A pyrolysis and stable isotopic approach to investigate the origin of methyltrimethyltridecylchromans (MTTCs)

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Abstract

Methyltrimethyltridecylchromans (MTTCs) have been widely detected in sediments and crude oils from various depositional settings and are established markers for palaeosalinities. A likely origin of these compounds, which show a distinctive isoprenoid substituted aromatic structure, seems to be condensation reactions of phytol with higher plant-derived alkyl phenols during early diagenesis. However, a direct biological origin from phytoplanktonic organisms cannot be excluded. To further investigate the potential origin from condensation reactions, an online pyrolysis-gas chromatography- isotope ratio mass spectrometry (PY-GC-irMS) method with the capacity to measure $\delta^{13}C$ in fragments (trimethylphenol and pristenes) generated from 5,7,8-trimethyl-MTTC was developed in this study. This straight forward technique poses a

great potential for the elucidation of chroman formation in geological samples as it possibly enables the distinction between the different proposed sources of isoprenoid and alkyl-phenol fragments (mainly phytoplankton and higher plants, respectively) based on their stable isotopic compositions. Furthermore, it might be useful for the investigation of products generated from MTTCs during thermal maturation of geological samples.

Keywords: Flash- pyrolysis, CSIA, palaeosalinity, phenols

1. Introduction

Methylated 2-methyl-2-trimethyltridecylchromans (MTTCs, **I** in **Figure 1**) in sediments or crude oils generally occur as distinct isomers of monomethyl, dimethyl and trimethyl homologues. They were first identified in geological samples by Sinninghe-Damsté et al. (1987), who also introduced them as palaeosalinity indicators. MTTCs have since been reported in a great variety of geological samples and the "chroman ratio" (5,7,8-trimethyl MTTC/total MTTCs) has been established as a powerful tool in salinity reconstructions (e.g. Schwark and Püttmann, 1990; Sinninghe Damsté et al., 1993; Grice et al., 1998; Schwark et al., 1998). However, their origin and geological formation pathway remain debated (Sinninghe Damsté et al., 1993; Li and Larter, 1995; Li et al., 1995, Sinninghe-Damsté and De Leeuw, 1995). Based on correlation of abundances and chroman ratios with other geological parameters and as an explanation for the limited number of naturally occurring isomers, a biosynthetic origin of MTTCs from phytoplanktonic organisms has been suggested (e.g. Sinninghe Damsté et al., 1993), although to date MTTCs or suitable direct precursors have not been found in organisms. An origin from higher plant tocopherols (**II**, **Figure**

49 **1**), which bear a strong structural similarity, has been ruled out due to their
50 comparatively low abundances in the geosphere and the presence of a phenolic
51 hydroxyl group at C-6 (Sinninghe Damsté et al., 1993; Li et al., 1995). Li et al.
52 (1995) alternatively proposed that MTTCs might form via early diagenetic
53 condensation reactions of the phytol side chain in chlorophylls with higher plant
54 derived phenols, which would imply largely different source organisms for the
55 isoprenoid and alkylphenol moiety of geological chromans. To further investigate
56 this potential formation pathway, we developed a pyrolysis-stable isotope
57 analytical method for $\delta^{13}C$ determination in isoprenoid and alkylphenol
58 fragments generated from MTTCs, which could possibly be used to establish the
59 relationship to the different proposed source organisms of these fragments on a
60 stable isotopic basis. Furthermore, tocopherols and MTTCs have been suggested
61 as an additional source of pristane in more mature sediments/crude oils
62 (Goossens et al., 1984; Li et al., 1995), which could also possibly be explored with
63 this technique. The method was initially investigated by thermal degradation of
64 an authentic 5,7,8-trimethyl-MTTC (triMeMTTC) standard in order to establish
65 the stable isotopic relationship between the parent compound and the distinctive
66 degradation products. Subsequently, chroman isolates from three Middle to
67 Upper Devonian sediments (Canning Basin, WA) were analysed to demonstrate
68 the applicability of the method in natural samples. Although pyrolysis products
69 of natural and artificial MTTCs and related compounds have been thoroughly
70 investigated by Li et al. (1995), there have been no previous isotopic based
71 studies of these compounds to establish the formation mechanism of MTTCs.

2. Experimental

The authentic 5,7,8-trimethyl MTTC standard was synthesised from 2,3,5-trimethylphenol and phytol according to Sinninghe-Damsté et al. (1987). Sediments (MWR-30.7 m, MWR-40.7 m and MWR-41.2 m) with high triMeMTTC abundances and exceptionally low maturities (e.g. T_{max} 405–413 °C; unpublished data) originated from basin facies associated with Middle to Upper Devonian reef systems in the Canning Basin, Western Australia. The powdered rock was Soxhlet extracted and the total lipid extract fractionated by silica gel column chromatography (for details see Grice et al., 2005; Supplementary material). Unsaturated compounds were separated from the aliphatic fraction by $AgNO_3$ silica column chromatography (10%) using hexane (saturated compounds) and DCM (unsaturated compounds) as eluents. *n*-Alkanes were subsequently removed with ZSM5 molecular sieve (e.g. Audino et al., 2001) to obtain a branched and cyclic fraction. 5,7,8-trimethyl MTTC was further isolated from the aromatic fractions of MWR-40.7 m and MWR-41.2 m by $AgNO_3$ thin layer chromatography (Eglinton and Murphy, 1969) using hexane as developer and the authentic chroman standard (visualized with rhodamine spray under UV-light) as reference. The MTTC containing silica band was scraped off, extracted with DCM and filtered through a glass sinter funnel under vacuum. The low amount of aromatic compounds in the MWR-30.7 m sample precluded a TLC isolate being obtained.

For bulk $\delta^{13}C$ analysis a Delta V Plus mass spectrometer connected to a Thermo Flush 1112 via Conflow IV (Thermo-Finnigan/Germany) was used. Analytes were combusted at 1020 °C.

Gas chromatography-mass spectrometry (GC-MS) was performed on an Agilent 5973 GC-MS equipped with a HP 6890 auto-sampler and a DB-5MS capillary column. The GC oven was heated from 40–310 °C or 325 °C at 3 °C/min with initial and final hold times of 1 min and 30 min, respectively. A CDS 5350 Auto-pyroprobe was used for flash pyrolysis (PY)-GC-MS. The pyrolysis chamber and injector were held at 300 °C and pyrolysis was separately performed at temperatures of 550 °C, 650 °C or 750 °C applied for 20 s. The pyrolysates were analysed with a 60:1 split. He carrier gas at a constant pressure of 17.5 psi was used and the GC oven was temperature programmed from -20 °C to 40 °C at 8 °C/min and then to 320 °C at 4 °C/min with initial and final hold times of 1 and 25 min, respectively. All other settings remained unchanged.

Gas chromatography-isotope ratio mass spectrometry (GC-irMS) was performed on a Micromass IsoPrime irMS interfaced to an Agilent 6890N GC fitted with a HP 7683 autosampler. GC parameters were similar to those used for GC-MS. For PY-GC-irMS a CDS-Pyroprobe 5000 was mounted directly on the vaporisation injector of the GC-irMS system. The pyrolysis chamber and injector were set to 300 °C. Analytes were pyrolysed at 650 °C for 20 s, injected with a 30:1 split or splitless (for increased sensitivity) and trapped in liquid nitrogen until the end of pyrolysis. The GC oven was programmed from 40–325 °C at 4 °C/min with initial and final hold times of 2 and 15 min, respectively. GC column and all other settings remained unchanged. Reference standards of known isotopic composition were regularly analysed to confirm accuracy of isotope analysis. All $\delta^{13}C$ values reported in this study are the average of at least two replicates and standard deviations were reported.

120 Further details about typical injector, carrier gas and MS/irMS settings as well
121 as GC column, interface (for GC-irMS) and instrument software used for GC-
122 MS/irMS can be found in Supplementary materials of Melendez et al. (2013).

123 **3. Results and discussion**

124 The aim of this study was to develop an online flash pyrolysis-GC-irMS method
125 which would allow stable isotopic correlation of MTTCs and related lower
126 molecular weight products for the elucidation of their sources and formation
127 pathways in geological samples. An authentic 5,7,8-triMeMTTC standard (often
128 the most abundant natural chroman) was first analysed by PY-GC-MS to
129 identify major degradation products of the parent structure and investigate
130 pyrolysis efficiency at different temperatures (550 °C, 650 °C and 750 °C) in
131 separate pyrolysis experiments. The major pyrolysates in all analyses were 2,3,5-
132 trimethylphenol (see appendix for compound identification) and pristenes as well
133 as the intact chroman (e.g. **Figure 2**a). The extent of pyrolytic degradation was
134 inferred from the ratio between the abundance (peak area) of the
135 trimethylphenol and all pristene products relative to the original chroman in
136 four replicate analyses. The highest degradation efficiency was achieved at a
137 pyrolysis temperature of 650 °C (ratios of 0.8, 1.6, 1.2 for 550 °C, 650 °C and 750
138 °C, respectively), which therefore was used in all subsequent analyses. However,
139 the replicates generally showed some variability which is typical of many
140 analytical pyrolysis studies. Li et al. (1995) conducted offline pyrolysis over 65 h
141 at 350 °C on isolates of 5,7,8-triMeMTTC which similarly showed high amounts
142 of pristenes, but contrary to present data generated tetramethylphenol instead of
143 trimethylphenol. This was also the main product we generated in preliminary

144 and unpublished pyrolysis experiments of the 5,7,8-triMeMTTC in sealed glass
145 tubes at temperatures of 330 and 360 °C over 72h. The different product
146 obtained from flash pyrolysis may be the result of the elevated pyrolysis
147 temperatures leading to a different bond cleavage in the chroman. In an earlier
148 study, tocopherols have also been shown to generate significant amounts of
149 pristenes during pyrolysis and have therefore been suggested as a contributor to
150 pristane in geological samples (Goossens et al., 1984).
151 Precision and accuracy of $\delta^{13}C$ values measured by PY-GC-irMS were tested with
152 five replicate analyses of the 5,7,8-triMeMTTC standard (using split and
153 splitless injections). Standard deviations between 0.2‰ and 0.4‰ for all
154 measured compounds confirmed an excellent precision (Table 1). $\delta^{13}C$ values
155 reported for prist-1-ene include a coeluting pristene isomer (*cf.* Figure 2a and
156 Figure 3a, b). Apart from that, good baseline separations, essential for GC-irMS
157 analysis, were achieved for all remaining products. $\delta^{13}C$ values of
158 trimethylphenol, pristenes and triMeMTTC in pyrolysates were comparable to
159 reference values obtained by elemental analysis (EA)-irMS of the chroman
160 standard as well as the phytol and trimethylphenol utilised for its synthesis
161 (Table 2). This confirmed both the accuracy of the data and the preservation of
162 the $\delta^{13}C$ signature of source compounds during condensation reactions and
163 pyrolysis. The slight systematic depletion of $\delta^{13}C$ values obtained from EA-irMS
164 in comparison to corresponding values measured on the GC-irMS system (in
165 pyrolysis products as well as in the chroman standard analysed by conventional
166 liquid injection; Table 2) can be attributed to instrumental bias. Similar
167 systematic variations between different systems for EA- and GC-irMS have

168 previously been reported (e.g. Zwank et al., 2003). Nevertheless, values obtained
169 from both methods are in accordance with the following mass balance equation:

170 $$\delta^{13}C_{triMeMTTC} = \frac{9 \times \delta^{13}C_{trimethylphenol} + 20 \times \delta^{13}C_{phytol/pristenes}}{29}$$

171 where "$\delta^{13}C_{phytol/pristenes}$" stands for $\delta^{13}C$ of phytol (for bulk-irMS) or average $\delta^{13}C$
172 of all pristenes (for PY-GC-irMS). The calculated $\delta^{13}C$ values for triMeMTTC of -
173 32.5‰ and -33.3‰ for PY-GC-irMS and EA-irMS, respectively, are almost
174 identical to the measured values (Table 1 and 2).
175 PY-GC-irMS was applied to the TLC-isolates from MWR-40.7 m and MWR-41.2
176 m (Figure 2c) and the whole aromatic fraction of MWR-30.7 m (containing
177 abundant triMeMTTC – **Figure 2**b). Figure 3c shows a typical GC-irMS trace of
178 pyrolysates obtained from these samples. Notable differences to the pyrolysate
179 distribution of the chroman standard include the absence of trimethylphenol and
180 prist-2-ene, which can probably be attributed to matrix effects, i.e. other
181 compounds present in the TLC isolates/aromatic fraction influencing thermal
182 behaviour, which can alter flash pyrolysis product distributions (e.g. Greenwood
183 et al., 2006). Further optimisation of the pyrolysis conditions for the challenges
184 of geological samples would be useful, but was not done here due to the limited
185 quantity of these samples. The $\delta^{13}C$ values of pristene (most likely prist-1-ene
186 and a second co-eluting isomer) measured by PY-GC-irMS of the three samples
187 was consistently similar to the corresponding values of pristane and phytane
188 obtained from traditional liquid injection GC-irMS. This correlation strongly
189 points to a common source for these products, most likely the phytol side chain in
190 chlorophylls (Table 3). Furthermore, the traditionally measured $\delta^{13}C$ values of

191 triMeMTTC were also similar to the isotopic signatures of these products,
192 although a very small ^{13}C enrichment was notable (Table 3). However, since the
193 $\delta^{13}C$ value of the alkylphenol moiety of the chroman standard could not be
194 measured, the suggested formation of chromans by biosynthesis in
195 phytoplanktonic organisms (Sinninghe Damsté et al., 1993) cannot be discounted
196 based on these results.

197 **4. Conclusions and outlook**

198 An online PY-GC-irMS method which enables $\delta^{13}C$ analysis of major thermal
199 breakdown products of triMe-MTTC (trimethylphenol and pristenes) was
200 developed. Initial application to a triMeMTTC standard confirmed high precision
201 and accuracy of the $\delta^{13}C$ data. Furthermore, the isotopic relationship of major
202 pyrolysis products to the parent chroman as well as to the corresponding source
203 compounds used for synthesis of the standard was established. Similar analyses
204 of triMeMTTC in isolates from immature sediments also generated a pristene
205 peak, however, trimethylphenol and prist-2-ene, which were obtained from the
206 standard in the previous analyses, were lacking. A more complete suite of MTTC
207 pyrolysis markers should be achievable with further optimisation of pyrolysis
208 conditions. Nevertheless, the few MTTC products detected in these initial
209 analyses of geological material show a great potential for the application of this
210 analytical method to probe the origin of MTTCs in geological samples.

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Figure captions

Figure 1. Chemical structures referred to in the text

Figure 2. Total ion chromatograms of a typical pyrolysate obtained from an authentic 5,7,8-trimethyl-2-methyl-2-trimethyltridecylchroman (triMeMTTC) standard (a), and triMeMTTC in isolates from natural samples (MWR-30.7 m, aromatic fraction; b, and MWR-40.7 m thin layer chromatography isolate from aromatic fraction (c), which were pyrolysed in subsequent experiments. TMP = trimethylphenol; * = Impurities in triMeMTTC standard.

Figure 3. Pyrolysis-gas chromatography-isotope ratio mass spectrometry (PY-GC-irMS) chromatograms of authentic 5,7,8-trimethyl-2-methyl-2-trimethyltridecylchroman (triMeMTTC) standard (a and b) and MTTC-isolate from the MWR-40.7 m natural sample (c).

Table captions

Table 1. $\delta^{13}C$ values of compounds in the pyrolysate obtained from five replicate analyses of an authentic chroman standard including average $\delta^{13}C$ values ± standard deviation. [a] injection with 30:1 split; [b] splitless injection; * joined peak of prist-1-ene and second, less abundant pristene isomer

	$\delta^{13}C$ [‰ VPDB]					
	run 1[a]	**run 2[a]**	**run 3[b]**	**run 4[b]**	**run 5[b]**	**Average**
trimethylphenol	-29.6	-29.9	-29.7	-29.4	-29.6	-29.6 ±0.2
prist-1-ene*	-33.5	-34.2	-34.1	-33.7	-33.9	-33.9 ±0.3
prist-2-ene	-33.4	-34.2	-33.9	-33.4	-34.0	-33.8 ±0.4
5,7,8-triMeMTTC	-32.2	-32.8	n.d.	n.d.	n.d.	-32.5 ±0.4

Table 2. $\delta^{13}C$ values of the synthesized chroman standard and source compounds ± standard deviations between 3 ([a]) or 2 ([b]) replicates obtained by elemental analysis-isotope ratio mass spectrometry (EA-irMS) and gas chromatography (GC)-irMS. n.d. = not determined

	$\delta^{13}C$ [‰ VPDB]		
	2,3,5-trimethylphenol	**phytol**	**5,7,8-triMeMTTC**
EA-irMS	-30.6 ±0.0[a]	-34.5 ±0.0[b]	-33.4 ±0.2[b]
GC-irMS	n.d.	n.d.	-32.9 ±0.1[a]

Table 3. $\delta^{13}C$ [‰ VPDB] of selected hydrocarbons in the aliphatic and aromatic fractions as well as pristenes generated by flash pyrolysis of the aromatic fraction ([a]) or isolated chroman ([b]) ± standard deviation of 2 replicate measurements. *Only measured once due to limited sample material.

	GC-irMS			**Py-GC-irMS**
Sample i.d.	**pristane**	**phytane**	**5,7,8-triMeMTTC**	**Pristenes**
MWR-30.7 m	-31.3 ±0.2	-29.9 ±0.4	n.d.	-31.2a*
MWR-40.7 m	-33.2 ±0.1	-32.9 ±0.4	-32.7 ±0.2	-33.0 ±0.1
MWR-41.2 m	-32.7 ±0.1	-32.6 ±0.0	-32.1 ±0.0	-32.4 ±0.0

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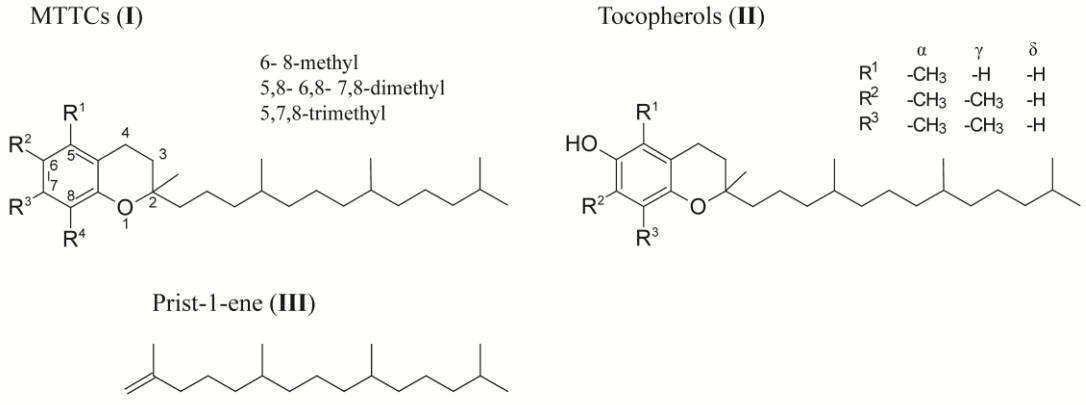
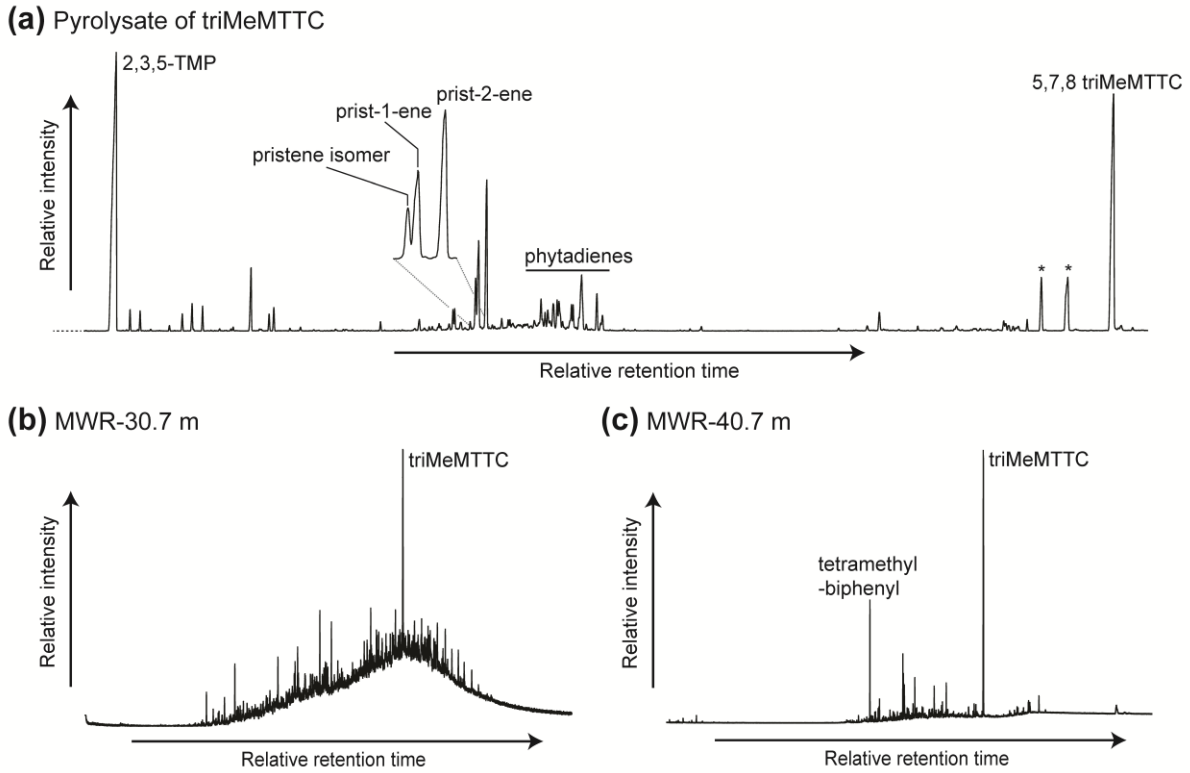
Figures





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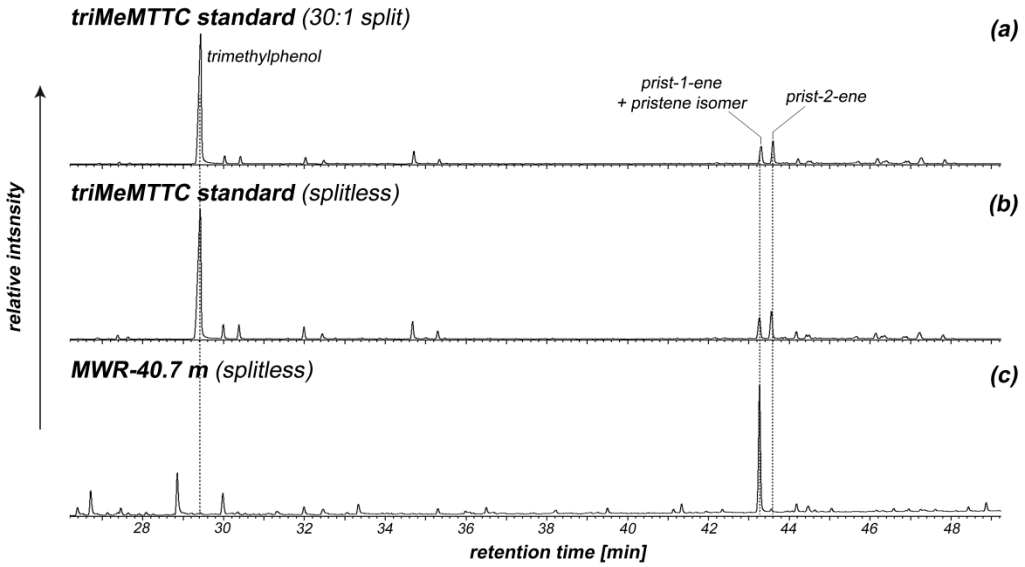

316
317

318 **Appendix**

319 **Identification of 2,3,5-trimethylphenol**

320 The identity of 2,3,5-trimethylphenol (TMP) generated by pyrolysis of the 5,7,8
321 triMe-MTTC standard was confirmed by the comparison of retention times with
322 an authentic 2,3,5-TMP standard. For this purpose a CDS-Pyroprobe 5000 was

mounted directly on the vaporisation injector of the GC-MS system described in the experimental section. Except for increasing the initial hold time at -20 °C to 2 min and the utilization of a different GC-column (ZB-5; Phenomenex) all GC-MS conditions were the same as described in the experimental section. Previous studies have shown that 2,3,5-TMP did not co-elute with other TMP isomers at comparable GC conditions (Bastow et al., 2005; Alexander et al., 2011), which enables an unequivocal identification of the generated TMP using this standard. The 5,7,8 triMe-MTTC standard was pyrolysed at 650 °C for 20s. For the analysis of the 2,3,5-TMPstandard the pyrolysis chamber was kept at 300 °C for 20s. Total ion chromatograms (TIC) of the 2,3,5-TMP standard and the MTTC pyrolysis product are displayed in Fig. A1. The mass spectrum of the TMP generated from MTTC pyrolysis is shown in Fig. A2.

Figure Captions Appendix

Figure A1:

Overlain TIC chromatograms of the 2,3,5-trimethylphenol (TMP) standard and the TMP in the pyrolysate of 5,7,8 trimethylmethyltrimethyltridecylchroman (triMeMTTC) analysed under the same GC-conditions confirming the identity of the latter

Figure A2:

Mass spectrum of the 2,3,5-trimethylphenol in the pyrolysate of 5,7,8 trimethylmethyltrimethyltridecylchroman (MTTC)

Figures Appendix

Figure A1

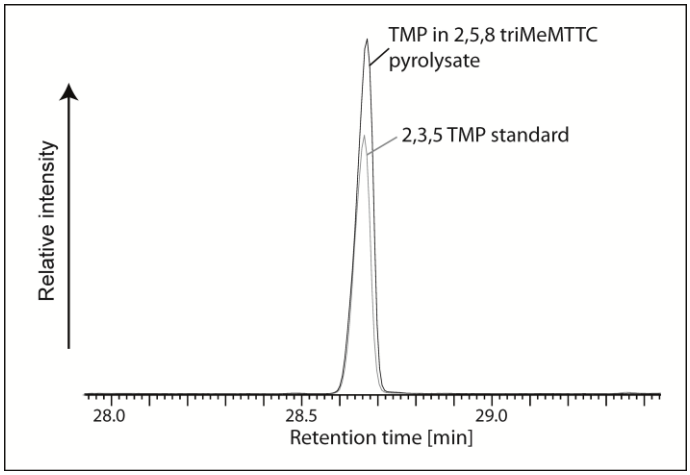

Figure A2