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The identification of mono-, di- and trimethyl 2-methyl-2-(4,8,12-trimethyltridecyl)chromans and their occurrence in the geosphere

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Abstract—A series of novel mono-, di- and trimethyl 2-methyl-2-(4,8,12-trimethyltridecyl)chromans (MTTC) have been identified in a number of sediment extracts and oils ranging from Pleistocene to Permian. The identifications were based on comparison of mass spectra and chromatographic data of synthetic methylated MTTC with those of geologically occurring methylated MTTC and coinjections with the synthetic standards. Although the methylated MTTC are structurally related to tocopherols, they do not appear to be their diagenetic derivatives. The distribution of methylated MTTC in sediments and oils seems to depend on the original environment of deposition and may be used as a palaeoenvironmental indicator, *e.g.* to assess the occurrence of palaeohypersalinity.

INTRODUCTION

THE CHROMAN SKELETON was first recognized in nature with the elucidation of the structure of α-tocopherol (vitamin E) (Table 1) by FERNHOLZ (1938). Ever since, considerable interest has arisen in this compound, especially in its biochemistry, and also in the structurally related β-, γ- and δ-tocopherols. Tocopherols are found in a variety of higher plant species (JANISZOWSKA and PENNOCK, 1976), algae (JENSEN, 1969), cyanobacteria (NEWTON *et al.*, 1977) and bacteria (GREEN *et al.*, 1959). They are natural anti-oxidants which protect lipids from excessive oxidation.

α-, γ- and δ-tocopherol have been encountered in a wide variety of sediment extracts (BRASSELL *et al.*, 1983; BRASSELL and EGLINTON, 1986). However, their usefulness as marker compounds is limited by their widespread biological occurrence. Tocopherols are geochemically significant in another respect; they can act as the precursors of pristane in ancient sediments and oils (GOOSSENS *et al.*, 1984).

Here we report the identification and occurrence of several related chroman derivatives in a number of sediments and oils of different geological ages.

EXPERIMENTAL

Samples. A number of samples have been investigated, as described briefly below.

A sediment sample from the Walvis Ridge was obtained from DSDP Hole 532, within the upwelling region along the Namibian Shelf (BRASSELL and EGLINTON, 1983).

The Sachrang sample from the south-western part of the Federal Republic of Germany was collected from an outcrop (BITTERLI, 1962) and is a manganiferous black shale deposited in a small basin underlain by Permian salt (H. C. JENKYNS, pers. commun.).

The Z2 sample is a hypersaline mudstone taken from a core collected *ca.* 40 km south of the Renqiu oil field in Hebei Province, China (BRASSELL *et al.*, 1987).

The Northern Apennines Marl (NAM) is from Miocene strata in the Perticara basin (Italy) which consist of varieties of gypsum deposits interbedded with bituminous marl layers. A 10 cm thick marl layer was sampled (see TEN HAVEN *et al.*, 1985, for details of sampling and geological setting) which is thought to have been deposited in a hypersaline environment.

Phosphoria Retort Shale is a phosphatic mudstone and dolomitic marlstone sequence of Permian age from the North-western part of Montana (U.S.A.) which was deposited in a large embayment with water depths of probably less than 40 meters (MCKELVEY *et al.*, 1959).

WX6-3 is a Palaeogene dark grey mudstone (depth 1704 m) from the Jianghan basin in the Southern part of Hubei Province, Eastern China, deposited in a hypersaline lacustrine environment (FU *et al.*, 1986).

The Rozel Point Oil is an oil from the North-western part of Utah (U.S.A.). Its source rock is thought to have been deposited in a playa lake environment (MEISSNER *et al.*, 1984), similar to that of WX6-3. Detailed analysis of the biological marker composition of this oil is presented elsewhere (SCHMID, 1986; SINNINGHE DAMSTÉ and DE LEEUW, 1987; TEN HAVEN *et al.*, 1987; SINNINGHE DAMSTÉ *et al.*, 1987).

The geological setting of the three related Sicily Seep Oils (Sicily, Italy) is described by PALMER and ZUMBERGE (1981). Briefly they seep out of marl layers of Upper Miocene evaporites deposited in an environment largely comparable with that described for the NAM (TEN HAVEN *et al.*, 1985, 1987).

G33 is an oil sample from a depth of 1829 m from the Jianghan basin (China). It is an immature oil (equivalent to an R_0 0.45–0.50%) thought to come from a hypersaline lacustrine source rock slightly more mature than WX6-3 (FU *et al.*, 1986). B1 and W1349 are petroleums from shallower depths (*ca.* 600 and 1200 m, respectively) and from different well sites within the Jianghan basin (BRASSELL *et al.*, 1987).

Extraction and fractionation. Detailed experimental procedures are described elsewhere, namely in BRASSELL and EGLINTON (1983) for the Walvis Ridge, BRASSELL *et al.* (1987) for Z2, SINNINGHE DAMSTÉ *et al.* (1986) for the NAM, TEN HAVEN *et al.* (1987) and SINNINGHE DAMSTÉ *et al.* (1987)

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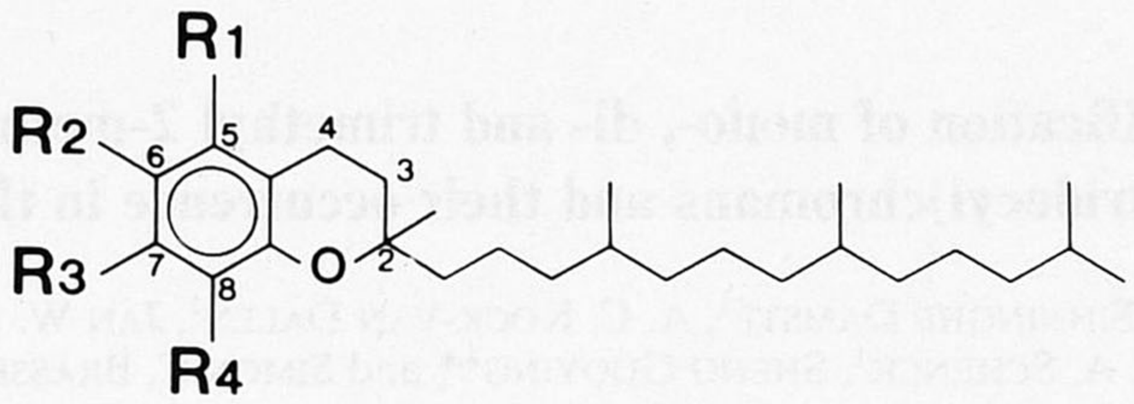
TABLE 1: TOCOPHEROLS AND SYNTHETIC CHROMANS



name	structure	code
TOCOPHEROLS:		
δ - tocopherol	R_2=OH, R_1=R_3=H, R_4=CH_3	-
β - tocopherol	R_2=OH, R_3=H, R_1=R_4=CH_3	-
γ - tocopherol	R_2=OH, R_1=H, R_3=R_4=CH_3	-
α - tocopherol	R_2=OH, R_1=R_3=R_4=CH_3	-
CHROMANS:		
2,5-dimethyl-2-(4,8,12-trimethyltridecyl)chroman	R_1=CH_3, R_2=R_3=R_4=H	5-Me-MTTC
2,6-dimethyl-2-(4,8,12-trimethyltridecyl)chroman	R_2=CH_3, R_1=R_3=R_4=H	6-Me-MTTC
2,7-dimethyl-2-(4,8,12-trimethyltridecyl)chroman	R_3=CH_3, R_1=R_2=R_4=H	7-Me-MTTC
2,8-dimethyl-2-(4,8,12-trimethyltridecyl)chroman	R_4=CH_3, R_1=R_2=R_3=H	8-Me-MTTC
2,5,8-trimethyl-2-(4,8,12-trimethyltridecyl)chroman	R_1=R_4=CH_3, R_2=R_3=H	5,8-diMe-MTTC
2,7,8-trimethyl-2-(4,8,12-trimethyltridecyl)chroman	R_3=R_4=CH_3, R_1=R_2=H	7,8-diMe-MTTC
2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman	R_1=R_3=R_4=CH_3, R_2=H	5,7,8-triMe-MTTC

for the Rozel Point Oil and the Sicily Seep Oils, FU *et al.* (1986) for WX6-3 and G33 and BRASSELL *et al.* (1987) for the B1 and W1349 samples. Phosphoria Retort Shale and Sachrang were extracted and their extracts fractionated as described for the NAM (SINNINGHE DAMSTÉ *et al.*, 1986) and for Z2 (BRASSELL *et al.*, 1987), respectively.

In brief, the extracts and oils were separated at Bristol by preparative thin layer chromatography, using hexane as a developer. At Delft the extracts or oils were separated into aliphatic, aromatic and heterocomponent fractions using column chromatography on silica/alumina (1:1). The aromatic fraction was further separated over alumina.

Syntheses. The methylated 2-methyl-2-(4,8,12-trimethyltridecyl)chromans were synthesized by a condensation reaction involving phytol (technical grade, Aldrich) and a phenol derivative (>95%). The phenol derivatives 3-methyl-, 4-methyl-, 2-methyl-, 2,5-dimethyl-, 2,3-dimethyl- and 2,3,5-trimethylphenol were used to synthesize 2,5- plus 2,7-dimethyl-; 2,6-dimethyl-; 2,8-dimethyl-; 2,5,8-trimethyl-; 2,7,8-trimethyl- and 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman, respectively.

As an example, synthesis of 8-Me-MTTC (see Table 1 for abbreviations) is described. Phytol (4.0 mmol), 2-methylphenol (5.9 mmol) and phosphorus pentoxide (10 mmol) were refluxed for 3.5 h in 10 ml toluene. The solution was cooled, the brownish toluene layer decanted and the residue washed with small amounts of toluene. Diethylether (20 ml) was added to the combined toluene layers and this mixture was subsequently washed three times with 5 ml NaCl-saturated 1 M KOH solution and several times with a 5% NaCl solution until this solution, after washing, was neutral (pH = 7). The clear toluene/diethylether solution was dried over anhydrous $MgSO_4$ and evaporated to give a light brown oil, which was purified by column chromatography (Al_2O_3; l = 10 cm, i.d. = 1.5 cm) using hexane as eluent. GC analysis showed a purity of ≈95%. The overall yield of the reaction was ≈80%. In the case of the reaction of phytol and 3-methylphenol a 1:1 mixture of 5-Me-MTTC and 7-Me-MTTC was obtained.

Mass spectra were obtained for all synthetic compounds using GC-MS. The ^{1}H NMR spectrum of synthetic 8-Me-MTTC (200 MHz, $CDCl_3$; δ (ppm): 1.76 (*t*, 1H (C-3), *J* = 6.5 Hz), 1.79 (*t*, 1H (C-3), *J* = 6.4 Hz), 2.16 (*s*, 3H (CH_3 at C-8)), 2.74 (*t*, 2H (C-4), *J* = 6.6 Hz), 6.70 (*t*, 1H (C-6), *J* = 7.5 Hz), 6.89 (*d*, 1H (C-5 or C-7), *J* = 7.5 Hz), 6.94 (*d*, 1H (C-7 or C-5), *J* = 7.5 Hz) shows the typical shifts and splitting patterns of aromatic protons and thereby confirms the structure of this compound and, hence, the general applicability of the synthetic method.

Gas chromatography. Gas chromatography was carried out on a Carlo Erba 4160 instrument equipped with a flame ionization detector and an on-column injection system. Two types of fused silica capillary columns were used. One (l = 25 m, i.d. = 0.32 mm) was coated with CP-Sil 5 (film thickness = 0.13 μm), the other, more polar column (l = 30 m, i.d. = 0.26 mm) was coated with DB-1701 (film thickness = 0.25 μm). Both columns were operated with He as carrier gas. Samples were injected at 100°C in ethylacetate. After solvent elution the oven temperature was programmed from 130°C to 330°C at 4°C/min. Coinjections were performed with small volumes of samples (≈0.5 μl) and small volumes (up to 0.4 μl) of standard solutions (0.1 mg/ml) of the synthetic isoprenoid chromans added to each other in the syringe. Retention indices were measured by coinjection of small volumes of standard solutions with a small volume of standard solution of *n*-alkanes.

Gas chromatography-mass spectrometry. GC-MS analyses were performed on a Varian 3700 gas chromatograph equipped with a fused silica capillary column (l = 25 m, i.d. = 0.25

mm) coated with CP-Sil 5 (film thickness = 0.12 μm) coupled to a MAT-44 quadrupole mass spectrometer operated at 80 eV with a cycle time of 1.5 s. He was used as carrier gas. The relative abundances of the methylated MTTC were determined from mass chromatography of *m/z* 121, 135 and 149, as appropriate, using the percentages of these ions in the total ion intensities of the synthetic methylated MTTC (6-Me-MTTC 18.3%; 8-Me-MTTC 19.9%; 5,8-diMe-MTTC 26.9%; 7,8-diMe-MTTC 33.2%; 5,7,8-triMe-MTTC 43.7%).

RESULTS AND DISCUSSION

Identification

In the aromatic fraction of the extract of the NAM (SINNINGHE DAMSTÉ *et al.*, 1986) three structurally related compounds were present as major components. They were characterized by ions at *m/z* 121, 161 and 386 (two compounds) and 135, 175 and 400 (one compound), respectively, in their mass spectra. Inspection of other sediment extracts and oils revealed the presence of two of these three compounds and two other related compounds. One of them also exhibited ions at *m/z* 135, 175 and 400 in its mass spectrum; the other was obviously a homologue with ions at *m/z* 149, 189 and 414.

A consistent difference of 40 daltons between the two major fragment ions, and the loss of 225 daltons ($C_{17}H_{35}$) from the molecular ion, are characteristic features of tocopherol mass spectra (SCHEPPELE *et al.*, 1972; ELLIOTT and WALLER, 1972). The molecular weight of δ-tocopherol (the least substituted naturally occurring tocopherol), however, is 400 daltons, 16 daltons greater than that of the two compounds with the lowest molecular weight occurring in the samples. This fact, and their fragmentation pattern, suggested that these novel compounds were methylated 2-methyl-2-(4,8,12-trimethyltridecyl)-chromans (MTTC), that is, tocopherols lacking their hydroxyl function.

These chroman derivatives were synthesized, using a simple one-step synthesis. Literature data (YAMADA *et al.*, 1971) confirmed that chromans substituted at position 2 with an isopranyl side chain and a methyl group can be synthesized from phenol and an isoprenoid alcohol *via* a condensation reaction. Using somewhat different reaction conditions the target compounds were obtained from phytol and several phenol derivatives in high yield. Thus, four monomethyl, two dimethyl- and one trimethyl substituted MTTC were synthesized (Table 1). They include compounds with structures similar to the four naturally occurring tocopherols, but lacking the phenolic hydroxyl group (8-Me-MTTC, 5,8- and 7,8-diMe-MTTC and 5,7,8-triMe-MTTC).

The mass spectra of five compounds are shown in Fig. 1. The mass spectra of the other two (5- and 7-Me-MTTC) are almost identical to those of 6- and 8-Me-MTTC. The fragmentation pathways are fully analogous to those reported for tocopherols (SCHEPPELE *et al.*, 1972; ELLIOTT and WALLER, 1972); α-cleavage of the isopranyl side chain yields ions at *m/z* 161 (5-, 6-, 7- and 8-Me-MTTC), *m/z* 175 (5,8- and 7,8-diMe-MTTC) or *m/z* 189 (5,7,8-triMe-MTTC) and cleavage through the non-aromatic portion of the chroman ring with hydrogen transfer yields ions at *m/z* 121 (5-, 6-, 7- and 8-Me-MTTC), 135 (5,8- and 7,8-diMe-MTTC) or 149 (5,7,8-triMe-MTTC).

The mass spectra of the synthetic compounds are identical to those obtained for compounds from geological samples. Since the mass spectra of the various positional isomers are virtually identical (only the relative intensities of the fragment ions differ to some extent), assignments could not be made solely based on mass spectral data.

Coinjections of the standards with three selected samples on two capillary columns coated with different stationary phases (Table 2), unequivocally established the identification of 6-Me-, 8-Me-, 5,8-diMe-, 7,8-diMe- and 5,7,8-triMe-MTTC (Fig. 2). The synthetic 5- and 7-Me-MTTC did not coelute with any of the geologically occurring compounds. Apart from these compounds a related compound was tentatively identified in the NAM: 2,8-dimethyl-(4,8-dimethylnonadecyl)chroman (*m/z* 316, 161, 121).

Occurrence

The methylated MTTC are present in a number of sediment extracts and oils from different geographical locations which range from Pleistocene to Permian (Table 3), suggesting a rather good survival potential. For instance the partial gas chromatograms (Fig. 3) of two subfractions of the aromatic fraction of the NAM and of a subfraction of the aromatic fraction of the Sachrang sample contain the methylated MTTC as major compounds. 2,7,8-triMe MTTC is present in the NAM as one of the most abundant lipids; its concentration in the NAM is of the same magnitude as that of phytane, the most abundant component in the hydrocarbon fraction of this sediment (TEN HAVEN *et al.*, 1985). Literature data for DSDP samples (RULLKÖTTER *et al.*, 1984a,b) further demonstrate the occurrence of methylated MTTC in oceanic sediments. These authors did not identify the compounds, but listed them as unknowns, mentioning the principal ions in their mass spectra.

The relative abundances of the methylated MTTC have been determined from mass chromatography of *m/z* 121, 135 and 149, as appropriate, and the respective percentages of these ions in the total ion intensities of the synthetic compounds. These data show a correlation between the presence of certain methylated MTTC and the environment of deposition of the sediment or source rock of the oil. The division into two groups of samples, *viz.* those from hypersaline and those from non-hypersaline depositional environments, is based on biological marker characteristics formulated by TEN HAVEN *et al.* (1985, 1987). These include a low pristane/phytane ratio, an even predominance in *n*-alkanes, C_{34} or C_{35} maxima in the distribution patterns for C_{31}–C_{35} hop-17(21)-enes and/or 17α(H),21β(H)-hopanes, and a high abundance of organic sulphur compounds. The Phosphoria Retort

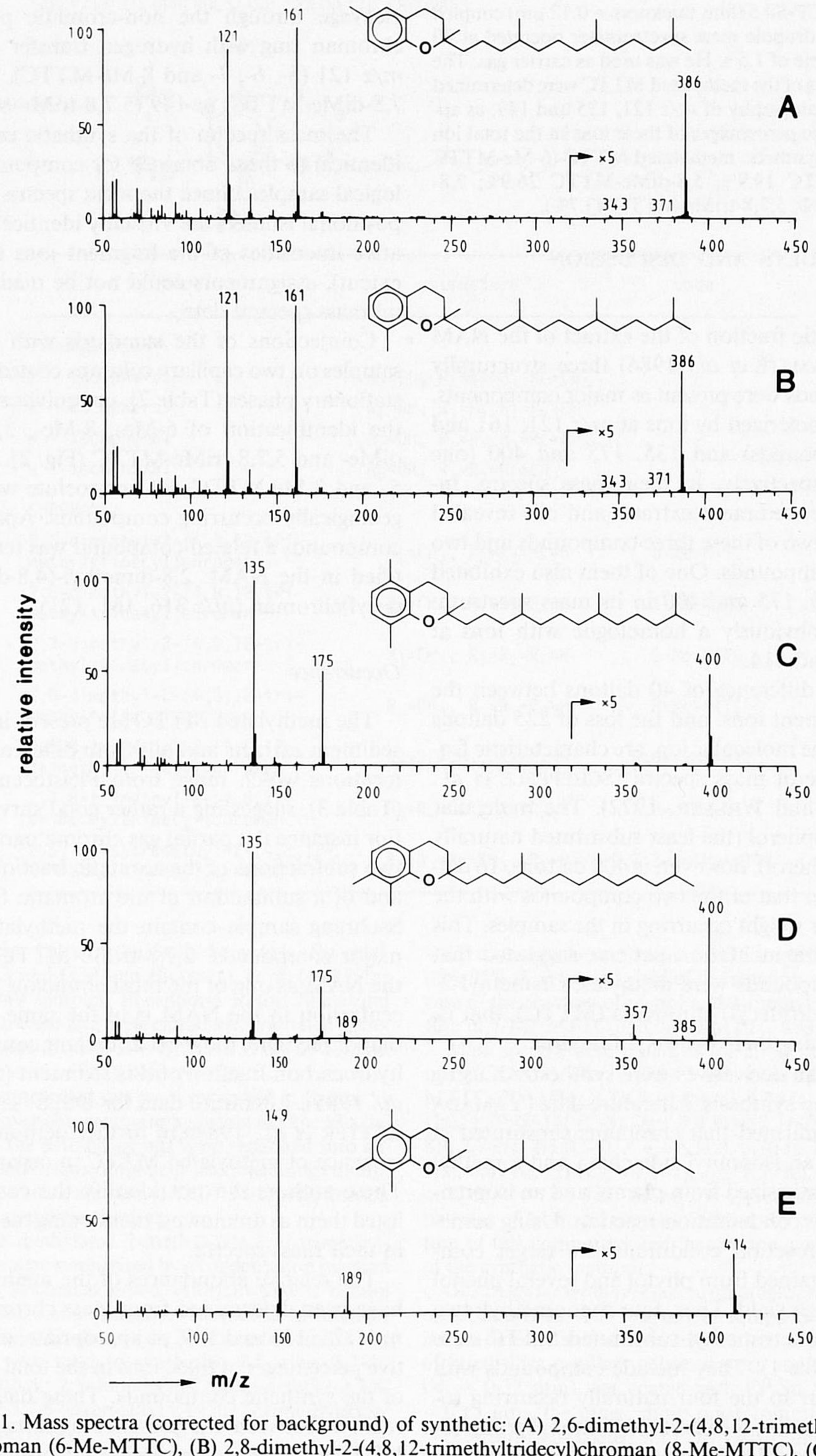


FIG. 1. Mass spectra (corrected for background) of synthetic: (A) 2,6-dimethyl-2-(4,8,12-trimethyltridecyl)chroman (6-Me-MTTC), (B) 2,8-dimethyl-2-(4,8,12-trimethyltridecyl)chroman (8-Me-MTTC), (C) 2,5,8-trimethyl-2-(4,8,12-trimethyltridecyl)chroman (5,8-diMe-MTTC), (D) 2,7,8-trimethyl-2-(4,8,12-trimethyltridecyl)chroman (7,8-diMe-MTTC) and (E) 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman (5,7,8-triMe-MTTC).

Shale is somewhat confusing in this respect, because there is no clear geological evidence for a hypersaline environment of deposition (MCKELVEY *et al.*, 1959), in contrast to its biological markers distribution, which shows the above mentioned characteristics.

The sediments from non-hypersaline environments of deposition show a dominance of 5,7,8-triMe-MTTC, whereas a feature of samples from hypersaline environments is the presence of 8-Me-MTTC, which is absent in samples from a non-hypersaline environment. The ratio 5,7,8-triMe-MTTC/8-Me-MTTC seems, empirically, to be useful as an indicator of the occur-

TABLE 2: SYNTHETIC CHROMAN DERIVATIVES: COINJECTIONS WITH SAMPLES AND KOVATS RETENTION INDICES.

	SAMPLE			STATIONARY PHASE			
COMPOUND	NAM 11-12[c]	NAM 14-15[c]	Sachrang[d]	CP-Sil 5	DB 1701	RI[a]	RI[b]
5- and 7-Me-MTTC	+[e]	+		x[f]	n.d.[g]	2641,2672[h]	2777,2828[h]
6-Me-MTTC		+		✓[i]	✓	2650	2786
8-Me-MTTC			+	✓	✓	2613	2745
8-Me-MTTC	+			✓	n.d.		
5,8-Me-MTTC			+	✓	n.d.	2720	2860
5,8-diMe-MTTC	+			✓	✓		
7,8-diMe-MTTC			+	✓	✓	2725	2863
7,8-diMe-MTTC	+			✓	n.d		
5,7,8-triMe-MTTC			+	✓	✓	2823	2974

[a] measured on CP-Sil 5, 130°C/ 4°C/min /300°C
[b] measured on DB 1701, 130°C/ 4°C/min /300°C
[c] sub-fractions of the aromatic fraction of the NAM (Sinninghe Damsté et al., 1986)
[d] see also Fig. 2
[e] + coinjection experiment
[f] x absent
[g] n.d. = not determined
[h] synthesis produced a mixture of compounds; no effort was made to establish their elution order
[i] ✓ coelution with synthetic standard confirmed

rence of palaeohypersalinity, although this observation is based on a relatively small suite of sample. A high 5,7,8-triMe-MTTC/8-Me-MTTC ratio (>100) points to a non-hypersaline environment of deposition, whereas a low ratio (<2) indicates a hypersaline environment of deposition.

Origin

The origin of these novel methylated MTTC is, as yet, unknown. They have not been reported to occur in organisms. BOGUTH and SERNETZ (1968) checked the vitamin-E activity of 5,7,8-tri-Me MTTC with a negative result. Because methylated MTTC are structurally related to tocopherols (which have a hydroxyl group at position 6 in the chroman ring system), an origin from tocopherols seems likely. However, two points argue against such an origin. First, removal of the phenolic hydroxyl group would require a relatively large amount of energy. Therefore, selective removal of the phenolic hydroxyl group during diagenesis, without any other structural modification seems highly improbable on chemical grounds. Secondly, the identification of 6-Me-MTTC (which has a methyl group at the tocopherol hydroxyl position; Table 1), although present in only one sample, also counters the hypothesis that tocopherols are the precursors of these geologically-occurring methylated MTTC. Thus, a biosynthetic origin for these compounds seems probable.

A useful method for assessing the possible biological origin of the methylated MTTC is the evaluation of the steric configuration at their chiral centres. We assume that a mixture of diastereoisomers (2R,4′R,8′R and 2S,4′R,8′R) was obtained upon synthesis. No separation of these diastereoisomers was, however, observed during GC analysis of the synthetic methylated MTTC. Thus, it is not possible to conclude whether either one or both diastereoisomers are present in the samples studied.

A possible biosynthetic pathway can be speculated by analogy with that reported for tocopherols (PENNOCK, 1983), but starting with phenylalanine rather than tyrosine, a structurally related amino acid. The occurrence of methylated MTTC in relatively shallow, little altered sediments (*e.g.* Walvis Ridge, DSDP Site 532, Pleistocene; see Table 3) is further supportive evidence for direct biosynthesis of these compounds, rather than a formation during diagenesis.

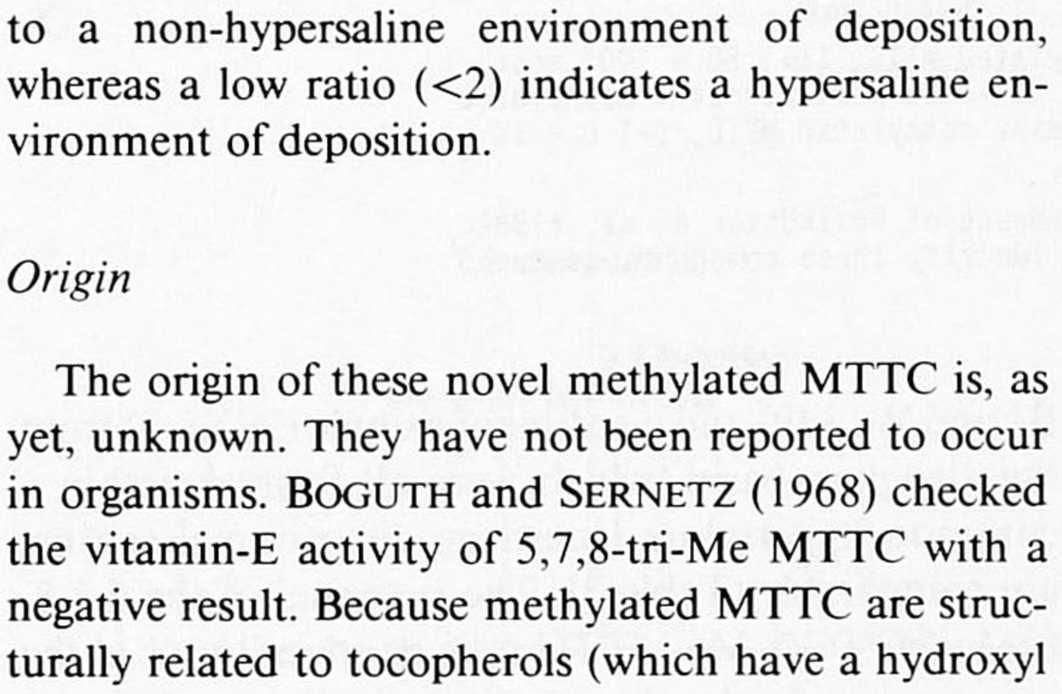


FIG. 2. Partial gas chromatograms (CP-Sil 5) of Sachrang fraction (A) and its coinjection with (B) 8-Me-MTTC, (C) 7,8-diMe-MTTC and (D) 5,7,8-triMe-MTTC. The increase of a peak area due to these coinjections is marked black.

TABLE 3: THE OCCURRENCE OF MONO-, DI- AND TRIMETHYL 2-METHYL-2-(4, 8,12-TRIMETHYLTRIDECYL) CHROMANS IN SEDIMENTS AND OILS

	SAMPLE	AGE	RELATIVE ABUNDANCE OF MTTC[a] 6-Me	8-Me	5,8-diMe	7,8-diMe	5,7,8-triMe
	SEDIMENTS						
non-hypersaline depositional environment	Mazagan escarpment[b] (DSDP, site 545)	late Miocene-late Aptian	-	-	+	+	+++
	Mazagan escarpment[b] (DSDP, site 547)	late Eocene-Albian	-	-	+	+	+++
	Angola basin[b] (DSDP, site 530A)	Coniacian-Albian/ Cenomanian	-	-	-	-	+++
	Walvis Ridge[b] (DSDP, site 532)	late Pliocene	-	-	-	-	+++
	Walvis Ridge (DSDP, site 532)	Pleistocene	-	-	+	+	+++
hypersaline depositional environment	Phosphoria Retort Shale	Permian	-	+	++	+	+++
	Sachrang	Toarcian	-	++	tr.	+++	+
	Z2	lower Tertiary	-	+	+	+++	-
	WX6-3	Palaeogene	-	+++	++	++	+
	Northern Apennines Marl	Miocene	+	+	+	+++	-
	OILS						
	Rozel Point Oil	Miocene	-	++	++	++	+++
	Sicily Seep Oils	Miocene	-	+++	-	++	++
	B1	Palaeogene	-	+++	+	++	+
	W1349	Palaeogene	-	+++	+	++	++
	G33	Palaeogene	-	+++	+	++	+

[a] key: (+++) most abundant methylated MTTC, (++) 50 - 100% most abundant methylated MTTC, (+) 10 - 50% most abundant methylated MTTC, (tr.) 1 - 10% most abundant methylated MTTC, (-) 0 - 1% most abundant methylated MTTC.

[b] derived from mass spectral evidence of Rullkötter et al. (1984a and b). These authors did not identify these compounds as such.

Environmental factors seem, empirically, to exert a marked influence on the composition of methylated MTTC, although this relationship is not yet understood and based on a relatively small suite of samples. A bacterial origin for 8-Me-MTTC, which only occurs in hypersaline environments, seems likely because of the presence of this compound in the Sachrang sample. This sediment was deposited in a small, but deep, basin overlying Permian salt (H. C. JENKYNS, pers. commun.). Leaching of salt into the bottom waters is thought to have created stratified hypersaline bottom waters, although the surface waters were unaffected. Since 8-Me-MTTC was produced in the deep bottom waters it is probably a biosynthetic product of non-photosynthetic bacteria.

Geochemical implications

Differences in environments of deposition seem to be reflected in the methylated MTTC signatures, which might indicate that these compounds have potential as diagnostic biomarkers. For instance, the distributions of methylated MTTC in three Chinese oils (G33, B1 and W1349) and a sediment sample (WX6-3) from the Jianghan basin, which were all formed within a common hypersaline lacustrine depositional setting, are comparable (Table 3). The potential of the 5,7,8-triMe-MTTC/8-Me-MTTC ratio as an indicator of the occurrence of palaeohypersalinity is discussed above. A future study in which more samples will be analyzed for methylated MTTC would specifically determine the usefulness of this ratio for assessing various levels of salinity ranging from fresh to brackish, normal marine to hypersaline. If validated, such a ratio would also aid recognition of the significance of hypersaline environments as oil source rocks. Given their survival in oils these compounds may also be of value in oil-source rock and oil-oil correlations.

Another aspect of the geochemistry of the methylated MTTC is their presence as relatively abundant components of samples from hypersaline environments. Here they can occur in concentrations comparable to phytane whereas they are found in relatively low concentrations in non-hypersaline environments. This observation might reflect the low diversity of organisms in hypersaline environments so that their bio-

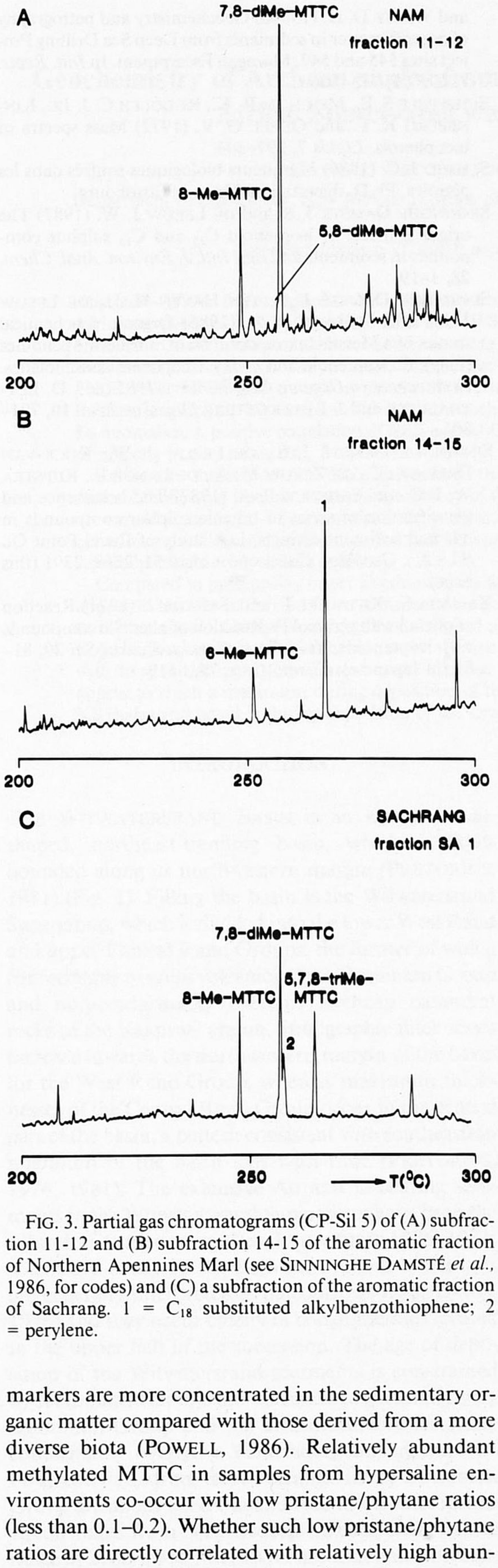


FIG. 3. Partial gas chromatograms (CP-Sil 5) of (A) subfraction 11-12 and (B) subfraction 14-15 of the aromatic fraction of Northern Apennines Marl (see SINNINGHE DAMSTÉ *et al.*, 1986, for codes) and (C) a subfraction of the aromatic fraction of Sachrang. 1 = C_{18} substituted alkylbenzothiophene; 2 = perylene.

markers are more concentrated in the sedimentary organic matter compared with those derived from a more diverse biota (POWELL, 1986). Relatively abundant methylated MTTC in samples from hypersaline environments co-occur with low pristane/phytane ratios (less than 0.1–0.2). Whether such low pristane/phytane ratios are directly correlated with relatively high abundances of methylated MTTC remains to be seen.

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