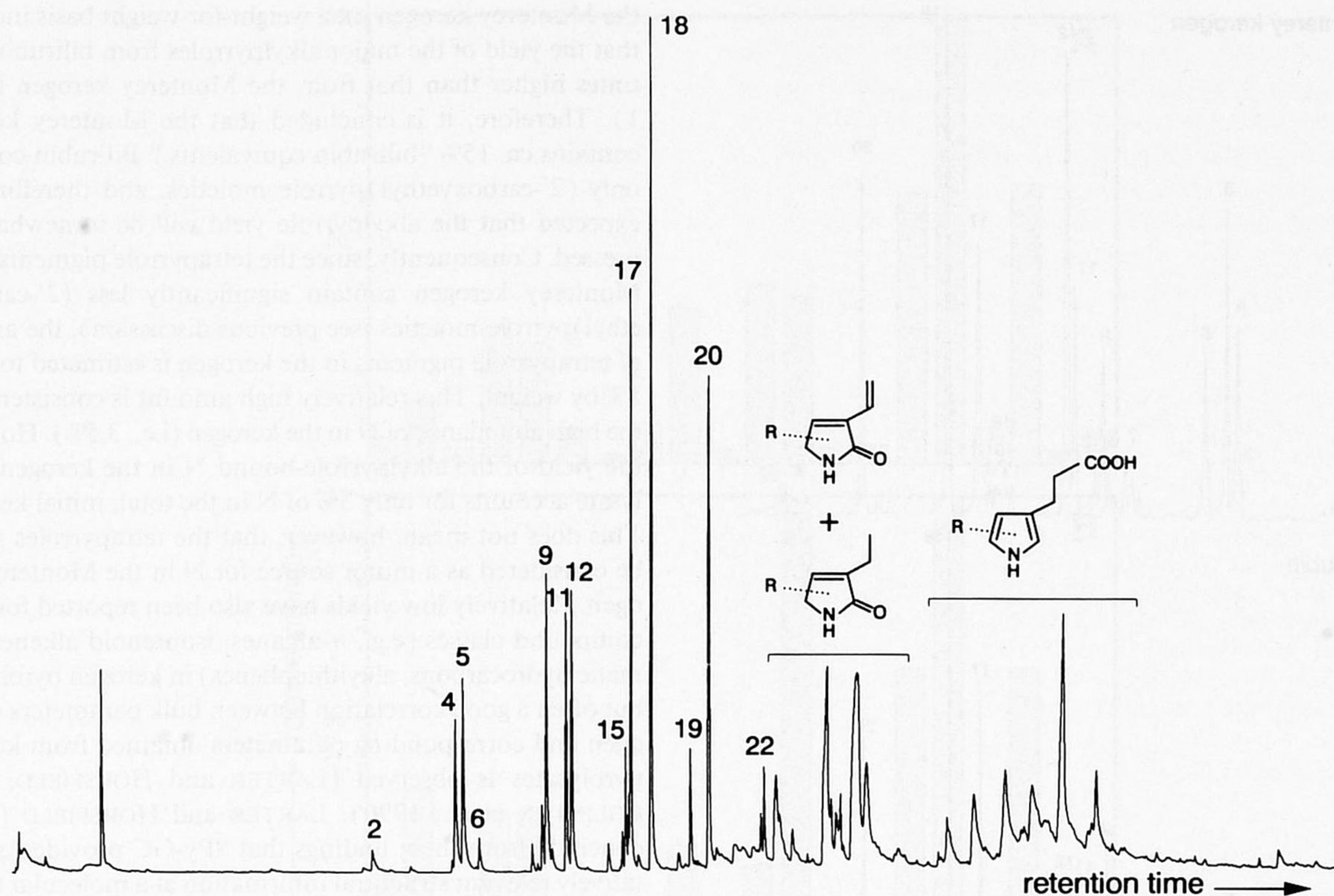


FIG. 3. Partial (0-75 min) TIC of the flash pyrolysate (610°C) of bilirubin. Peak numbers refer to alkylpyrroles listed in Table 1.

12, 17, 18, and 20 (Table 1) were the major pyrroles identified at the temperatures examined (in the range 420–770°C).

Flash pyrolysis of free base octaethylporphyrin (VII, R_1 - R_8 = ethyl) and the metallo-porphyrins, vanadyl octaethylporphyrin, nickel octaethylporphyrin and nickel ETIO-porphyrin III did not generate alkylpyrroles. This is consistent with the findings of MEUZELAAR et al. (1982). These authors measured the Py-MS spectrum of tetraethyltetramethylporphyrin (VII; R_1 = R_3 = R_5 = R_7 = methyl, R_2 = R_4 = R_6 = R_8 = ethyl) and did not note any fragment ions which could be ascribed to alkylated pyrroles. Probably both the free base and the metalloporphyrins are thermally stable and evaporate from the pyrolysis wire before they start to degrade. Their thermal stability is also attested by their GC-amenability using high temperatures (400°C; BLUM et al., 1988).

These experiments seem to indicate that acid or ester groups (the latter may be transformed into acid groups upon thermal degradation) may play a critical role in determining the thermal stability of tetrapyrroles and for "cyclic" structures (i.e., porphyrin like) in dictating the breakdown of the tetrapyrrole nuclei (cf. breakdown products of protoporphyrin-IX with those of octaethylporphyrin). However, the degradation pathway of the functionalized tetrapyrroles is by no means clear. The formation of alkylpyrroles requires multiple bond cleavage at the *meso* positions of the tetrapyrrole. It is suggested that the degradation proceeds by an initial hydrogenation to the corresponding, not fully conjugated porphyrinogens (hexahydroporphyrins) followed by a subsequent breakdown into alkylpyrroles. Since this process

requires a lot of hydrogen, this has to be furnished by other tetrapyrroles, which may explain the relatively low yield of alkylpyrroles from bilirubin (Table 1). The proposed degradation pathway is based on a mass spectrometry study of porphyrinogens (BUDZIEKIWICZ and PESCH, 1976) which revealed that these compounds upon electron impact ionization yield more fragment ions (including those of alkylpyrroles) than the corresponding porphyrins. Chemical ionization-mass spectrometry with H_2 or NH_3 reagent gases (SHAW et al., 1981; SUNDARARAMAN et al., 1984; JIANG et al., 1984; WOLFF et al., 1984; VAN BERKEL et al., 1989a) also leads to hydrogenation of porphyrins and thus promotes formation of tri-, di-, and monopyrrolic fragment ions. The proposed thermal degradation pathway should also apply to macro-molecularly bound nonfunctionalized tetrapyrroles (i.e., ETIO- and DPEP-porphyrins; VI and VII). It is well documented that such macromolecularly bound porphyrins do occur in kerogen (e.g., VAN BERKEL and FILBY, 1987; BEATO et al., 1991).

A comparison of the Py-MS spectrum of the Monterey kerogen with that published for bilirubin (MEUZELAAR et al., 1982) indicates that the tetrapyrrole moieties in the kerogen contain less 2'-carboxyethyl groups than bilirubin since the intensity of the ion at m/z 60 (ascribed to acetic acid derived from the 2'-carboxyethyl groups; MEUZELAAR et al., 1982) relative to m/z 123 is significantly less in the Py-MS spectrum of the Monterey kerogen (cf. Fig. 2a, b). Furthermore, m/z 60 in the Py-MS spectrum of the kerogen can also have other sources (e.g., COS). Lastly, 3,4-dehydro-2-

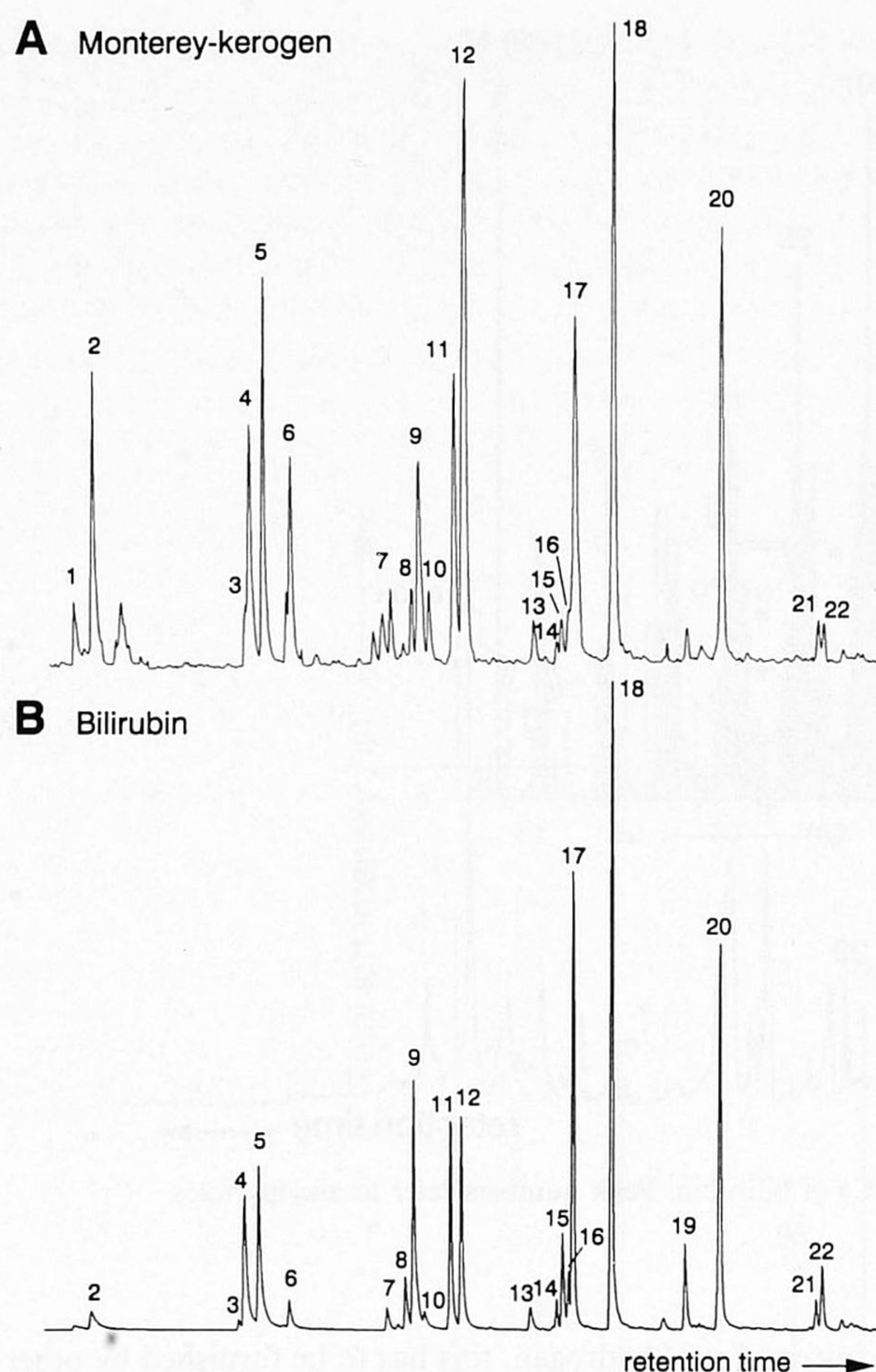


FIG. 4. Accurate (mass window 0.01 amu) summed mass chromatograms of m/z 80.07 + 81.08 + 94.08 + 95.09 + 108.10 + 109.11 + 122.11 + 123.12 + 136.13 + 137.13 + 150.14 + 151.14 for the flash pyrolysate (610°C) of (A) the Monterey kerogen and (B) bilirubin. Peak numbers refer to alkylpyrroles listed in Table 1.

pyrrolidone and (2'-carboxyethyl)pyrrole derivatives were not detected in the Monterey kerogen pyrolysate, indicating that unaltered bilirubin, phycocyanobilin, or phycoerythrobilin cannot be important precursors for the alkylated pyrroles.

These findings indicate that macromolecularly bound, cyclic tetrapyrrole pigments may act as precursor structures for the specific alkylpyrroles observed in the Monterey kerogen and asphaltene pyrolysates. Alternatively, "free" functionalized tetrapyrrole pigments may be associated with the kerogen in salt and hence unextractable form. If the tetrapyrrole pigments are macromolecularly bound in the kerogen, it may be speculated that such binding of pigments occurs via sulphur bridges, since the sample contains a high amount of organically bound sulphur as revealed by the abundance of alkylthiophenes in the flash pyrolysate (Fig. 1; EGLINTON et al., 1990; SINNINGHE DAMSTÉ et al., 1990).

Quantitative Pyrolysis

Quantitative flash pyrolysis (using a polymer internal standard; LARTER and SENFTLE, 1985) of both bilirubin and

the Monterey kerogen on a weight-for-weight basis indicates that the yield of the major alkylpyrroles from bilirubin is six times higher than that from the Monterey kerogen (Table 1). Therefore, it is concluded that the Monterey kerogen contains ca. 15% "bilirubin equivalents." Bilirubin contains only (2'-carboxyethyl)pyrrole moieties, and therefore it is expected that the alkylpyrrole yield will be somewhat suppressed. Consequently, since the tetrapyrrole pigments in the Monterey kerogen contain significantly less (2'-carboxyethyl)pyrrole moieties (see previous discussion), the amount of tetrapyrrole pigments in the kerogen is estimated to be ca. 5% by weight. This relatively high amount is consistent with the high abundance of N in the kerogen (i.e., 3.5%). However, the yield of the alkylpyrrole-bound N in the kerogen pyrolysate accounts for only 3% of N in the total, initial kerogen. This does not mean, however, that the tetrapyrroles should be considered as a minor source for N in the Monterey kerogen. Relatively low yields have also been reported for other compound classes (e.g., *n*-alkanes, isoprenoid alkenes, aromatic hydrocarbons, alkylthiophenes) in kerogen pyrolysates, but often a good correlation between bulk parameters of kerogen and corresponding parameters obtained from kerogen pyrolysates is observed (LARTER and HORSFIELD, 1992; EGLINTON et al., 1990). LARTER and HORSFIELD (1992) conclude from these findings that "Py-GC provides quantitatively relevant structural information at a molecular level." Therefore, it is thought that cyclic tetrapyrroles contribute significantly to the organic matter of the Monterey sediment sample.

The estimation that the Monterey kerogen contains ca. 5 wt% tetrapyrrole pigments is also not unreasonable from another point of view. VAN BERKEL et al. (1989b) reported the nickel and vanadium concentrations in the New Albany kerogen. If we assume that the nickel and vanadium in the kerogen is predominantly complexed with porphyrin, a similar value for tetrapyrrole pigment abundance is obtained. Thus, other kerogens may contain the same high concentrations of tetrapyrrole pigments.

Geochemical Implications

Several hundreds of sediment samples representing a wide range of depositional environments and diagenetic stages have been analyzed by flash pyrolysis in our laboratory in the course of various geochemical studies. Despite these extensive investigations, high yields of alkylpyrroles have not previously been observed. These results described here thus indicate the unique character of the Monterey kerogen studied. Other samples from the Monterey Formation investigated in this laboratory did not generate significant amounts of alkylpyrroles upon flash pyrolysis. However, BARAKAT and YEN (1989) reported recently that major amounts of 3-ethyl-4-methyl-1H-pyrrole-2,5-dione and, to a lesser extent, 3,4-dimethyl-1H-pyrrole-2,5-dione were formed upon controlled stepwise oxidation of a Monterey kerogen from the Santa Maria basin. The same products were also identified in the oxidation mixture of Green River shale kerogen. These compounds are thought to be derived from oxidation of entrapped ETIO-porphyrins (VII). However, in view of our observa-

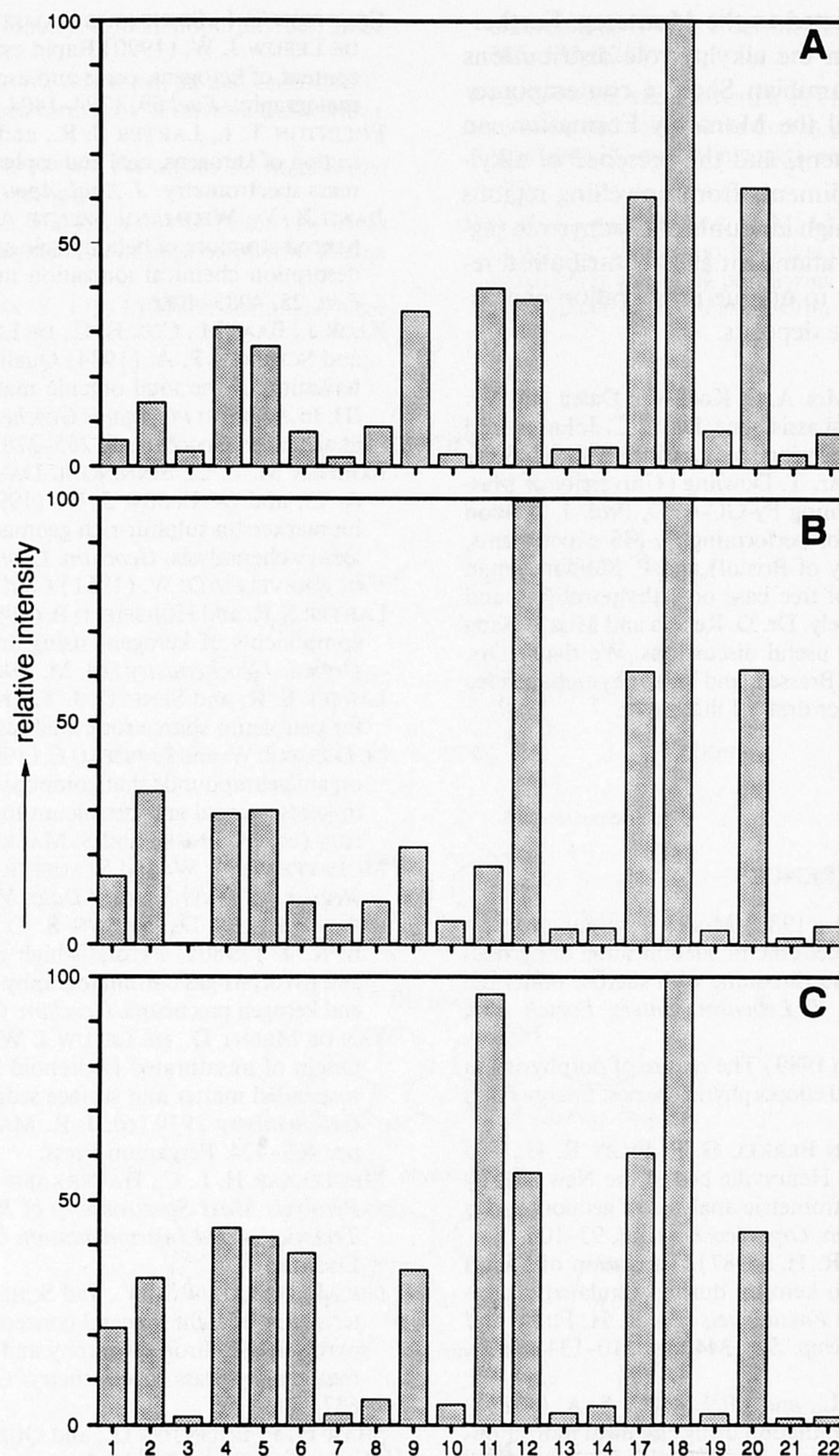


FIG. 5. Bar charts showing the distributions of alkylpyrroles generated by flash pyrolysis (770°C, 1.5 s) using the Horizon system of (A) bilirubin (III), (B) chlorophyll-*a* (I), and (C) protoporphyrin-IX (II). Numbers indicate alkylpyrroles indicated in Table 1. Data were obtained by integration of summed mass chromatograms of m/z 80 + 81 + 94 + 95 + 108 + 109 + 122 + 123 + 136 + 137 + 150 + 151.

tions, it can also be argued that they derive from oxidation of macromolecularly bound tetrapyrrole pigments or tetrapyrrole salts. KLOK et al. (1984) reported alkylpyrroles in the flash pyrolysate of the residue obtained from a Recent diatomaceous ooze from the Namibian Shelf obtained after acid treatment and subsequent extraction. Although the authors did not report the exact structures, their measured retention indices are in good agreement with those described in this work (Table 1) and indicate that 2,3,4-trimethylpyrrole, 3-ethyl-4-methylpyrrole, 2,3-dimethyl-4-ethylpyrrole, 2,4-dimethyl-3-ethylpyrrole, and 3-ethyl-2,3,5-trimethylpyr-

role are the most abundant alkylpyrroles in the pyrolysate. This distribution is similar to the alkylpyrrole distribution of both the Monterey kerogen and the tetrapyrrole pigment pyrolysates. Alkylpyrroles have also been detected in pyrolysates of sediments from the Oman and Peru upwelling region (Whelan, pers. commun.). BRACEWELL et al. (1987) recorded the Py-MS spectra of humic material isolated from Cretaceous chalks and reported the presence of alkylpyrroles in some of their pyrolysates.

These scattered literature reports indicate that the occurrence of tetrapyrrole pigments in macromolecular organic

matter fractions is not restricted to the Monterey. Furthermore, the similarity between the alkylpyrrole distributions of the kerogen from the Namibian Shelf, a contemporary upwelling environment, and the Monterey Formation, an ancient upwelling environment, and the presence of alkylpyrroles in other Recent sediments from upwelling regions indicates that the relatively high amounts of tetrapyrrole pigments may be related to the abundant algal contribution received by both sediments or to unique preservation characteristics associated with these deposits.

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APPENDIX

