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**Structure-Odor Activity Studies on
Monoterpenoid Mercaptans Synthesized by
Changing the Structural Motifs of the Key
Food Odorant 1-*p*-Menthene-8-thiol**

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- 2 -

1 **ABSTRACT.** 1-*p*-Menthene-8-thiol (**1**) has been discovered as the key odorant in
2 grapefruit juice several decades ago and contributes to the overall odor of the fruit
3 with an extremely low odor threshold of 0.000034 ng/L in air. This value is among the
4 lowest odor thresholds ever reported for a food odorant. In order to check whether
5 modifications in the structure of **1** would lead to changes in odor threshold and odor
6 quality, thirty-three mercapto-containing *p*-menthane and 1-*p*-menthene derivatives
7 as well as several aromatic and open-chain mercapto monoterpenoids were
8 synthesized. Eighteen of them are reported for the first time in literature, and their
9 odor thresholds and odor qualities as well as analytical data are supplied. A
10 comparison of the sensory data with those of **1** showed that hydrogenation of the
11 double bond led to a clear increase in the odor threshold. Furthermore, moving the
12 mercapto group into the ring always resulted in higher odor thresholds compared to
13 thiols with a mercapto group in the side chains. Although all tertiary thiols always
14 exhibited low odor thresholds, none of the 33 compounds reached the extremely low
15 threshold of **1**. Also none of the synthesized mercapto monoterpenoids showed a
16 similar odor quality resembling grapefruit. While the saturated and aromatic
17 analogues exhibited similar scents as **1**, the aromas of the majority of the other
18 compounds were described as sulfury, rubber-like, burned, soapy, or even
19 mushroom-like. NMR and MS data as well as retention indices of the twenty-three
20 newly reported sulfur-containing compounds might aid in future research to identify
21 terpene derived mercaptans possibly present in trace levels in foods.

22

23 **KEYWORDS.** 1-*p*-Menthene-8-thiol, mercaptan, *p*-menthane derivatives, 1-*p*-
24 menthene derivatives, mercapto monoterpenoids, structure/odor activity

25

26 INTRODUCTION

27 Although mercaptans often occur in very low concentrations in foods, they are
28 known as key contributors to many food aromas due to their often extremely low odor
29 thresholds. While thiols in higher concentrations usually exhibit quite unpleasant
30 odors, in lower concentrations often tropical fruit, or even coffee-like odors are
31 elicited. So far, more than one hundred odor-active thiols have been identified in
32 foods including low-molecular alkane thiols and various alkene thiols, e.g., 3-methyl-
33 2-butene-1-thiol. The latter has been found to be responsible for the so called sun-
34 struck off-flavor in beer.¹ Also polyfunctional thiols, like mercapto alkanols, mercapto
35 alkyl esters, or mercapto alkanones have been identified in foods, and for example,
36 3-mercaptohexan-1-ol has been reported to contribute to the overall aroma of
37 passion fruit,² wine,³ and guava.⁴ But, so far, only three mercapto monoterpenoids
38 have been reported as food aroma compounds. The grapefruit-like smelling 1-*p*-
39 menthene-8-thiol, which is one of the most potent food odorants ever reported, was
40 first detected in grapefruit juice.⁵ Later it was also identified in orange juice,⁶ grape
41 must,⁷ wine,⁸ and guava puree.⁹ The second naturally occurring mercapto
42 monoterpenoid, 8-mercapto-*p*-menthane-3-one, exhibits a characteristic catty, black
43 currant-like odor, and is only known as constituent of the oil from the leaves of the
44 South African buchu bush.¹⁰ Furthermore, 3-mercapto-3,7-dimethyl-6-octenyl acetate
45 has been reported as a burnt, rubber-like, and grapefruit-like smelling compound in
46 lemons.¹¹ It is, however, unclear, why in particular the presence of a mercapto group
47 in a volatile food constituent often causes a low odor threshold. Because this attribute
48 must be related to the complementary structure of specific odorant receptors in the
49 human olfactory system, the clarification of the structural motifs necessary for a
50 efficient detection by humans is an important goal in structure/odor activity studies.
51 However, so far only a few studies were performed on structure/odor correlations

52 among thiols. Wannagat et al.¹² were among the first to show that the replacement of
53 a hydroxyl group by a thiol group led to a complete change in odor often resulting in
54 an unpleasant aroma perception. Polak et al.¹³ proposed that a tertiary mercapto
55 amyl substructure should be responsible for a catty odor, and Node et al.¹⁴ previously
56 found that the odor activity of alkane-1-thiols decreased with increasing chain length.
57 Sakoda and Hayashi¹⁵ determined the odor qualities of alkane-1-thiols and alkane-2-
58 thiols, as well as their corresponding alcohols and found some analogies in the odor
59 qualities. Recently Polster and Schieberle¹⁶ performed a comprehensive study on
60 structure/odor relationships in seven homologous series of alkane thiols and thio
61 ethers. They demonstrated that steric effects had an important influence on the odor
62 thresholds, and in all homologous series synthesized a minimum was observed for
63 thiols with five to seven carbon atoms, while molecules with longer alkyl chains
64 showed an exponential increase in their odor thresholds. Furthermore, substitution of
65 the thiol group by a hydroxy or a thiomethyl group led to a significant increase in odor
66 thresholds. The authors also confirmed results of Meilgaard¹⁷ that tertiary thiols
67 exhibit significantly lower thresholds than the primary and secondary mercaptans. In
68 a study on 4-mercapto-2-alkanones Wakabayashi et al.¹⁸ also confirmed the clear
69 influence of the chain length on odor thresholds.

70 Due to the outstanding position of **1** among food odorants, the aim of the present
71 study was to elucidate which structural features in 1-*p*-menthene-8-thiol are causing
72 its extremely low odor threshold. For this purpose, several mercapto-containing *p*-
73 menthane and 1-*p*-menthene derivatives as well as aromatic and open-chain
74 mercapto monoterpenoids were synthesized. Their structures were confirmed by
75 mass spectrometry and NMR measurements and, on the basis of the odor thresholds
76 and odor qualities, structure/odor activity correlations were done. As during food
77 processing the reaction of terpenoid compounds with either cysteine or H₂S might

78 lead to yet unknown terpenes with a mercapto group another aim of this study was to
79 generate analytical data to facilitate the identification of such unknown thiols possibly
80 occurring in foods.

81

82 **MATERIALS AND METHODS**

83 **Chemicals and Reference Odorants.** Chemicals for syntheses as well as some
84 reference odorants were purchased from ABCR (Karlsruhe, Germany), Alpha-Aesar
85 (Karlsruhe, Germany), Otava Chemicals (Kiev, Ukraine), Sigma-Aldrich (Steinheim,
86 Germany), and TCI Europe Laboratory Chemicals (Eschborn, Germany). Solvents
87 were obtained from VWR (Darmstadt, Germany) and deuterated solvents were
88 supplied by Euriso-top (Saarbruecken, Germany). Dichloromethane, diethyl ether,
89 and pentane were freshly distilled prior to use.

90 **Syntheses.** In total thirty-three mercaptans, diastereoisomers, and enantiopure
91 thiols were synthesized. The reactions were carried out in dry glassware under an
92 argon atmosphere. Details on the synthetic procedures are available in the
93 supplementary information.

94 One general synthetic route started from the corresponding alcohols of which
95 eight were synthesized.

96 *Synthesis of Alcohols.* Dihydro terpinen-4-ol, *p*-menthane-9-ol diastereomers,
97 tetrahydro carveol and tetrahydro linalool were obtained by hydrogenation of
98 terpinen-4-ol, (4*S*,8*R*)-*p*-menthene-9-ol, dihydro carveol, and linalool, respectively.
99 (1*R*,4*R*)-*p*-Menthane-7-ol and piperitol were prepared by reduction of (1*R*,4*R*)-4-
100 isopropylcyclohexane-1-carboxylic acid and piperitone, respectively.

101 *Synthesis of Racemic 1-p-Menthene-8-thiol (1a) and its Enantiomers (1b and 1c;*
102 *Figure 1A).* These were prepared from the corresponding alcohols following the

103 method described by Nishio¹⁹ with some modifications. For purification a SAFE-
104 distillation was used.²⁰

105 *Synthesis of 2 (Figure 1A), 6-9 (Figure 1B), 12 (Figure 1C), 15 and 16 (Figure*
106 *1D), 18 (Figure 1E) and 22 (Figure 1F).* Most of these thiols were synthesized from
107 the corresponding alcohols or from the respective stereoisomers using a slightly
108 modified method previously reported²¹ consisting of tosylation, thioacetylation, and
109 reduction (Figure 2). Compounds exhibiting a stereocenter at the carbon bearing a
110 hydroxyl group led to thiols with a different stereochemistry because of the Sn2
111 mechanism known for thioacetylation.

112 *Synthesis of 5 and 10 (Figure 1B), 11 and 13 (Figure 1C), 17 (Figure 1D), 23 and*
113 *24 (Figure 1E).* To synthesize tertiary thiols and compounds with a thiol group in an
114 α -position to a double bond, a strategy used by Ott and Kindel²² was followed.
115 However, after direct thioacetylation and reduction (Figure 3) the chiral information
116 was lost for compounds showing a stereocenter at the thiol group.

117 *Synthesis of 1-p-Menthene-4-thiol (3; Figure 1A).* This compound was prepared
118 from terpinolene in a three-step synthesis by epoxidation, transformation to the
119 episulfide, and reduction, following a previously published procedure²² with some
120 modifications (Figure 4).

121 *Synthesis of Two Diastereomers of 1-p-Menthene-3-thiol (4a and 4b; Figure 1A).*
122 The compounds were synthesized from linalool by a direct thioacetylation followed by
123 reduction.

124 *Synthesis of Thio Geraniol (19; Figure 1E) and Thio Nerol (21; Figure 1E).* Both
125 were synthesized following the method by Helminger et al.²³ starting from linalool as
126 the educt (Figure 5).

127 *Synthesis of Thio Linalool (20; Figure 1E).* The synthesis was performed by a
128 method described by Sigg-Gruetter and Wild²⁴ starting from geraniol.

129 **Gas Chromatography-Flame Ionization Detection (GC/FID) and Gas**
130 **Chromatography/Olfactometry (GC/O).** GC/FID and GC/O analyses were
131 performed by means of a Trace Ultra gas chromatograph (Thermo Scientific,
132 Bremen, Germany) using helium as the carrier gas. Capillaries used were DB-5 and
133 DB-FFAP (each 30 m × 0.32 mm i.d., 0.25 µm film thickness, 75 kPa head pressure)
134 (J&W Scientific, Chromatographie-Handel Mueller, Fridolfing, Germany). The
135 samples were applied by the cold-on-column injection technique (injection volume
136 1 µL) at 40 °C. After 2 min, the temperature of the oven was raised at 8 °C/min to
137 230 °C (DB-FFAP) or 240 °C (DB-5), respectively, and then held for 5 min. At the end
138 of the capillary, the effluent was split 1:1 into an FID and a sniffing port using a
139 deactivated Y-shaped glass splitter and two deactivated fused silica capillaries (50
140 cm × 32 mm i.d.). The FID and the sniffing port were held at 250 °C or 200 °C,
141 respectively. The FID was operated with hydrogen (20 mL/min) and air (200 mL/min).
142 Nitrogen (30 mL/min) was used as the make-up gas. During a GC/O run, the
143 panelist's nose was placed closely above the sniffing port, and the odor quality was
144 evaluated. If an odor was recognized, the retention time was marked in the
145 chromatogram, and the odor quality was annotated. Retention indices were
146 calculated using a series of *n*-alkanes.

147 **Gas Chromatography/Mass Spectrometry (GC/MS).** Mass spectra were
148 recorded by means of a 5890 series gas II chromatograph (Hewlett-Packard,
149 Waldbronn, Germany) connected to an MAT 95 S sector field mass spectrometer
150 (Finnigan, Bremen, Germany). Mass spectra in the electron ionization mode (MS-EI)
151 were recorded at 70 eV ionization energy and mass spectra in the chemical
152 ionization mode (MS-CI) at 115 eV with isobutane as the reactant gas.

153 **Determination of Odor Thresholds in Air.** Thresholds in air were determined by
154 aroma extract dilution analysis of a mixture containing known amounts of the

155 respective thiol and (*E*)-2-decenal as the internal standard. Thresholds were
156 calculated from the flavor dilution (FD) factors determined by using a previously
157 published method²⁵ and a threshold of 2.7 ng/L for (*E*)-2-decenal.²⁶

158 **NMR-Spectroscopy.** The ¹H, ¹³C, and 2D NMR experiments (COSY, HSQC,
159 HMBC) were performed using a 400 MHz Avance III spectrometer (Bruker,
160 Rheinstetten, Germany) at 297 K with deuterated chloroform (+ 0.03%
161 tetramethylsilane) as the solvent.

162

163 RESULTS

164 **Odor Thresholds in Air.** Odor thresholds are often determined in water or oil,
165 respectively, however, trace impurities may influence the results and lead to false
166 conclusions.²⁷ To overcome this problem, a method using GC/olfactometry with an
167 internal standard is the method of choice.²⁶ Furthermore, different volatilities of the
168 compounds depending on the matrices do not play a role, and in particular,
169 thresholds of enantiomers can simultaneously be determined using a chiral stationary
170 phase. The reliability of the method was verified by the determination of threshold
171 values of 8 mercapto-containing compounds by 8 panelists. The values only differed
172 by factors of 2 to 6, and the relative standard deviation was between 45 and 95%,
173 thus demonstrating a very good precision for the olfactory method.

174 **1-*p*-Menthene-8-thiol and Displacement of its Thiol Group.** In a first series of
175 experiments the influence of the position of the mercapto group in the 1-*p*-menthene
176 structure on odor threshold and odor quality was studied. For this purpose, first both
177 enantiomers of 1-*p*-menthene-8-thiol (**1b** and **1c**) as well as compounds **2**, **3** and **4a**
178 and **4b** were synthesized (Figure 1A).

179 The mass spectrum of 1-*p*-menthene-8-thiol (**1a**) as well as the spectrum of the
180 enantiomers (**1b** and **1c**; Figure 6A) revealed a signal for the molecular ion M⁺

181 (m/z 170) and a weak signal for $[M - CH_3]^+$ (m/z 155). The release of hydrogen
182 sulfide resulted in $[M - H_2S]^+$ (m/z 136) and further quite intense signals for the
183 fragments at m/z 121 and m/z 93, which are caused by the fragmentation of the
184 carbon chain. The racemic **1a** showed a grapefruit-like odor quality and a very low
185 odor threshold of 0.000034 ng/L in air (Table 1). The (*R*)-enantiomer showed a
186 slightly higher odor threshold compared to the (*S*)-enantiomer (Table 1). However,
187 the odor quality of both enantiomers was described as grapefruit-like. (*R*)- α -Terpineol
188 and (*S*)- α -terpineol, the corresponding alcohols, exhibited lilac-like and fir-like scents
189 and showed much higher odor thresholds of 4600 and 570 ng/L, respectively (Table
190 1).

191 (*4S,8R*)-1-*p*-Menthene-9-thiol (**2**; Figure 1A), 1-*p*-menthene-4-thiol (**3**, Figure 1A)
192 and the two diastereomers of 1-*p*-menthene-3-thiol (**4a** and **4b**, Figure 1A) were
193 subsequently synthesized to elucidate the influence of the position of the mercapto
194 group in the 1-*p*-menthene substructure. The mass spectrum of (*4S,8R*)-1-*p*-
195 menthene-9-thiol (Figure 6B) showed a quite intense signal for the molecular ion (m/z
196 170). The loss of H_2S is displayed by a signal at m/z 136, and the fragmentation of
197 the carbon skeleton produced signals at m/z 121, m/z 107 and the very distinct
198 signals at m/z 93, m/z 94, and m/z 95. For 1-*p*-menthene-4-thiol (Figure 6C),
199 however, only a small signal for M^+ (m/z 170) was observed, while the elimination of
200 H_2S (m/z 136) also occurred; the most intense signal m/z 93 was caused by $[M - H_2S$
201 $- CH_3 - CH_2 - CH_2]^+$. 1-*p*-Menthene-3-thiol only showed a few signals: Besides a
202 very small one for the molecular ion (m/z 170) two strong signals were found at m/z
203 137 and m/z 81 resulting from the cleavage of the thiol group and all of the side
204 chains, respectively (data not shown). The odor qualities for the four mercapto-
205 containing 1-*p*-menthenes differed significantly (Table 1). While (*4S,8R*)-1-*p*-
206 menthene-9-thiol (**2**) showed a soapy, fatty, and mushroom-like odor quality, for both

207 diastereomers of 1-*p*-menthene-3-thiol (**4a** and **4b**) unpleasant sulfury notes were
208 detected. By contrast, a catty and black currant-like odor was elicited by 1-*p*-
209 menthene-4-thiol (**3**; Table 1). However, again none of the compounds reached the
210 low odor threshold of 1-*p*-menthene-8-thiol (**1**). Although a low value was shown by
211 (4*S*,8*R*)-1-*p*-menthene-9-thiol (**2**), its threshold of 0.094 ng/L was still by three powers
212 of ten higher compared to **1**. Interestingly, 1-*p*-menthene-4-thiol (**3**) exhibited a quite
213 high threshold of 31 ng/L, and also the diastereomers of 1-*p*-menthene-3-thiol (**4**)
214 showed comparatively high odor thresholds between 2.8 and 4.5 ng/L. The odor
215 thresholds of the respective alcohols were always clearly higher than those of the
216 mercapto monoterpenoids ranging between 23 ng/L for (4*S*,8*R*)-1-*p*-menthene-9-ol
217 and 1200 ng/L for (+)-terpinen-4-ol (Table 1). While the retention indices of the
218 primary thiol **2** were significantly higher than those of **1**, both tertiary thiols were
219 eluted from the GC column much closer to **1** (Table 1).

220 **Hydrogenation of the Double Bond and Displacement of the Thiol Group.** In
221 a next series of experiments, the influence of the double bond in 1-*p*-menthene-8-
222 thiol (**1**) on the sensory attributes was studied followed by a displacement of the
223 mercapto group from position 8 to other carbons in the 1-*p*-menthane substructure. A
224 total of six thiols was prepared, and first, (1*R*,4*R*)-*p*-menthane-8-thiol (**5**; Figure 1B)
225 was synthesized. Its mass spectrum (Figure 7A) revealed nearly no molecular ion,
226 but strong signals at m/z 139 ($[M - SH]^+$) and m/z 75 ($C_3H_7S^+$), which is caused by
227 the propyl group bearing the thiol group. A comparison with **1** showed that
228 hydrogenation of the double bond in **1** led to a loss of the grapefruit-like odor quality,
229 but a citrus-like odor was kept (Table 2). Along with this small change in structure, a
230 significant increase in the odor threshold (0.59 ng/L) was found. The corresponding
231 alcohol, (1*R*,4*R*)-*p*-menthane-8-ol was described as fir needle-like and peppermint-
232 like and showed a high odor threshold of 830 ng/L in air (Table 2).

233 Besides (1*R*,4*R*)-*p*-menthane-8-thiol, further mercapto-containing *p*-menthane
234 derivatives were investigated, including compounds with a thiol group in the side
235 chain such as the diastereomers of *p*-menthane-9-thiol (**6a** and **6b**; Figure 1A) and
236 (1*R*,4*R*)-*p*-menthane-7-thiol (**7**; Figure 1B). In addition, mercaptans with a mercapto
237 group attached at the saturated ring, such as the *p*-menthane-2-thiol enantiomers (**8a**
238 and **8b**; Figure 1B), the 3 *p*-menthane-3-thiol stereoisomers (**9a** and **9c**; Figure 1B),
239 and *p*-menthane-4-thiol (**10**; Figure 1B) were synthesized.

240 The mass spectra of **6a**, **6b** and **7** were very similar showing quite intense signals
241 for m/z 172 (M^+) and m/z 138 ($[M - H_2S]^+$) as well as further fragments at m/z 123,
242 m/z 109, m/z 95, and m/z 81, which are due to the fragmentation of the carbon chain.
243 The only difference appeared for m/z 95, which was significantly higher in *p*-
244 menthane-7-thiol (**7**). *p*-Menthane-2-thiol (**8**) and the 3 *p*-menthane-3-thiol
245 stereoisomers (**9**) also revealed nearly identical fragments. As shown for **9** in Figure
246 7C, the molecular ion caused a considerable signal at m/z 172 and the loss of
247 hydrogen sulfide gave m/z 138 ($[M - H_2S]^+$). Further signals were caused by
248 fragmentation of the carbon chain, with the strongest signal at $[M - H_2S - CH_3 - CH_2$
249 $- CH_2]^+$ (m/z 95). However, for *p*-menthane-4-thiol, besides a very small signal for M^+
250 (m/z 172), a clear signal at m/z 139 ($[M - SH]^+$) was displayed (data not shown).

251 The *p*-menthane derivatives with thiol groups in the side chain clearly differed in
252 their odor qualities (Table 2). While (1*R*,4*R*)-*p*-menthane-8-thiol (**5**) was described as
253 sulfury and citrus-like, (1*R*,4*R*)-*p*-menthane-7-thiol (**7**) showed a rubber-like, burned
254 scent and both diastereomers of *p*-menthane-9-thiol (**6**) surprisingly exhibited soapy,
255 fatty and mushroom-like odor qualities. The thresholds of both isomers, however,
256 differed significantly by a factor of nearly 200. The respective alcohols showed clearly
257 higher thresholds between 48 and 830 ng/L (Table 2).

258 Most of the sulfur-containing *p*-menthane derivatives with a thiol group at the ring
259 (**8-10**) showed a rubber-like odor quality. Some of them were additionally perceived
260 as burned, e.g., (*1R,2S,4R*)-*p*-menthane-2-thiol (**8a**), while the (*1S,2R,4S*)-*p*-
261 menthane-2-thiol (**8b**) showed an onion-like odor. The three diastereomers of *p*-
262 menthane-3-ol (**9a-9c**; Table 2) smelled rubber-like, but (*1R,3R,4R*)- and (*1S,3R,4R*)-
263 *p*-menthane-3-thiol showed an additional bell-pepper like odor, while (*1R,3S,4S*)-*p*-
264 menthane-3-thiol (**9a**) and *p*-menthane-4-thiol (**10**) showed an additional orange-like,
265 citrus-like odor quality. Surprisingly, the odor thresholds for all *p*-menthane-2-thiols
266 and *p*-menthane-3-thiols were very high and ranged between 57 and 450 ng/L in air,
267 while the only tertiary thiol among these six compounds, *p*-menthane-4-thiol (**10**),
268 exhibited the lowest threshold of 0.19 ng/L. Interestingly, the corresponding alcohols
269 of the thiols **8a**, **8b**, **9a**, **9b**, and **9c** showed lower odor thresholds than the
270 mercaptans, although with clearly different odor qualities (Table 2).

271 **Aromatization and Displacement of the Thiol Group.** To investigate the
272 influence of a further modification of the ring system, some aromatic analogues were
273 studied. First, *p*-cymene-8-thiol (**11**; Figure 1C), the aromatic analog of 1-*p*-
274 menthene-8-thiol, was synthesized. The molecular ion (*m/z* 166) in the mass
275 spectrum was nearly absent (Figure 8A). By contrast, the signal for [M – SH]⁺ (*m/z*
276 133) was very strong and besides *m/z* 117 and *m/z* 105, another weak signal at *m/z*
277 91 was displayed, which is explainable by the aromatic tropylium cation. Whilst **1**
278 showed a grapefruit-like scent, its aromatic analog was described as sulfury and
279 passion fruit-like (Table 3). Additionally, **11** exhibited a low odor threshold of 0.051
280 ng/L, which was, however, still by far higher than that of **1** (Table 3). *p*-Cymene-8-ol,
281 the corresponding alcohol showed an apple-like as well as bitter almond-like odor
282 and a high odor threshold of 330 ng/L (Table 3).

283 Displacement of the thiol group within the aromatic ring finally gave *p*-cymene-9-
284 thiol (**12**), *p*-cymene-7-thiol (**13**) and *p*-cymene-3-thiol (**14**) (Figure 1C). The mass
285 spectra of these three compounds again revealed signals at *m/z* 91 for the aromatic
286 tropylium cation and a quite strong signal for the molecular ion (*m/z* 166). For **14**, the
287 signal at *m/z* 151 ($[M - CH_3]^+$) was the most intense, while for **13** the most intense ion
288 was *m/z* 133 ($[M - SH]^+$) and for **12** it was *m/z* 119 ($[M - SH - CH_2]^+$). Clear
289 differences in thresholds were determined within the three aromatic mercapto
290 monoterpenoids. *p*-Cymene-3-thiol showed a quite high odor threshold of 73 ng/L
291 and, thus, a significantly higher threshold than the compounds with thiol groups in the
292 side chain (**12** and **13**; Table 3). The odor qualities also differed in a certain way;
293 while **14** and **12** showed rubber-like and citrus-like odor qualities, **13** exhibited a
294 soapy and mushroom-like odor (Table 3). The thresholds of the corresponding
295 alcohols ranged between 4.6 ng/L for thymol and 2500 ng/L for *p*-cymene-9-ol (Table
296 3).

297 **8-Menthene Mercaptans.** Very recently it was suggested that 1-*p*-menthene-8-
298 thiol should be considered as an artifact from limonene and hydrogen sulfide formed
299 by the thermal treatment of fruit juices.²⁸ It can, thus, be speculated that an addition
300 of H₂S at the ring carbon 2 could also occur during food processing. Therefore,
301 (1*R*,2*S*,4*R*)- (**15a**) and (1*S*,2*R*,4*S*)-8-*p*-menthene-2-thiol (**15b**; Figure 1D) were
302 synthesized. To evaluate the influence of further structural modifications, also
303 (1*R*,3*S*,4*S*)- (**16a**) and (1*S*,3*R*,4*R*)-8-*p*-menthene-3-thiol (**16b**) were investigated
304 (Figure 1D).

305 Besides the low signals for M⁺ (*m/z* 170) and $[M - CH_3]^+$ (*m/z* 155), the mass
306 spectra of (1*R*,2*S*,4*R*)- and (1*S*,2*R*,4*S*)-8-*p*-menthene-2-thiol (**15**; Figure 8B) showed
307 a very strong signal at *m/z* 136, which indicates the loss of hydrogen sulfide ($[M -$
308 H₂S]⁺), and *m/z* 121, *m/z* 107, *m/z* 93, and *m/z* 79, which are all due to the

309 fragmentation of the carbon chain. For the corresponding 8-*p*-menthene-3-thiols (**16a**
310 and **16b**) the signals were quite the same, but the intensities differed significantly.
311 Here the signals at *m/z* 155 and *m/z* 81 were the strongest (see supplementary
312 information). In contrast to a suggested addition of H₂S to limonene at carbon 8
313 resulting in 1-*p*-menthene-8-thiol, an addition at carbon 2 would lead to significant
314 different odor qualities and higher odor thresholds as (1*R*,2*S*,4*R*)- (**15a**) and
315 (1*S*,2*R*,4*S*)-8-*p*-menthene-2-thiol (**15b**) exhibited rather rubber-like, onion-like, and
316 burned scents and showed higher thresholds of 1.1 and 35 ng/L, respectively (Table
317 4). A displacement of the thiol group to the ring carbon 3 neither led to a significant
318 change in odor qualities nor in odor thresholds. The isomers **16a** and **16b** also
319 exhibited burned and rubber-like odors and thresholds of 3.9 and 8.6 ng/L. The
320 enantiomers of the respective alcohols dihydro carveol and isopulegol showed odor
321 thresholds between 150 and 440 ng/L (Table 4).

322 **Structural Motif of Thio Carveol.** Since carveol is a naturally occurring volatile
323 compound, the corresponding mercaptan (4*R*)-1,8-*p*-menthadiene-6-thiol (**17**) (Figure
324 1D) was also synthesized. MS data showed again the typical fragmentation pattern
325 for mercapto-containing 1-*p*-menthene derivatives. The most intense signals at *m/z*
326 134, *m/z* 119 and *m/z* 93 resulted from the decomposition of the carbon chain,
327 whereas the smaller signals at *m/z* 168 and *m/z* 153 are due to the molecular ion and
328 the [M – CH₃]⁺ (Figure 8C). **17** showed a rubber-like, burned and onion-like odor
329 quality and an odor threshold of 0.45 ng/L (Table 4). The diastereomers of the
330 corresponding (-)-carveol exhibited thresholds of 120 and 170 ng/L and were
331 described as caraway- and peppermint-like, respectively.

332 **Open-chain Mercapto Monoterpenoids.** To complete the study on mercapto
333 terpenoids, thiol analogues of naturally occurring open-chain compounds such as

334 thio citronellol (**18**), thio geraniol (**19**), thio linalool (**20**) and thio nerol (**21**) (Figure 1E)
335 were prepared.

336 The mass spectra of thio geraniol and thio nerol were nearly identical (Figure 9A).
337 The molecular ion M^+ was nearly absent in **19** and further fragments like $[M - CH_3]^+$,
338 $[M - SH]^+$ only showed small intensities, whereas the fragment at m/z 69, which is
339 due to $C_5H_9^+$, resulted in by far the strongest signal. Thio linalool revealed a similar
340 fragmentation pattern with strong signals at m/z 93 and m/z 69 (Figure 9B). The two
341 enantiomers of thio citronellol showed only small signals for M^+ (m/z 172) and $[M -$
342 $H_2S]^+$ (m/z 138), but distinct signals at m/z 129, m/z 115, and m/z 69. The former two
343 fragments resulted from the split-off of $C_3H_7^+$ and $C_4H_9^+$, respectively. Thio geraniol
344 as well as (3*R*)- (**18a**) and (3*S*)- β -thio citronellol (**18b**) were described as soapy, fatty
345 and mushroom-like and also thio nerol exhibited a soapy odor quality, but an
346 additional peach-like scent was recognized (Table 5). The thresholds of thio geraniol,
347 of the thio citronellol enantiomers, and of thio linalool, which showed a rubber-like
348 and citrus-like odor, all ranked between 5.1 and 13 ng/L, whereas thio nerol had a
349 low odor threshold of 0.014 ng/L, which was the second-lowest threshold value
350 among all the 33 mercapto monoterpenoids investigated. Most of the corresponding
351 alcohols were described as rose-like and citrus-like, however, linalool shows a
352 bergamot-like scent and nerol a balm-like odor. The highest odor threshold was
353 shown by nerol (61 ng/L), whereas geraniol exhibited a very low value of 0.067 ng/L
354 (Table 5).

355 **Hydrogenated Open-chain Mercapto Monoterpenoids.** In a last series of
356 experiments, the hydrogenated analogues of thio citronellol (**22**), thio linalool (**23**)
357 and thio myrcenol (**24**; Figure 1E) were synthesized.

358 Mass spectra of the three compounds did not differ clearly. In all spectra, a small
359 signal for M^+ (m/z 174) was detected and a bunch of signals for fragments with a

360 mass-to-charge-ratio less than m/z 85 were measured. Dihydro thio citronellol
361 showed a quite intense signal at m/z 140, whereas tetrahydro thio linalool and
362 tetrahydro thio myrcenol showed a signal at m/z 141. These signals resulted from the
363 fragments $[M - H_2S]^+$ and $[M - SH]^+$, respectively. The odor thresholds were
364 comparatively high and ranged between 63 ng/L for tetrahydro thio myrcenol and 340
365 ng/L for tetrahydro thio linalool (Table 5). Dihydro thio citronellol, showing a threshold
366 value of 71 ng/L, was described as soapy, fatty and mushroom-like and the other two
367 compounds as burned and rubber-like. Dihydro citronellol, tetrahydro linalool and
368 tetrahydro myrcenol were all described as citrus-like, with the latter two compounds
369 showing thresholds of 2.4 and 8.8 ng/L, respectively, while dihydro citronellol
370 exhibited a higher threshold of 140 ng/L (Table 5).

371

372 DISCUSSION

373 The results revealed that 1-*p*-menthene-8-thiol (**1**) showed by far the lowest odor
374 threshold among the 33 monoterpene derived mercaptans. Modifications of the
375 structure of **1** clearly indicated that the double bond in position 1 of the ring and a
376 tertiary thiol group at position 8 of the structure are key odotopes for the
377 characteristic grapefruit-like odor as well as for its extremely low odor threshold.
378 However, it could be found that only a double bond at the right position in the ring
379 does not necessarily lead to a low odor threshold, because (4*S*,8*R*)-1-*p*-menthene-9-
380 thiol (**2**) did not reach the low value of 1-*p*-menthene-8-thiol. 1-*p*-Menthene-4-thiol (**3**)
381 and two diastereomers of 1-*p*-menthene-3-thiol (**4a** and **4b**) even exhibited
382 comparatively high odor thresholds between 2.8 and 31 ng/L.

383 A general observation was, however, that the unsaturated compounds showed
384 considerably lower thresholds than the saturated analogues, e.g., (1*R*,4*R*)-*p*-
385 menthane-8-thiol had a threshold of 0.59 ng/L, which was by 4 powers of ten higher

386 compared to the grapefruit-like smelling **1**. Also the thresholds of (*4R*)-1,8-*p*-
387 menthadiene-6-thiol (**17**), the two diastereomers of 1-*p*-menthene-3-thiol, and
388 (*4S,8R*)-1-*p*-menthene-9-thiol were lower than those of the respective *p*-menthane
389 derivatives. One exception was 1-*p*-menthene-4-thiol, which showed by a factor of
390 nearly 200 higher threshold value than its saturated analog.

391 Apart from the thresholds, also the odor qualities changed in most cases except
392 the soapy, fatty, and mushroom-like scents, which stayed the same for (*4S,8R*)-1-*p*-
393 menthene-9-thiol and both diastereomers of *p*-menthane-9-thiol (**6a** and **6b**). Thus,
394 as a first conclusion, a double bond in the ring is needed to reach lower odor
395 thresholds in mercaptans with a *p*-menthane structure.

396 However, also a 1-*p*-menthene basic structure does not consequently induce a
397 low odor threshold in thiols. Apart from the double bond in the ring the tertiary thiol
398 group at the side chain at carbon C8 is a necessary odotope. This structural element
399 seems to be a very important component to reach a low odor threshold as seven of
400 the ten compounds with the lowest thresholds had a thiol group in the side chain (**1**,
401 **2**, **5**, **6b**, **11**, **12**, **13**). By contrast, 1-*p*-menthene and *p*-menthane derivatives with
402 thiol groups attached at the ring exhibited clearly higher thresholds. In comparison to
403 the *p*-menthane-2-thiols (**8a** and **8b**) and *p*-menthane-3-thiols (**9a** and **9b**) showing
404 thresholds between 57 and 450 ng/L, the *p*-menthane derivatives with thiol groups in
405 the side chain showed thresholds between 0.13 and 25 ng/L. An exception was
406 found for *p*-menthane-4-thiol, but its very low odor threshold of 0.19 ng/L could
407 possibly be explained by the tertiary thiol group, as suggested by Meilgaard¹⁷ as well
408 as by Polster and Schieberle.¹⁶ Also 1-*p*-menthene-8-thiol and (*4S,8R*)-1-*p*-
409 menthene-9-thiol showed lower thresholds than the 1-*p*-menthene derivatives with a
410 thiol group in the ring. The same trend was observed for the aromatic mercapto
411 monoterpenoids (Table 3). In this group, also compounds with a thiol group in the

412 side chain showed significantly lower thresholds than, e.g., *p*-cymene-3-thiol (**11**)
413 with a thiol group in the ring. However, the odor threshold of the tertiary mercaptan
414 *p*-cymene-8-thiol was again the lowest among the aromatic compounds and these
415 three analogues ranked among the eight most potent mercapto monoterpenoids
416 analyzed.

417 The odor qualities of the structurally similar compounds 1-*p*-menthene-8-thiol,
418 (1*R*,4*R*)-*p*-menthane-8-thiol, and *p*-cymene-8-thiol were also similar, but in contrast
419 to the compounds mentioned that also showed fruity scents, 1-*p*-menthene-8-thiol
420 lost the repellent sulfury odor quality in dilution and the odor intensity stayed quite
421 high up to the threshold value. However, it should be stressed that for none of the
422 investigated thiols the characteristic grapefruit-like odor of 1-*p*-menthene-8-thiol was
423 found.

424 Not only a double bond in the ring, but also a double bond in the side chain
425 induced lower thresholds in mercapto-containing monoterpenoids. The thresholds of
426 (1*R*,3*S*,4*S*)- (**16a**) and (1*S*,3*R*,4*R*)-8-*p*-menthene-3-thiol (**16b**) were ~ 20 to 40 times
427 lower than those of the saturated analogues. The same was true for the 8-*p*-
428 menthene-2-thiols, although here an additional double bond in the ring, e.g., in (4*R*)-
429 1,8-*p*-menthadiene-6-thiol (**17**), again caused a lower threshold.

430 The open-chain thiols mainly showed soapy, fatty, or burned and rubber-like
431 smelling compounds with thresholds between 5.1 and 340 ng/L which was in good
432 agreement with the results of Polster and Schieberle.¹⁶ For thiols containing ten
433 carbon atoms they determined odor thresholds between 40 and 270 ng/L.
434 Surprisingly, thio nerol (**21**) exhibited a very low odor threshold of 0.014 ng/L, which
435 was the second lowest value among the thiols studied. Also its peach-like odor
436 quality was unique among the open-chain mercapto monoterpenoids. Taking into
437 account the data collected in the recent study, it was conspicuous that tertiary thiols

438 did not exhibit the lowest odor thresholds, but rather double bonds in the molecules
439 caused again a decrease, such as for tetrahydro thio linalool (**23**) and thio linalool
440 (**20**), and for dihydro thio citronellol (**22**) and β -thio citronellol (**18a**, **18b**).

441 Besides the odor qualities and odor thresholds of the mercapto monoterpenoids,
442 those of the respective monoterpene alcohols were also determined to study the
443 influence of the thiol group on odor thresholds. Almost half of the alcohols exhibited
444 slightly lower or similar thresholds as the thiols, especially the open-chain mercapto
445 monoterpenoids and a few *p*-menthane derivatives. This was also previously
446 reported for longer-chain thiols.¹⁶ For example alkane-1-thiols, alkane-2-thiols,
447 alkane-3-thiols, and 2-methylalkane-2-thiols containing 8 to 10 carbons showed
448 nearly the same odor thresholds as the respective alcohols.¹⁵ However, for the
449 shorter-chain compounds threshold values were lower by up to 6 decimal powers.

450 On the other hand, approximately half of the thiols examined in our study showed
451 significantly lower odor thresholds than the corresponding alcohols. The greatest
452 difference occurred for 1-*p*-menthene-8-thiol and its respective alcohol α -terpineol.
453 Whilst the (*S*)-enantiomer showed by far the lowest threshold among the sulfur-
454 containing compounds, (*R*)- α -terpineol exhibited the highest value among all alcohols
455 studied. For the respective enantiomers differences by factors of approximately 50
456 and 90 millions, respectively, were determined. So, despite the quite high number of
457 carbons, the cyclic 1-*p*-menthene, *p*-menthane, and *p*-cymene structures also seem
458 to be effective odotopes to generate low odor thresholds.

459 In general, the study has shown that a double bond in the ring of the *p*-menthane
460 structure, and in particular a tertiary thiol group in the side chain of a cyclic structure
461 are necessary prerequisites to generate low odor thresholds in mercapto
462 monoterpenoids.

- 20 -

463 However, the results do still not explain why none of the synthesized compounds
464 with similar structures showed an extraordinary low threshold in the same order of
465 magnitude as found for **1**. For some of the *p*-menthane derivatives the values were
466 even higher by 7 powers of ten. It can, thus, be speculated that probably human
467 olfactory receptors must have been developed in close correlation to the naturally
468 occurring volatile compounds. There would be no other way to explain why even very
469 structurally similar, but not naturally occurring thiols show so much higher thresholds
470 as found for **1**.

471

472 **ASSOCIATED CONTENT**

473 **Supporting Information.** Experimental procedures and spectral data (NMR, MS) of
474 the synthesized compounds and intermediates. In Figures S1, S4, S38, S55, S58,
475 and S63 the synthetic routes of the reactions are illustrated. Figures S2, S3, S5-S37,
476 S39-S54, S56, S57, S59-S62, and S64-S67 show the NMR spectra of the
477 synthesized sulfur compounds. This material is available free of charge via the
478 Internet at <http://pubs.acs.org>.

479

480 **Notes.** The authors declare no competing financial interest.

481

482 **ABBREVIATIONS USED.** CI, chemical ionization; COSY, correlated spectroscopy;
483 EI, electron ionization; FFAP, free fatty acid phase; FID, flame ionization detector;
484 GC-O, gas chromatography-olfactometry; HMBC, heteronuclear multiple bond
485 correlation; HSQC, heteronuclear single quantum coherence; 1-*p*MT, 1-*p*-menthene-
486 8-thiol; M_r , relative molecular mass; MS, mass spectrometry; NMR, nuclear magnetic
487 resonance; RI, retention index; SAFE, solvent assisted flavor evaporation.

488

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573

574

575 **FIGURE CAPTIONS**

576

577 **Figure 1A.** Structural formulas of 1-*p*-menthene thiols.578 **Figure 1B.** Structural formulas of *p*-menthane thiols.579 **Figure 1C.** Structural formulas of aromatic mercapto monoterpenoids.580 **Figure 1D.** Structural formulas of 8-menthene mercaptans and thio carveol.581 **Figure 1E.** Structural formulas of open-chain mercapto monoterpenoids.582 **Figure 2.** Synthetic route used in the preparation of primary and secondary thiols.583 **Figure 3.** Synthetic route used in the preparation of tertiary thiols and compounds
584 with a thiol group in conjugation to a double bond.585 **Figure 4.** Synthetic route used in the preparation of 1-*p*-menthene-4-thiol.586 **Figure 5.** Synthetic route used in the preparation of thio geraniol and thio nerol.587 **Figure 6.** Mass spectra (MS-EI) of 1-*p*-menthene-8-thiol (**A**), (4*R*,8*R*)-1-*p*-menthene-
588 9-thiol (**B**), and 1-*p*-menthene-4-thiol (**C**).589 **Figure 7.** Mass spectra (MS-EI) of *p*-menthane-8-thiol (**A**) and (1*R*,3*S*,4*S*)-*p*-
590 menthane-3-thiol (**B**).591 **Figure 8.** Mass spectra (MS-EI) of *p*-cymene-8-thiol (**A**), (1*S*,2*R*,4*S*)-8-*p*-menthene-
592 2-thiol (**B**), and (4*R*)-1,8-*p*-menthadiene-6-thiol (**C**).593 **Figure 9.** Mass spectra (MS-EI) of thio nerol (**A**) and thio linalool (**B**).

594

Table 1. Retention Indices and Sensory Properties of Mercapto-Containing 1-*p*-Menthene Derivatives and Sensory Properties of the Respective Alcohols

no. ^a	compound	RI		odor quality ^b	odor threshold (ng/L in air)	respective alcohol	odor quality ^{b,c}	odor threshold (ng/L in air) ^c
		FFAP	DB-5					
1a	1- <i>p</i> -menthene-8-thiol, <i>mixture of enantiomers</i>	1577	1285	grapefruit-like	0.000034			
1b	(<i>R</i>)-1- <i>p</i> -menthene-8-thiol	1577	1285	grapefruit-like	0.000090	(<i>R</i>)- α -terpineol	citrus-like, lilac-like	4600
1c	(<i>S</i>)-1- <i>p</i> -menthene-8-thiol	1577	1285	grapefruit-like	0.0000066	(<i>S</i>)- α -terpineol	flowery, conifer-like	570
2	(4 <i>S</i> ,8 <i>R</i>)-1- <i>p</i> -menthene-9-thiol	1710	1364	soapy, fatty, mushroom-like	0.094	(4 <i>S</i> ,8 <i>R</i>)-1- <i>p</i> -menthene-9-ol	rose-like, citrus-like	23
3	1- <i>p</i> -menthene-4-thiol	1535	1260	catty, black currant-like	31	(+)-terpinen-4-ol	fir needle-like, peppermint-like	1200
						(-)-terpinen-4-ol	fir needle-like, peppermint-like	220
4a	1- <i>p</i> -menthene-3-thiol, <i>diastereomer 1</i>	1533	1268	sulfury, roasty	4.5	piperitol	peppermint-like	340
4b	1- <i>p</i> -menthene-3-thiol, <i>diastereomer 2</i>	1544	1280	sulfury, citrus- like	2.8			

^a Compound numbers correspond to the numbers in Figure 1. ^b Odor quality as perceived at the sniffing port during GC/O at threshold level.

^c Sensory properties of the respective alcohol.

Table 2. Retention Indices and Sensory Properties of Mercapto-Containing *p*-Menthane Derivatives and Sensory Properties of the Corresponding Alcohols

no. ^a	compound	RI		odor quality ^b	odor threshold (ng/L in air)	respective alcohol	odor quality ^{b, c}	odor threshold (ng/L in air) ^c
		FFAP	DB-5					
5	(1 <i>R</i> ,4 <i>R</i>)- <i>p</i> -menthane-8-thiol	1436	1232	sulfury, citrus-like	0.59	(1 <i>R</i> ,4 <i>R</i>)- <i>p</i> -menthane-8-ol	fir needle-like, peppermint-like	830
6a	<i>p</i> -menthane-9-thiol, <i>diastereomer 1</i>	1548	1307	soapy, fatty, mushroom-like	25	<i>p</i> -menthane-9-ol, <i>diastereomer 1</i>	rose-like, citrus-like	96
6b	<i>p</i> -menthane-9-thiol, <i>diastereomer 2</i>	1577	1324	soapy, fatty, mushroom-like	0.13	<i>p</i> -menthane-9-ol, <i>diastereomer 2</i>	citrus-like	66
7	(1 <i>R</i> ,4 <i>R</i>)- <i>p</i> -menthane-7-thiol	1601	1330	rubber-like, burned	7.0	(1 <i>R</i> ,4 <i>R</i>)- <i>p</i> -menthane-7-ol	rose-like, citrus-like, peppermint-like	48
8a	(1 <i>R</i> ,2 <i>S</i> ,4 <i>R</i>)- <i>p</i> -menthane-2-thiol	1491	1272	rubber-like, burned, onion-like	57	(-)-tetrahydro carveol	musty, peppermint- like	45
8b	(1 <i>S</i> ,2 <i>R</i> ,4 <i>S</i>)- <i>p</i> -menthane-2-thiol	1485	1271	onion-like, rubber-like	450	(+)-tetrahydro carveol	peppermint-like, fecal	100
9a	(1 <i>R</i> ,3 <i>S</i> ,4 <i>S</i>)- <i>p</i> -menthane-3-thiol	1461	1241	rubber-like, orange-like	170	(-)-menthol	peppermint-like	43
9b	(1 <i>R</i> ,3 <i>R</i> ,4 <i>R</i>)- <i>p</i> -menthane-3-thiol	1520	1274	rubber-like, bell pepper- like	59	(+)-isomenthol	peppermint-like	20
9c	(1 <i>S</i> ,3 <i>R</i> ,4 <i>R</i>)- <i>p</i> -menthane-3-thiol	1461	1241	rubber-like, bell pepper- like	150	(+)-menthol	peppermint-like	19
10	<i>p</i> -menthane-4-thiol	1438	1237	rubber-like, citrus-like	0.19	Dihydro terpinen-4-ol	fir needle-like, peppermint-like	240

^a Compound numbers correspond to the numbers in Figure 1. ^b Odor quality as perceived at the sniffing port during GC/O at threshold level.

^c Sensory properties of the respective alcohol.

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Table 3. Retention Indices and Sensory Properties of Aromatic Mercapto Monoterpenoids and Sensory Properties of the Respective Alcohols

no. ^a	compound	RI		odor quality ^b	odor threshold (ng/L in air)	respective alcohol	odor quality ^{b,c}	odor threshold (ng/L in air) ^c
		FFAP	DB-5					
11	<i>p</i> -cymene-8-thiol	1722	1280	sulfury, passion fruit-like	0.051	<i>p</i> -cymene-8-ol	apple-like, bitter almond-like	330
12	<i>p</i> -cymene-9-thiol	1813	1324	soapy, rubber-like, citrus-like	0.28	<i>p</i> -cymene-9-ol	peppermint-like, musty	2500
13	<i>p</i> -cymene-7-thiol	1857	1345	soapy, mushroom-like	0.27	<i>p</i> -cymene-7-ol	smoky, phenolic	54
14	<i>p</i> -cymene-3-thiol	1867	1315	rubber-like, citrus-like	73	thymol	thyme-like	4.6

^a Compound numbers correspond to the numbers in Figure 1. ^b Odor quality as perceived at the sniffing port during GC/O at threshold level.

^c Sensory properties of the respective alcohol.

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Table 4. Retention Indices and Sensory Properties of 8-Menthene Mercaptans as well as Thiocarveol and Sensory Properties of the Respective Alcohols

no. ^a	compound	RI		odor quality ^b	odor threshold (ng/L in air)	respective alcohol or educt, respectively	odor quality ^{b,c}	odor threshold (ng/L in air) ^c
		FFAP	DB-5					
15a	(1 <i>R</i> ,2 <i>S</i> ,4 <i>R</i>)-8- <i>p</i> -menthene-2-thiol	1592	1282	rubber-like, onion-like, minty	1.1	(-)-dihydro carveol	musty, peppermint-like	160
15b	(1 <i>S</i> ,2 <i>R</i> ,4 <i>S</i>)-8- <i>p</i> -menthene-2-thiol	1591	1282	burned, onion-like	35	(+)-dihydro carveol	peppermint-like, fecal	300
16a	(1 <i>R</i> ,3 <i>S</i> ,4 <i>S</i>)-8- <i>p</i> -menthene-3-thiol	1558	1266	burned, rubber-like	8.6	(-)-isopulegol	peppermint-like	440
16b	(1 <i>S</i> ,3 <i>R</i> ,4 <i>R</i>)-8- <i>p</i> -menthene-3-thiol	1558	1267	burned, rubber-like	3.9	(+)-isopulegol	peppermint-like	150
17	(4 <i>R</i>)-1,8- <i>p</i> -menthadiene-6-thiol	1650	1279	rubber-like, burned, onion-like	0.45	(-)-carveol, <i>diastereomer 1</i>	musty, peppermint-like	170
						(-)-carveol, <i>diastereomer 2</i>	musty, caraway-like	120

^a Compound numbers correspond to the numbers in Figure 1. ^b Odor quality as perceived at the sniffing port during GC/O at threshold level.

^c Sensory properties of the respective alcohol.

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Table 5. Retention Indices and Sensory Properties of Open-Chain Mercapto Monoterpenoids and Sensory Properties of the Corresponding Alcohols

no. ^a	compound	RI		odor quality ^c	odor threshold (ng/L in air)	respective alcohol	odor quality ^{b,c}	odor threshold (ng/L in air) ^c
		FFAP	DB-5					
18a	(3 <i>R</i>)- β -thio citronellol	1541	1278	soapy, fatty, mushroom-like	5.1	(3 <i>R</i>)- β -citronellol	rose-like, citrus-like	1.1
18b	(3 <i>S</i>)- β -thio citronellol	1541	1278	soapy, fatty, mushroom-like	13	(3 <i>S</i>)- β -citronellol	rose-like, citrus-like	0.57
19	Thio geraniol	1599	1287	soapy, fatty, mushroom-like	5.2	geraniol	rose-like, citrus-like	0.067
20	thio linalool	1439	1194	rubber-like, citrus-like	5.3	linalool	citrus-like, bergamot-like	0.26
21	thio nerol	1573	1271	soapy, peach-like	0.014	nerol	balm-like	61
22	dihydro thio citronellol	1440	1242	soapy, fatty, peach-like	71	dihydro citronellol	rose-like, citrus-like	140
23	tetrahydro thio linalool	1320	1181	burned, rubber-like, citrus-like	340	tetrahydro linalool	citrus-like, bergamot-like	2.4
24	tetrahydro thio myrcenol	1310	1177	burned, rubber-like	63	tetrahydro myrcenol	citrus-like, soapy	8.8

^a Compound numbers correspond to the numbers in Figure 1. ^b Odor quality as perceived at the sniffing port during GC/O at threshold level.

^c Sensory properties of the corresponding alcohol.

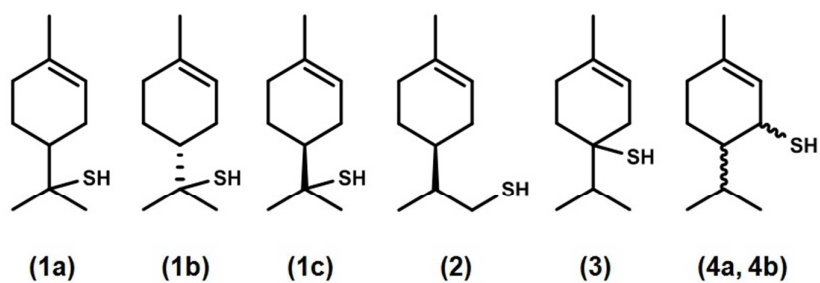


Figure 1A

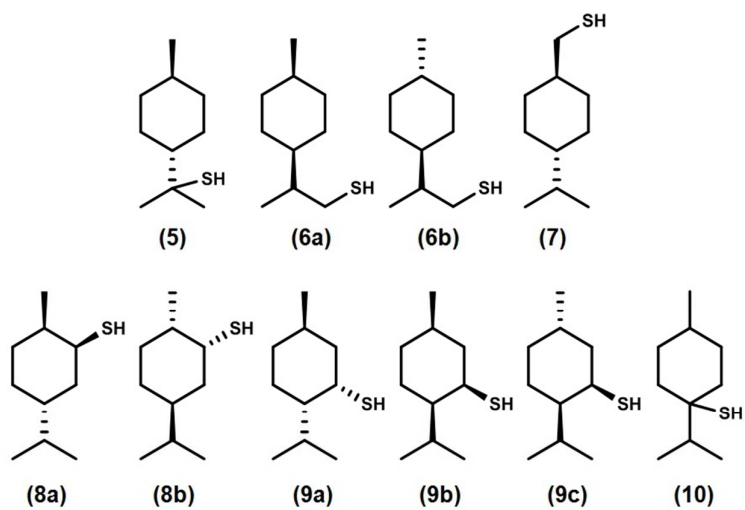


Figure 1B

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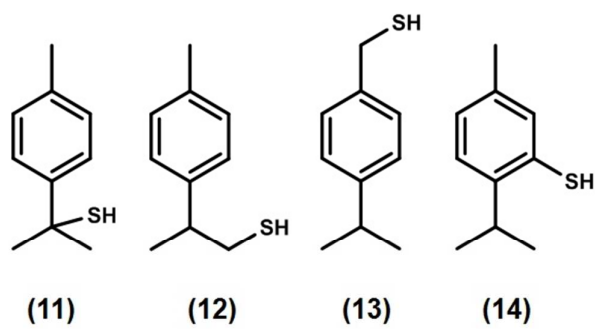


Figure 1C

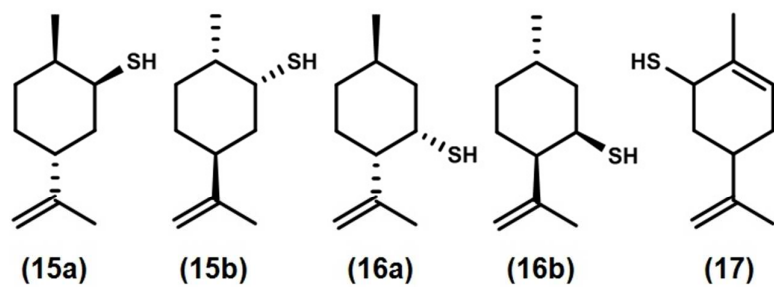


Figure 1D

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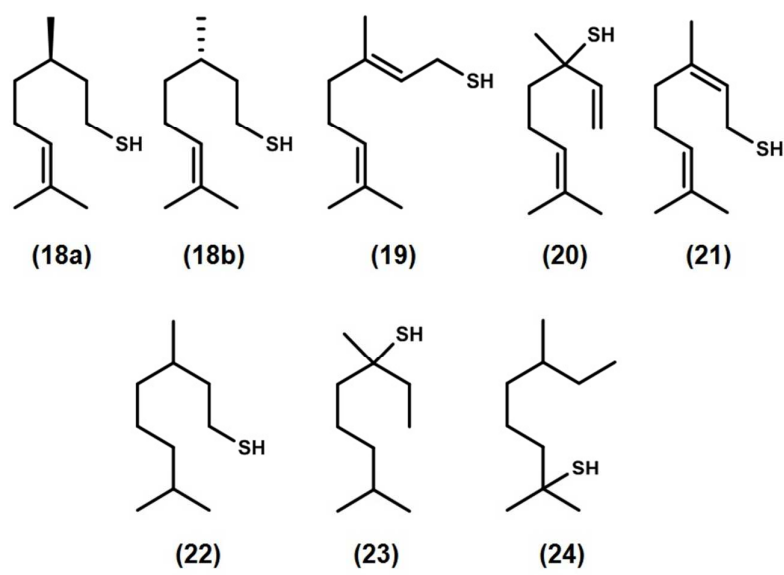


Figure 1E

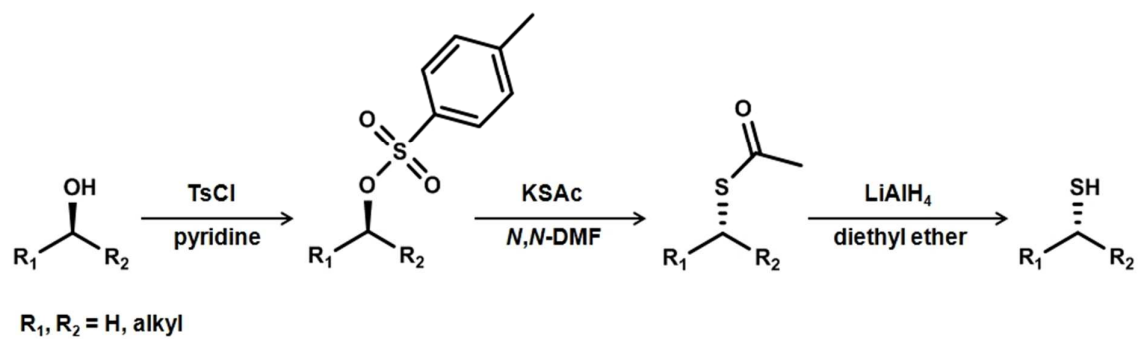


Figure 2

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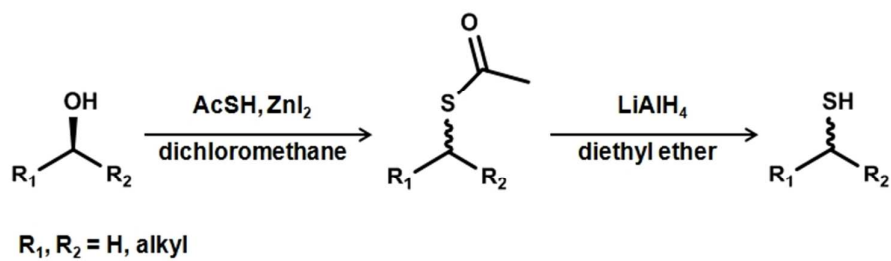


Figure 3

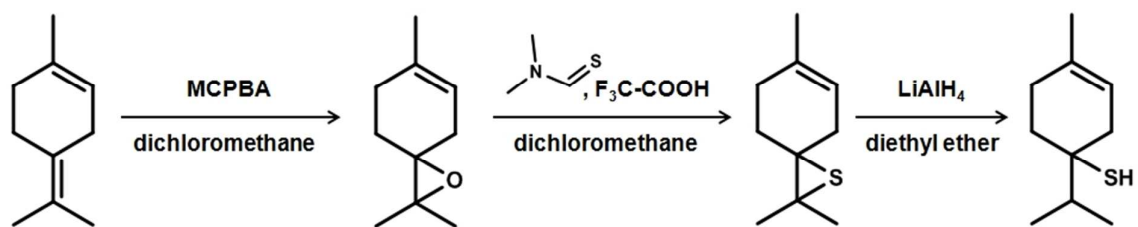


Figure 4

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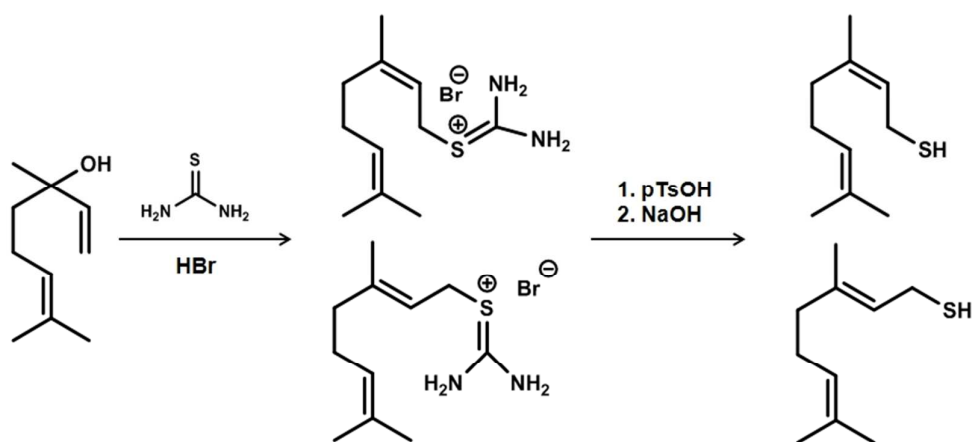


Figure 5

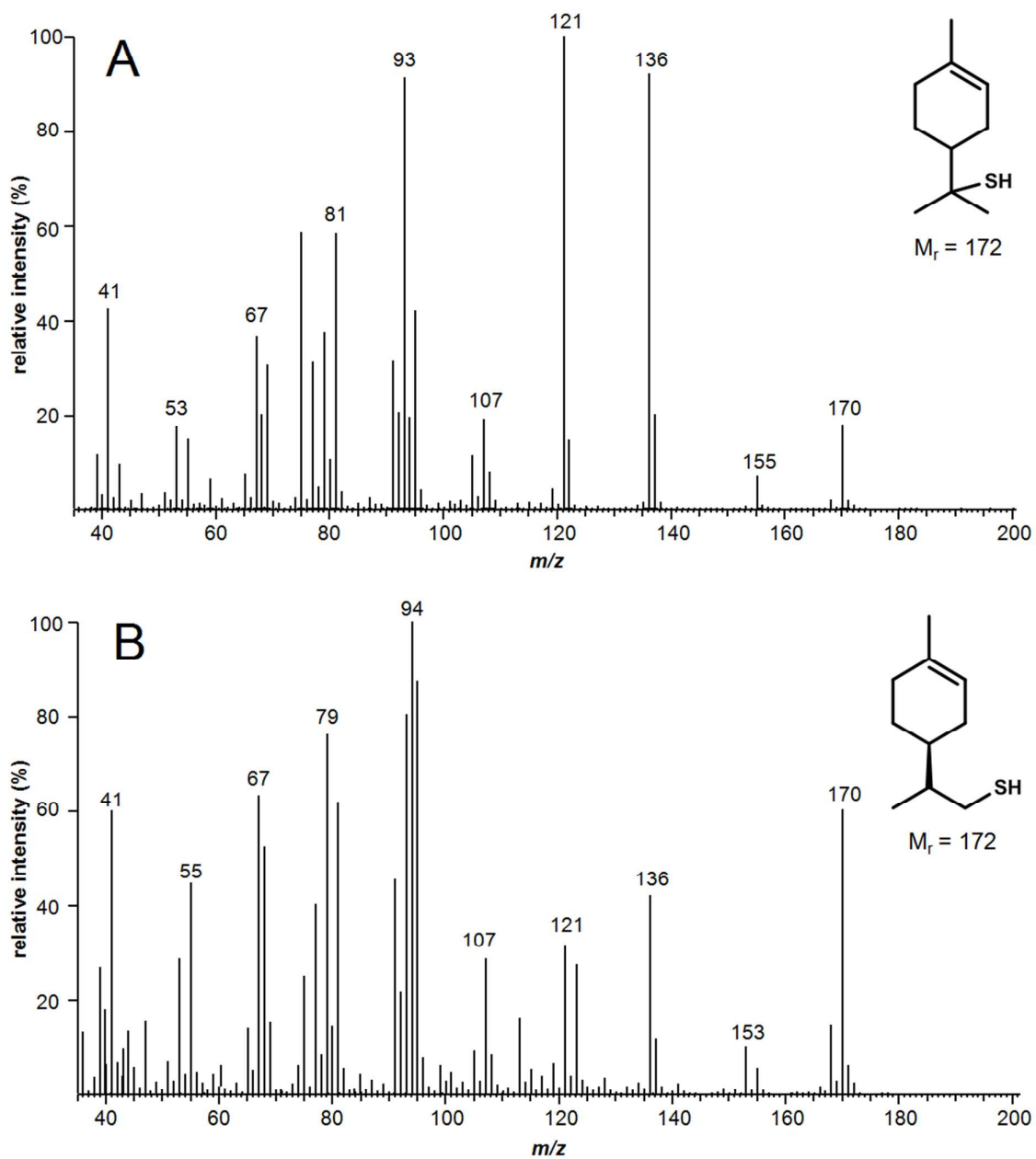


Figure 6

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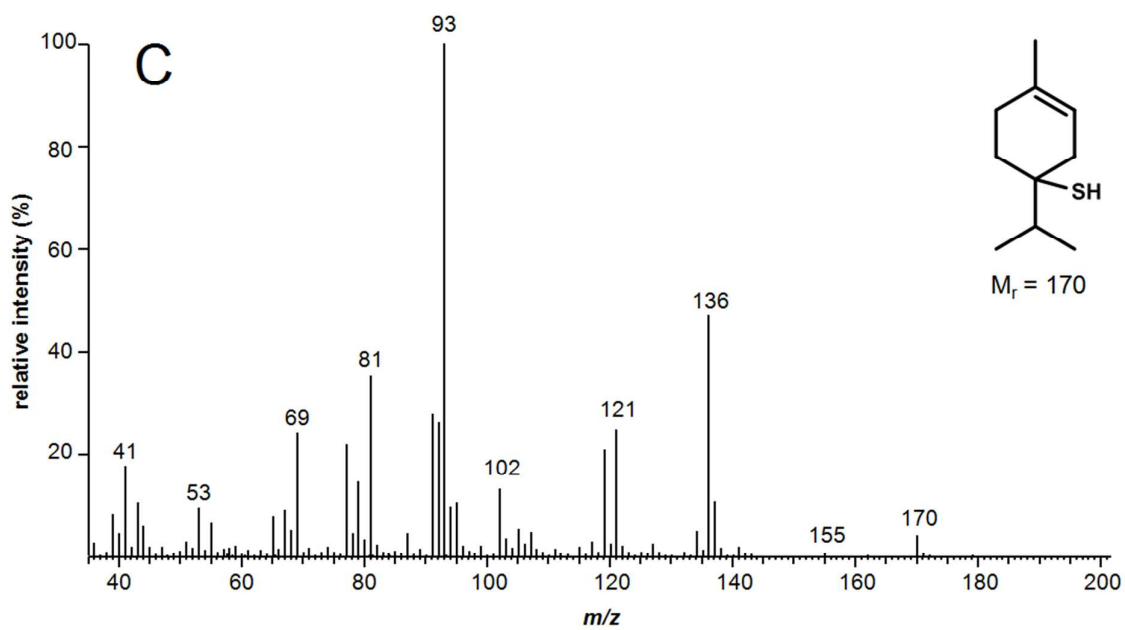


Figure 6

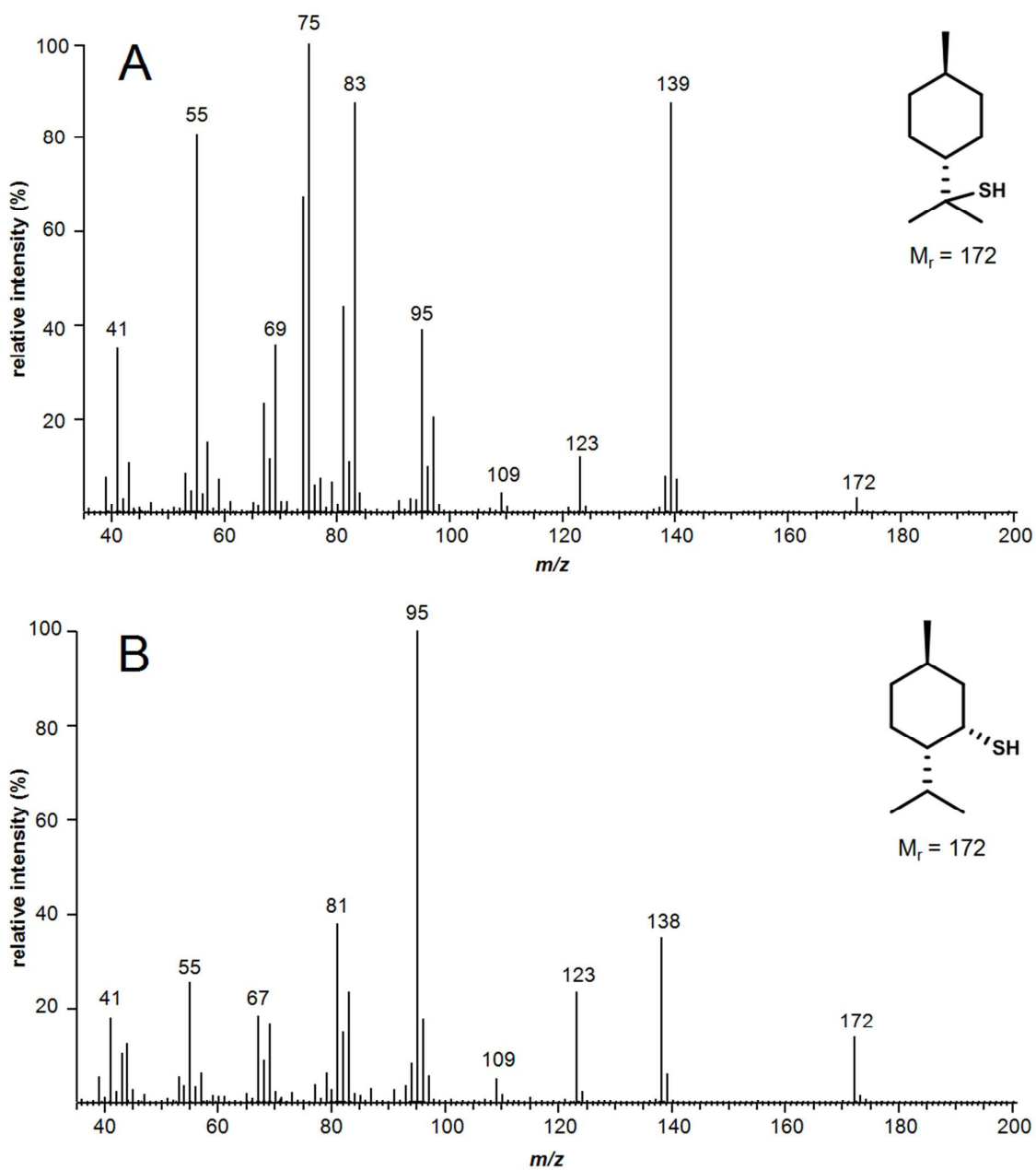


Figure 7

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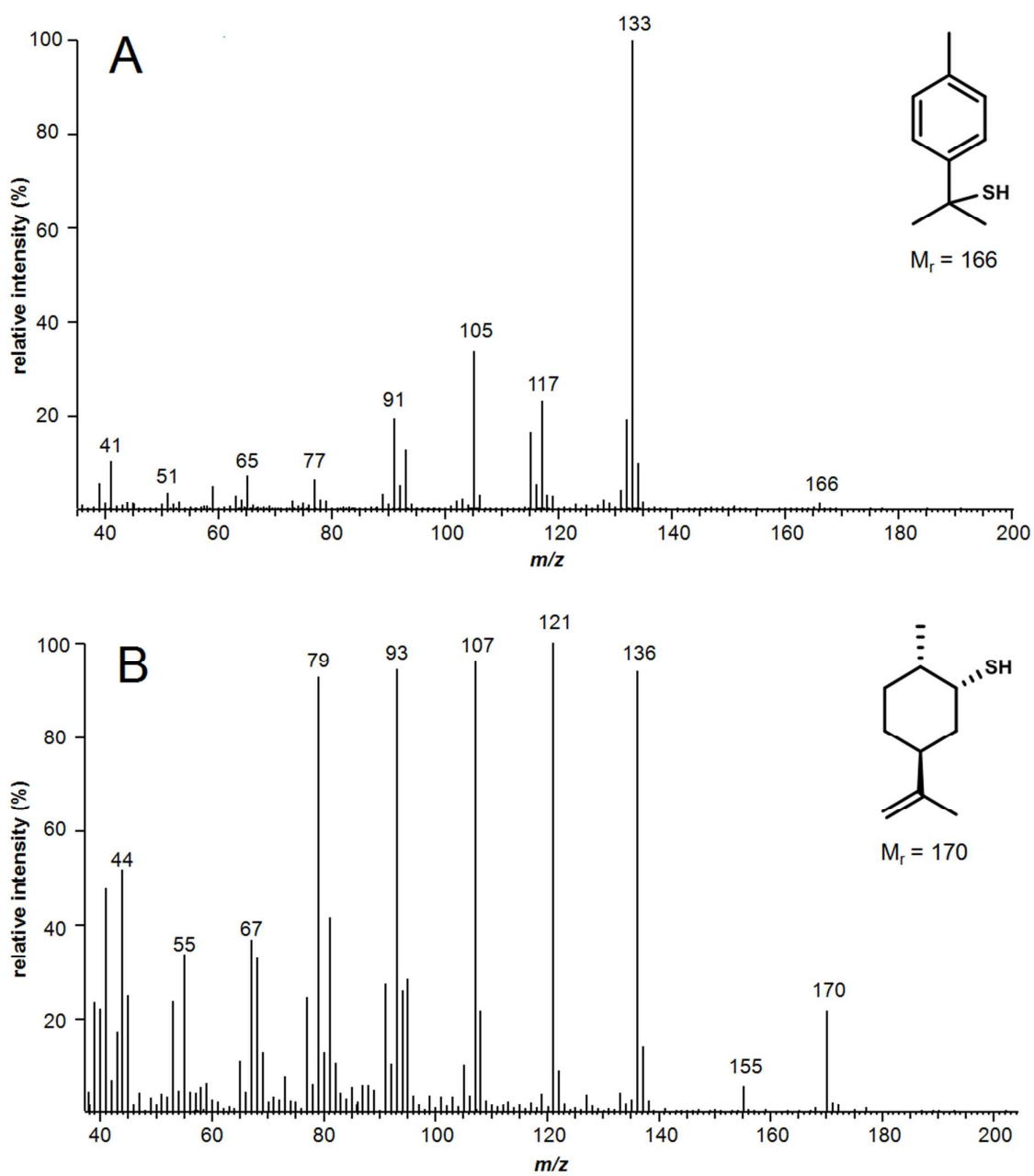


Figure 8

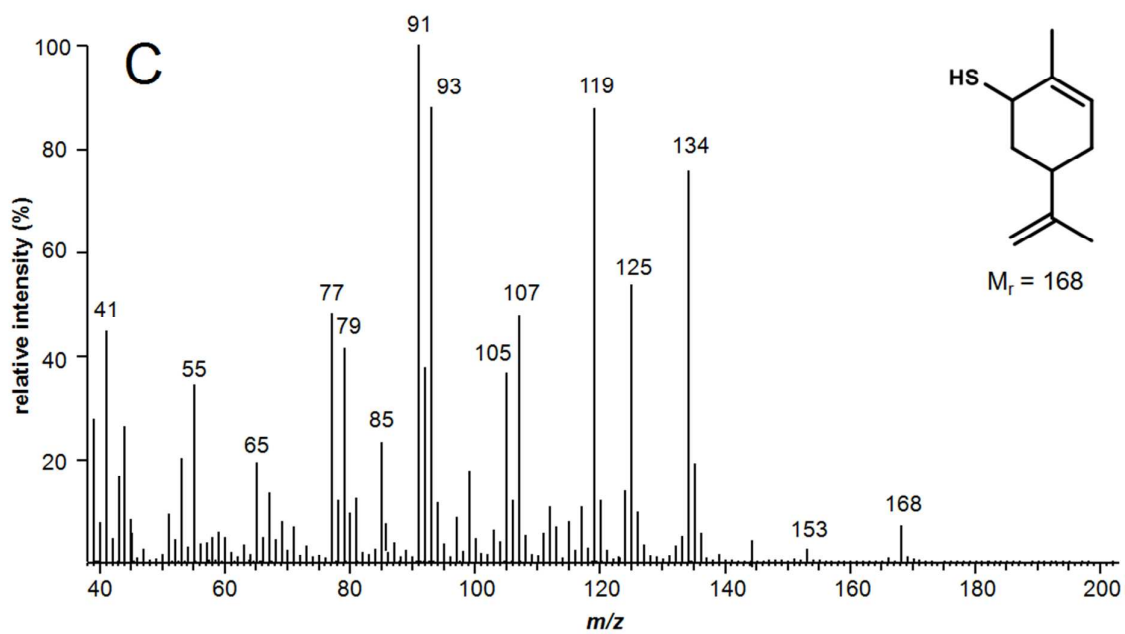


Figure 8

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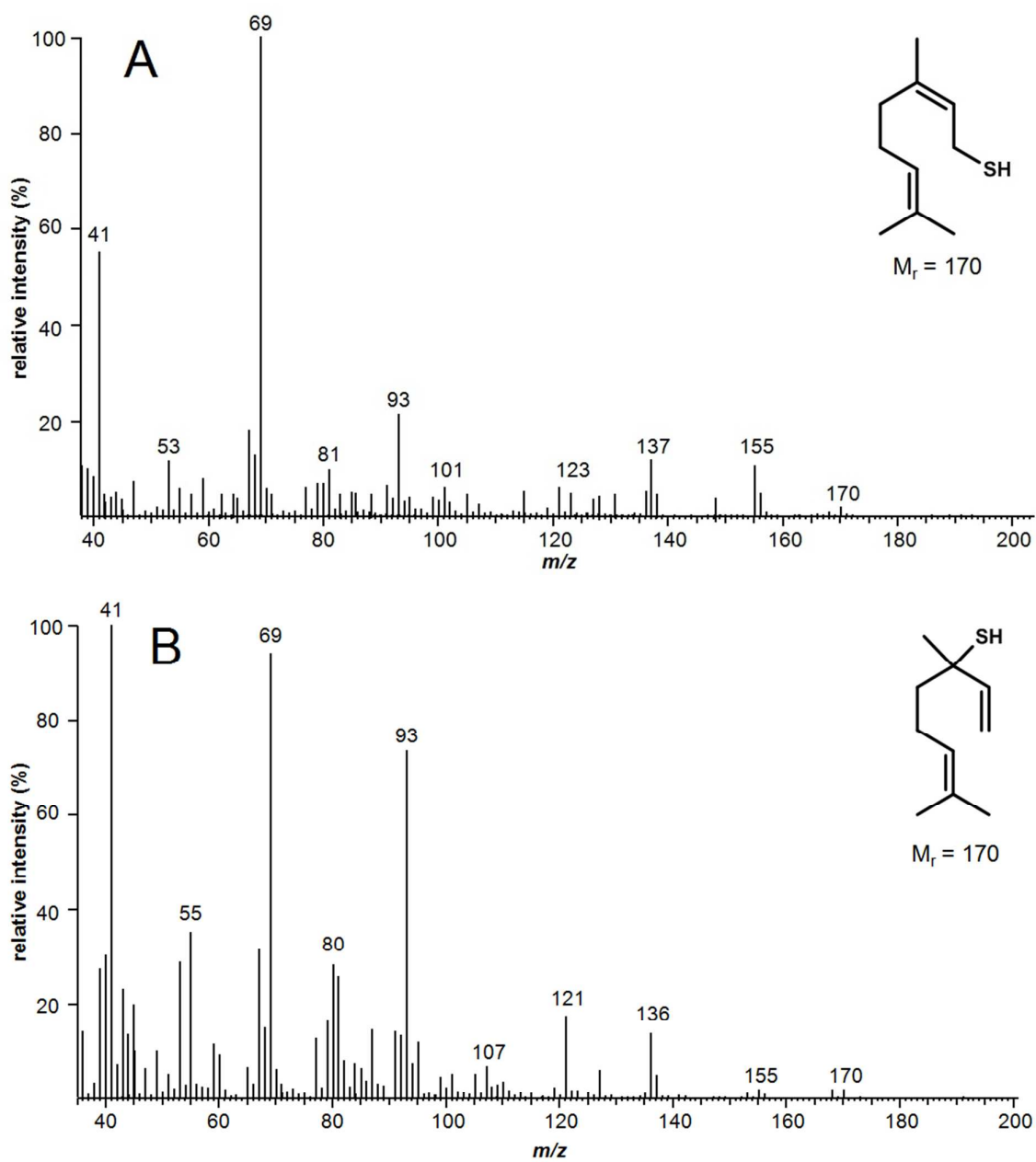
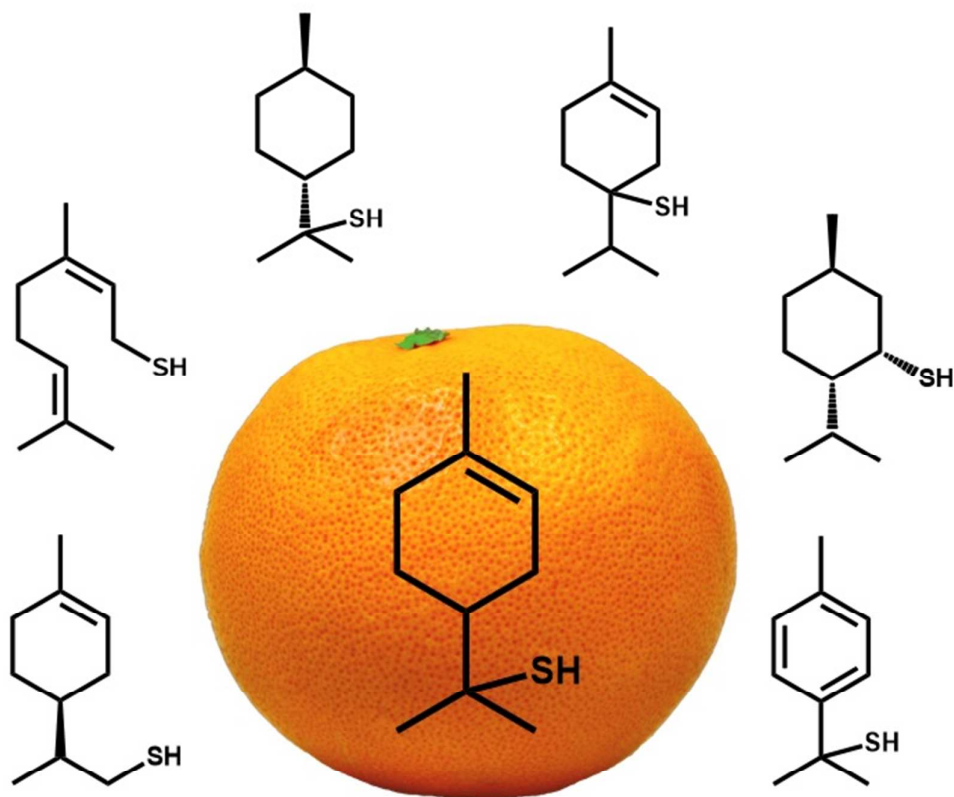


Figure 9



TOC graphic