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**EIMS Fragmentation and detection of autoxidation products
of 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-
pentadec-5-ene in Arctic sediments**

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Abstract:	2,6,10,14-Tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5(Z/E)-en-4-ols were identified after autoxidation of the HBI alkene 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5-ene. CID-MS/MS analyses and accurate mass measurement allowed EIMS fragmentations of their TMS derivatives to be elucidated. Some specific fragment ions and chromatographic retention times were also useful for further characterization. As an application of some of the described fragmentations, TMS derivatives of these metabolites were characterized and quantified in MRM mode in Arctic sediments.

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4 1 **EIMS Fragmentation and detection of autoxidation**
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8 **enyl)-pentadec-5-ene in Arctic sediments**
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28 Abstract

29 **RATIONALE:**

30 Some highly branched isoprenoid (HBI) alkenes are commonly used as proxies for
31 palaeoceanographic reconstructions. However, there is a need to identify compounds that are
32 sufficiently stable and abundant to be used as tracers of HBI oxidation in sediments. 2,6,10,14-
33 tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5(*Z/E*)-en-4-ols resulting from 2,6,10,14-
34 tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5-ene appear to be useful for a-this purpose.

36 **METHODS:**

37 Comparison of EIMS mass spectra and retention times with those of standards allowed formal
38 identification of autoxidation products of 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-
39 pentadec-5-ene. EIMS fragmentations of TMS ethers of the main oxidation products (2,6,10,14-
40 tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5(*Z/E*)-en-4-ols) were deduced by GC-EI-MS,
41 low energy CID-MS/MS and accurate mass measurements. These compounds were then
42 quantified in Arctic sediment samples in MS/MS MRM mode using transitions based on the
43 main fragmentation pathways elucidated.

45 **RESULTS:**

46 2,6,10,14-Tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5(*Z/E*)-en-4-ols were identified after
47 autoxidation of- the HBI alkene 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5-
48 ene. Low energy CID-MS/MS analyses and accurate mass measurement allowed the bEIMS
49 fragmentation pathways of their TMS derivatives to be elucidated. Some specific fragment ions
50 and chromatographic retention times were also useful for further characterization. As an
51 application of some of the described fragmentations, TMS derivatives of these metabolites were
52 characterized and quantified in MRM mode in Arctic sediments.

53

CONCLUSIONS:

Due to: (i) their production in high proportion during autoxidation of their parent HBI diene, (ii) their apparent stability in sediments, and (iii) their specific EIMS fragmentations, (*Z* and *E*) 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5-en-4-ol TMS derivatives appeared to be useful tracers of HBI autoxidation in sediments.

RUNNING TITLE: Mass fragmentations of autoxidation products of an HBI diene.**KEYWORDS:** Autoxidation; HBI diene; (*Z* and *E*) 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5-en-4-ol TMS derivatives; EIMS fragmentation; Sediments.

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1. INTRODUCTION

Highly branched isoprenoid alkenes (HBIs), which are biosynthesized by a relatively small number of diatom taxa belonging to the *Haslea*, *Navicula*, *Pleurosigma*, *Berkeleya*, *Rhizosolenia* and *Pseudosolenia* genera,¹⁻⁸ are nonetheless common constituents of marine and lacustrine sediments.⁹⁻¹¹ Due to their source specificity and relative stability within the geological record, some HBIs are now commonly used as proxies for palaeoceanographic reconstructions, especially in the Polar Regions.¹² Some mono- and di-unsaturated HBIs have been proposed as proxy measures of past seasonal sea ice in the Arctic and Antarctic,^{5,12} while some tri-unsaturated HBIs have been proposed as possible proxies for the open waters of the marginal ice zone in the Polar Regions.¹²

Application of such proxies requires careful consideration of alteration and preservation between their source and sedimentary environments. According to the number, the position and the ionization potential of their double bonds and the strength of their allylic C–H bonds, HBIs may be affected more or less intensively by photooxidation in the sunlit layer of oceans^{13,14} and by autoxidation in oxic environments such as the water column and surficial sediments,^{14,15} prior to being longer-term preserved in anoxic sediments.¹² Although some oxidation tracers of individual HBIs have been identified and characterised,¹⁵⁻¹⁷ they are often either too susceptible to secondary oxidation (e.g. for tri-unsaturated HBIs with *bis*-allylic double bonds¹⁵) or are produced in too low proportion (e.g. for mono- and di-unsaturated HBIs^{16,17}) to permit meaningful quantification. There is thus a real need to identify HBI oxidation products that are sufficiently stable and abundant to estimate the impact of oxidative degradation processes on the preservation of these lipid biomarkers in marine environments.

The present work focuses on the oxidation of 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5-ene (**1**, Scheme 1). This HBI diene has been reported in diatom cultures,^{7,18}

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3 89 and sediments from various regions.^{7,8,18-20} It may also result from isomerisation of 2,6,10,14-
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5 90 tetramethyl-7-(3-methylpent-4-enyl)-pentadec-6(17)-ene (IPSO₂₅) (**2**) (Scheme 1), a common
6
7 91 constituent of Arctic and Antarctic sea ice and surface sediments.^{5,12,21,22} Electron ionization
8
9 92 (EI) fragmentation pathways of trimethylsilyl (TMS) ethers of (*Z* and *E*) 2,6,10,14-tetramethyl-
10
11 93 7-(3-methylpent-4-enyl)-pentadec-5-en-4-ols (**3** and **4**) arising from autoxidation of HBI **1**
12
13
14
15 94 (Scheme 1) were elucidated by using GC-EI-MS, low-energy collision-induced dissociation
16
17 95 (CID)-MS/MS and accurate mass measurements. These compounds were then quantified in
18
19 96 Arctic sediment samples in MS/MS multiple reaction monitoring (MRM) mode using
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21 97 transitions based on the main fragmentation pathways elucidated and proposed as valuable
22
23 98 tracers of HBI autoxidation in sediments.
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100 2. EXPERIMENTAL

101 2.1 Chemicals

102 A small-scale sample of HBI **1** was obtained from a sediment extract described
103 previously.⁸ The sediment extract was further purified here using silver-ion chromatography
104 (Supelco, 250 mg, dichloromethane:acetone (3:1, v/v), 5 mL) to provide a few micrograms of
105 HBI **1** (>93%; GC-MS). HBI **2** (IPSO₂₅) (containing approximately 4% of HBI **1**) was
106 obtained from a culture of the marine diatom *Haslea ostrearia* as described previously.²¹

107 Oxidation of HBI **1** using RuCl₃ and *tert*-butyl hydroperoxide in cyclohexane at room
108 temperature for 16 h²³ and subsequent NaBH₄-reduction in ether-methanol (4:1, v/v) produced
109 (*Z* and *E*) 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5-en-4-ols (**3** and **4**) in low
110 yield. This method involving oxidation by the bulky *tert*-butyl hydroperoxyl radical avoided
111 oxidation of the sterically hindered allylic C-7.

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3 112 Treatment of HBI 1 with a stoichiometric amount of perchloroperbenzoic acid in dry
4
5 113 dichloromethane (4 h at 50°C) afforded 5,6-epoxy-2,6,10,14-tetramethyl-7-(3-methylpent-4-
6
7 114 enyl)-pentadecane (**5**).

8
9
10 115 The synthesis of the highly structurally related 2,6,10,14,18-pentamethylnonadec-5-en-
11
12 116 4-ol (**8**) employed as a standard required two steps: (i) oxidation of (*E*)-phytol (Sigma Aldrich,
13
14 117 St. Quentin Fallavier, France) with CrO₃/pyridine in dry dichloromethane,²⁴ and (ii)
15
16 118 condensation of the resulting (*E*)-phytenal with isobutyl magnesium bromide (Sigma Aldrich,
17
18 119 ~~St. Quentin Fallavier, France~~) in dry diethyl ether. This method strongly favoured 1,2- vs. 1,4-
19
20
21
22 120 addition.

25 121 2.2 Autoxidation of HBI 1

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27
28 122 Autoxidation experiments were performed under an atmosphere of air in 15-mL screw-
29
30 123 cap flasks containing HBI 1 (amount too low to be weighed) or a mixture of HBIs 1 and 2 (1
31
32 124 mg), *tert*-butyl hydroperoxide (300 ~~mL~~ mL of a 6.0 M solution in decane), di-*tert*-butyl nitroxide
33
34 125 (1.2 mg) and hexane (2 mL). After stirring, the flask was incubated in the dark at 65°C. Aliquots
35
36 126 (200 µL) were withdrawn from the reaction mixture after incubation for different times. Each
37
38 127 sub-sample was evaporated to dryness under a stream of nitrogen and analyzed by gas
39
40 128 chromatography–electron ionization mass spectrometry (GC–EI-MS) after NaBH₄ reduction
41
42
43
44 129 and silylation.

47 130 2.3 Reduction of oxidation products

48
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50 131 Hydroperoxides resulting from HBI oxidation were reduced to the corresponding alcohols
51
52 132 by reaction with excess NaBH₄ in diethyl ether:methanol (4:1, v/v) at room temperature (1 h).
53
54 133 After reduction, a saturated solution of NH₄Cl (10 mL) was added cautiously to remove any
55
56 134 unreacted reducing agent; the pH was adjusted to 1 with dilute HCl (2 M) and the mixture
57
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3 135 shaken and extracted with hexane:chloroform (5 mL, 4:1, v/v; ×3). The combined extracts were
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5 136 dried over anhydrous Na₂SO₄, filtered and evaporated to dryness under a stream of nitrogen.
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7

8 137 **2.4 Sampling and treatment of sediments**

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11 138 Our sampling location for sediment material corresponds to Barrow Strait (Station 4,
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14 139 74°16'12"N, 91°46'12"W, *ca.* 345 m water depth) in the Canadian Arctic. Box cores were
15
16 140 collected, sectioned on board, with sub-samples (1-cm resolution) then freeze-dried before
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18
19 141 storage (< 4°C) prior to analysis. The Redox boundary layer was identified previously at *ca.* 2
20
21 142 cm.¹⁶ Sediment sub-samples from sectioned box cores were placed in methanol (15 mL) and
22
23 143 the hydroperoxides were reduced to the corresponding alcohols with excess NaBH₄ (70 mg, 30
24
25 144 min at 20°C). Following the reduction step, water (15 mL) and KOH (1.7 g) were added and
26
27
28 145 the mixture saponified by refluxing (2 h). After cooling, the contents of the flask were acidified
29
30 146 (HCl, to pH 1) and extracted three times with dichloromethane (30 mL). The combined
31
32 147 dichloromethane extracts were dried over anhydrous Na₂SO₄, filtered and concentrated to give
33
34
35 148 the total lipid extract (TLE). Since the HBI oxidation product content was quite low relative to
36
37 149 other lipids, accurate quantification required further separation of the TLE using column
38
39 150 chromatography (silica; Kieselgel 60, 8 × 0.5 cm). The HBIs were obtained by elution with
40
41 151 hexane (10 mL) and their oxidation products by subsequent elution with dichloromethane (10
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44 152 mL).
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47 153 **2.5 Silylation**

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50 154 Dichloromethane eluates of sediments, reduced subsamples of autoxidation experiments
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52 155 (evaporated to dryness) and standard alcohol **8** were derivatized by dissolving them in 300 μL
53
54 156 pyridine/bis-(trimethylsilyl)trifluoroacetamide (BSTFA; Supelco; 2:1, v/v) and silylated (50°C,
55
56
57 157 1 h). After evaporation to dryness under a stream of N₂, the derivatized residue was dissolved
58
59 158 in ethyl acetate/BSTFA (to avoid desilylation) and analysed by mass spectrometric methods.
60

2.6 Gas chromatography/electron ionization tandem mass spectrometry

GC-/EI-MS and GC-/EI-MS/MS experiments were performed using an Agilent 7890A/7000A tandem quadrupole gas chromatograph system (Agilent Technologies, ~~Pare Technopolis~~ ~~ZA Courtaboeuf~~, Les Ulis, France). A cross-linked 5% phenylmethylpolysiloxane (Agilent; HP-5MS-Ultra Inert) (30 m × 0.25 mm, 0.25 μm film thickness) capillary column was employed. Analyses were performed with an injector operating in pulsed splitless mode set at 270°C and the oven temperature programmed from 70°C to 130°C at 20°C min⁻¹, then to 250°C at 5°C min⁻¹ and ~~then finally~~ to 300°C at 3°C min⁻¹. The pressure of the carrier gas (He) was maintained at 0.69 × 10⁵ Pa until the end of the temperature program and then programmed from 0.69 × 10⁵ Pa to 1.49 × 10⁵ Pa at 0.04 × 10⁵ Pa min⁻¹. The following mass spectrometric conditions were employed: electron energy, 70 eV; transfer line ~~temperature~~, 300°C; source temperature, 230°C; quadrupole 1 temperature, 150°C; quadrupole 2 temperature, 150°C; collision gas (N₂) flow ~~rate~~, 1.5 mL min⁻¹; quench gas (He) flow ~~rate~~, 2.25 mL min⁻¹; mass range, ~~m/z 50-700-Dalton~~; cycle time, 313 ms. Collision induced dissociation (CID) was optimized by using collision energies at 5, 10, 15 and 20 eV.

Due to the very low amounts of HBI **1** available, compounds **3** and **4** could not be produced in sufficient amounts to permit quantification, although comparison of their mass fragmentations and retention times with ~~those of~~ compounds detected in sediments allowed their unambiguous identification. Quantification of ~~the~~ TMS ethers of alcohols **3** and **4** was thus carried out with a standard of the highly structurally related 2,6,10,14,18-pentamethylnonadec-5-en-4-ol (**8**; TMS derivative) in multiple reaction monitoring (MRM) mode. A correction factor that took into account the proportion of the selected precursor ion (*m/z* 379 for compounds **3** and **4** and *m/z* 367 for compound **8**) in the EIMS ~~spectra~~ of each compound (Figs-~~ures~~ 1B and 1C) and that of the selected MRM transition in each CID-MS ~~spectrum~~ was employed.

184 2.7 Gas chromatography/electron ionization quadrupole time of flight mass spectrometry

185 Accurate mass measurements were carried out in full scan mode with an Agilent
186 7890B/7200 GC/QTOF System. ~~(Agilent Technologies, Parc Technopolis – ZA Courtaboeuf, Les Ulis, France).~~
187 A cross-linked 5% phenyl-methylpolysiloxane (Macherey-Nagel, Hoerd,
188 France; Optima-5MS Accent) (30 m × 0.25 mm, 0.25 μm film thickness) capillary column was
189 employed. Analyses were performed with an injector operating in pulsed splitless mode set at
190 270°C and the oven temperature programmed from 70°C to 130°C at 20°C min⁻¹ and then to
191 300°C at 5°C min⁻¹. The pressure of the carrier gas (He) was maintained at 0.69 × 10⁵ Pa until
192 the end of the temperature program. Instrument temperatures were 300°C ~~for~~for the transfer
193 line and 230°C for the ion source. Nitrogen (flow rate of 1.5 mL min⁻¹) was used as the collision
194 gas. Accurate mass spectra were recorded across the range *m/z* 50-700 at 4 GHz with the
195 collision gas valve opened. The QTOF-MS instrument provided a typical resolution ranging
196 from 8009 to 12252 from *m/z* 68.9955 to 501.9706. Perfluorotributylamine (PFTBA) was
197 utilized for daily MS calibration.

198

199 3. RESULTS AND DISCUSSION

200 3.1 Autoxidation of HBI 1

201 Comparison of retention times and EI mass spectra with those of synthesized standards
202 allowed identification of isomeric (*Z* and *E*) 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-
203 pentadec-5-en-4-ols (**3** and **4**) (Fig. ~~ure~~ure 1B) and 5,6-epoxy-2,6,10,14-tetramethyl-7-(3-
204 methylpent-4-enyl)-pentadecane (**5**) (Fig. ~~ure~~ure 1A) after incubation of HBI **1** in hexane in the
205 presence of *tert*-butyl hydroperoxide (radical enhancer) and di-*tert*-butyl nitroxide (radical
206 initiator)²⁵ at 65°C and subsequent NaBH₄-reduction and silylation. Allylic hydrogen
207 abstraction and addition of peroxy radical to the double bonds generally compete during the

208 autoxidation of alkenes.²⁶ Formation of alcohols **3** and **4** results from hydrogen abstraction at
209 the allylic C-4 of HBI **1**, and epoxide **5** following peroxy radical addition to the C5-C6 double
210 bond (Scheme 1). The lack of hydrogen abstraction at the allylic carbon 7 probably results likely
211 from steric hindrance during hydrogen abstraction by the bulky *tert*-butylperoxy radicals
212 employed during the incubation.¹⁷

213 Comparison of autoxidation rates of the two isomeric HBIs **1** and **2** shows that HBI **1** is
214 oxidized 1.4 times faster than IPSO₂₅ (**2**). While autoxidation of IPSO₂₅ (**2**) mainly afforded
215 1,2-epoxy-2-(4-methylpentyl)-3-(3-methylpent-4-enyl)-6,10-dimethylundecane (**7**) and, to a
216 lesser extent, 6-methylidene-2,10,14-trimethyl-7-(3-methylpent-4-enyl)-pentadecan-5-ol (**6**)
217 (ratio **6/7** = 0.1)¹⁷ (Scheme 1), allylic hydrogen abstraction appeared to be more favoured during
218 autoxidation of HBI **1** (ratio (**3+4**)/**5** = 1.2). This difference in reactivity of allylic C-4 of HBI
219 **1** and C-5 of IPSO₂₅ (**2**) towards hydrogen abstraction is in good agreement with EPR
220 spectroscopy results obtained previously by Camara et al.²⁷

221 Due to the well-known lability of epoxides in sediments¹⁷ and during their treatment,²⁸
222 the production of a higher proportion of allylic alcohols **3** and **4** during autoxidation of HBI **1**
223 strengthens the tracer potential of autoxidation products of this alkene.

225 **3.2 EIMS fragmentations of 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-** 226 **5(Z/E)-en-4-ol TMS ether derivatives (3 and 4)**

227 The TMS ethers of the *Z* and *E* isomers **3** and **4** exhibited the same EI mass spectra (Fig-
228 ure 1B), with weak peaks at *m/z* 436 and *m/z* 421 corresponding to the molecular ion (**a**⁺) and
229 [M – CH₃]⁺ (**b**⁺), respectively. Intense and interesting peaks were also observed at *m/z* 379, *m/z*
230 289, *m/z*-199, *m/z*-163, *m/z*-143 and *m/z*-109. α-Cleavage relative to the ionized ether group
231 affords fragment ion **c**⁺ at *m/z* 379, which may lose a neutral molecule of trimethylsilanol
232 (TMSOH) after 1,5-hydrogen shift from C-17 to the ionized ether group. Subsequent 1,4-

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3 233 cyclization yields ion **d**⁺ at *m/z* 289 (Scheme 2), which can then be cleaved to the fragment ion
4
5 234 **e**⁺ at *m/z* 163 following 1,5-hydrogen shift from C-10 to the charged cyclobutyl ring and
6
7
8 235 concerted ring extension (Scheme 2). Cleavage of ion **f**⁺ at *m/z* 379 (mesomer of ion **c**⁺)
9
10 236 involving a 1,3-hydrogen shift from C-8 to the carbocation may be at the origin of the formation
11
12 237 of the strongly stabilized ion **g**⁺ at *m/z* 143 (Scheme 2).

13
14 238 Ionization of TMS ethers of the *Z* and *E* isomers **3** and **4** can also take place at the 5-6
15
16 239 double bond affording ion **h**⁺ at *m/z* 436, which can be cleaved to the strongly stabilized ion **i**⁺
17
18 240 at *m/z* 199 after a 1,3-hydrogen shift from C-4 to the ionized tertiary C-6 and subsequent
19
20 241 cleavage of the C6-C7 bond (Scheme 2). Ion **i**⁺ can then either lose a neutral molecule of
21
22 242 TMSOH after a 1,3-hydrogen shift from C-17 and subsequent 1,4-cyclization to produce the
23
24 243 fragment ion **j**⁺ at *m/z* 109, or be converted to ion **g**⁺ at *m/z* 143 following a 1,3-hydrogen shift
25
26 244 from tertiary C-2 and cleavage of the C3-C4 bond (Scheme 2).

27
28
29
30 245 The proposed fragmentation pathways are supported further by the results of CID
31
32 246 analyses of precursor ions **a**⁺ and **h**⁺ at *m/z* 436, **c**⁺ and **f**⁺ at *m/z* 379, **d**⁺ at *m/z* 289 and **i**⁺ at
33
34 247 *m/z* 199 (Table 1). Moreover, the accurate masses of ions **a**⁺-**j**⁺ showed only minor deviations
35
36 248 (ranging from 0.7 to 5.7 ppm) from the calculated theoretical masses (Table 2), thus confirming
37
38 249 the elemental composition of the fragment ions in each case.

250

251 3.3 MRM quantification of compounds **3** and **4** in sediment samples

252 The mass spectral transitions employed for the quantification of oxidation products were
253 *m/z* 379 → 143 for TMS ethers of compounds **3** and **4**, and *m/z* 367 → 143 for the TMS ether
254 of the standard **8**. Transitions *m/z* 379 → 163 and *m/z* 379 → 289 were used as qualifiers (i.e.
255 to confirm qualitatively the presence of TMS ethers of compounds **3** and **4**). It may be noted
256 that transitions resulting from the cleavage of ion **i**⁺ at *m/z* 199 appeared to be insufficiently
257 specific for the analysis of sediment extracts and were thus discarded.

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3 258 The limit of quantification (150 pg) was determined according to a signal-to-noise ratio
4
5 259 greater than 3. The linear range was determined using values that met the standard analysis
6
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8 260 criteria of less than 15% deviation across the concentration range. Linear responses were
9
10 261 obtained over 2 to 3 orders of magnitude. Due to: (i) the relatively low amounts of sediments
11
12 262 available and (ii) the low concentrations of analytes, the reproducibility of our analyses could
13
14 263 not be determined. Despite the relatively weak concentration of HBI **1** in sediments from
15
16 264 Barrow Strait (Table 3), compounds **3** and **4** could be readily detected and quantified (Table 3,
17
18 265 Figure 2). It is interesting to note that the detection of these compounds, which eluted just after
19
20 266 phytol (chlorophyll phytyl side chain) TMS ether, is also possible by GC-QTOF (by extracting
21
22 267 the accurate mass of ion f^+) but not by GC-EI-MS (due to the complexity of the organic extracts
23
24 268 of sediments). The proportion of such allylic alcohols relative to the parent HBI (up to 26%)
25
26 269 (Table 3) appeared to be two orders of magnitude higher than that of the alcohol **6** relative to
27
28 270 the parent IPSO₂₅ (**2**) in the same sediments (up to 0.2%)¹⁷. The decrease of the ratio **3/4**
29
30 271 observed in sediments relative to the autoxidation experiment (Figure 2) was attributed to
31
32 272 allylic rearrangement of the corresponding hydroperoxides to 2,6,10,14-tetramethyl-7-(3-
33
34 273 methylpent-4-enyl)-pentadec-4(*E*)-en-6-hydroperoxide (**9**) (Scheme 1) inhibited by high
35
36 274 concentration of *tert*-butyl-hydroperoxide during the autoxidation experiment²⁵ but not in
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38 275 sediments. Indeed, it was previously observed that rearrangement of *E*-allylperoxyls was
39
40 276 reversible, but this was not the case for *Z*-allylperoxyls²⁹ (Scheme 1).
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49 278 4. CONCLUSIONS

50
51 279 The main autoxidation products of the HBI diene 2,6,10,14-tetramethyl-7-(3-
52
53 280 methylpent-4-enyl)-pentadec-5-ene (**1**) were identified as (*Z* and *E*) 2,6,10,14-tetramethyl-7-(3-
54
55 281 methylpent-4-enyl)-pentadec-5-en-4-ols (**3** and **4**) and 5,6-epoxy-2,6,10,14-tetramethyl-7-(3-
56
57 282 methylpent-4-enyl)-pentadecane (**5**). CID-MS/MS and accurate mass measurements allowed
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3 283 the EI mass fragmentations of TMS ethers of alcohols **3** and **4** to be elucidated. On the basis of
4
5 284 these fragmentations, some MRM transitions were selected and applied to lipid extracts of
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7
8 285 Arctic sediments. Although the reproducibility of analyses could not be determined, these
9
10 286 compounds appeared to be present in quite high proportions relative to the parent HBI (**1**) (up
11
12 287 to 26%). The apparent stability of compounds **3** and **4** in sediments, their production in high
13
14 288 proportion during autoxidation of HBI **1** and the potential isomerization of the widely
15
16 289 distributed IPSO₂₅ (**2**) to their parent HBI **1** under environmental conditions supports the use of
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19 290 these alcohols as tracers of HBI autoxidation in sediments.
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3 379 **FIGURE AND SCHEME CAPTIONS**

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8 381 **Figure 1.** EI mass spectra of 5,6-epoxy-2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-
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10 382 pentadecane (**5**) (A), 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-5(*E*)-en-4-ol
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12 383 TMS derivative (**4**) (B) and 2,6,10,14,18-pentamethylnonadec-5-en-4-ol TMS derivative (**8**)
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14 384 (C).

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19 386 **Figure 2.** MRM chromatograms (m/z 379 \rightarrow 143, m/z 379 \rightarrow 163 and m/z 379 \rightarrow 289) of
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21 387 silylated HBI **1** autoxidation products **3** and **4** (produced during autoxidation experiment) (A)
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23 388 and DCM fraction obtained from the 2-3 cm (B) and 10-11 cm (C) layer of the core sediment
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25 389 from Barrow Strait.

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31 392 **Scheme 1.** Autoxidation and interconverting of HBI dienes **1** and **2**.

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35 394 **Scheme 2.** Proposed fragmentation mechanisms of alcohols **3** and **4** TMS derivatives.

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Table 1. CID analyses of the different fragment ions.

Code	<i>m/z</i>	Collision energy (eV)	Product ions
i⁺	199	5	199(100), 181(8), 157(5), 143(41), 129(7), 109(19), 99(9), 87(6), 75(38), 73(36)
d⁺	289	5	289(100), 199(23), 171(24), 163(45), 149(33), 127(14), 121(26), 107(29), 97(13), 95(26), 83(19), 81(39)
c⁺ and f⁺	379	5	379(100), 289(17), 269(11), 163(49), 149(14), 143(40), 129(17), 121(11), 109(22), 107(18), 103(14), 95(25), 81(18), 69(15)
a⁺ and h⁺	436	7	436(100), 379(37), 295(4), 275(6), 253(45), 225(30), 199(75), 129(23), 69(5)

Table 2. High-accuracy mass spectral data for ions **a⁺-j⁺**

Code	Formula	<i>m/z</i> calculated	<i>m/z</i> observed	Δ (ppm)
j⁺	C ₈ H ₁₃	109.1012	109.1011	-0.9
g⁺	C ₇ H ₁₅ OSi	143.0887	143.0886	-0.7
e⁺	C ₁₂ H ₁₉	163.1481	163.1485	+2.4
i⁺	C ₁₁ H ₂₃ OSi	199.1513	199.1516	+1.5
d⁺	C ₂₁ H ₃₇	289.2890	289.2896	+2.1
c⁺ and f⁺	C ₂₄ H ₄₇ OSi	379.3391	379.3401	+2.6
b⁺	C ₂₇ H ₅₃ OSi	421.3890	421.3866	-5.7
a⁺ and h⁺	C ₂₈ H ₅₆ OSi	436.4095	436.4102	+1.6

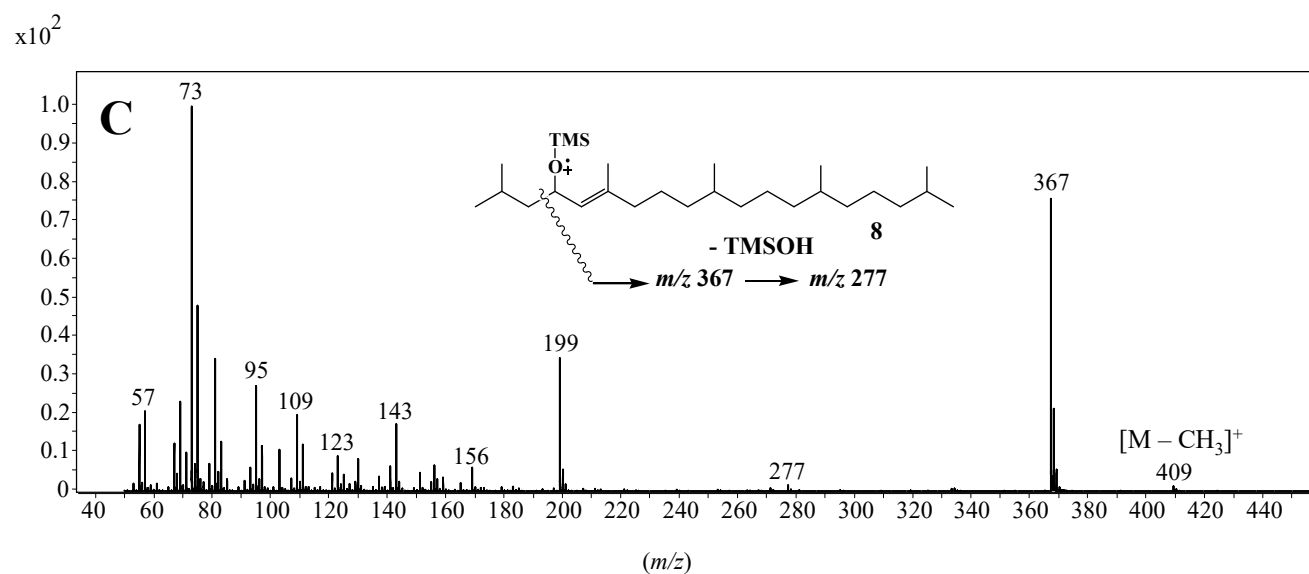
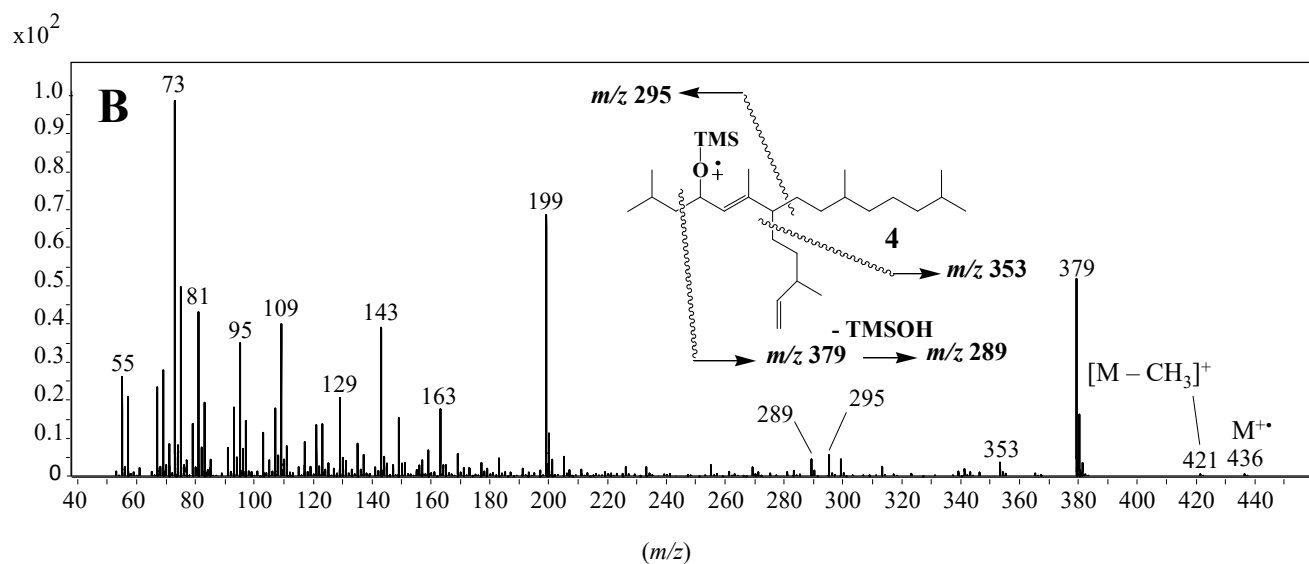
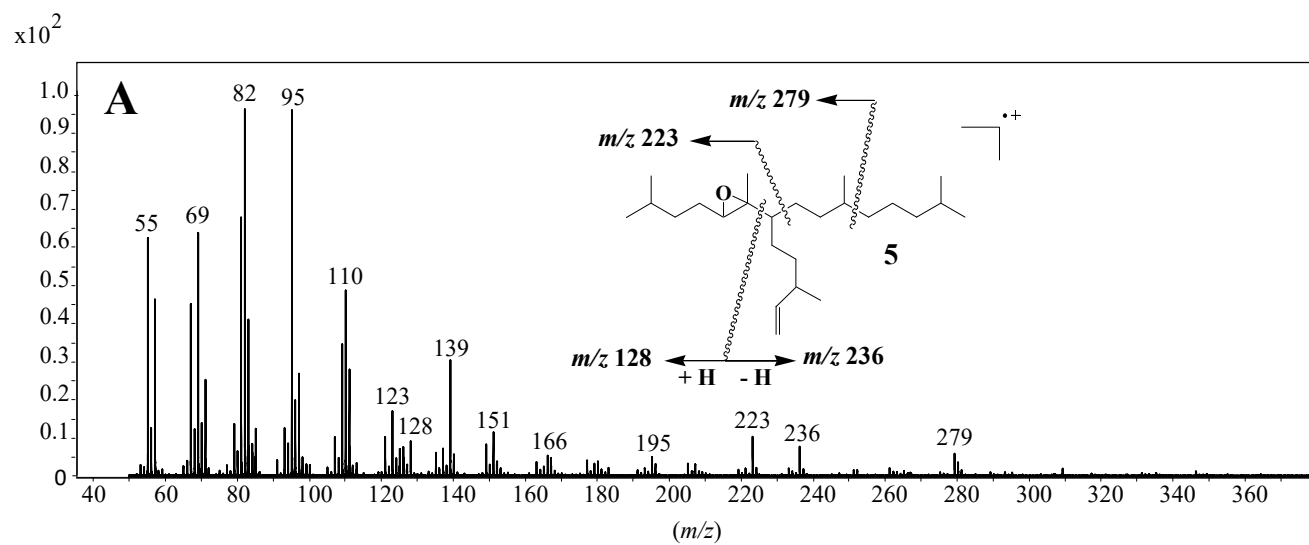
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Table 3. Concentration of HBI **1** and its autoxidation products **3** and **4** in sediments from the Arctic station 4 (Barrow Strait)

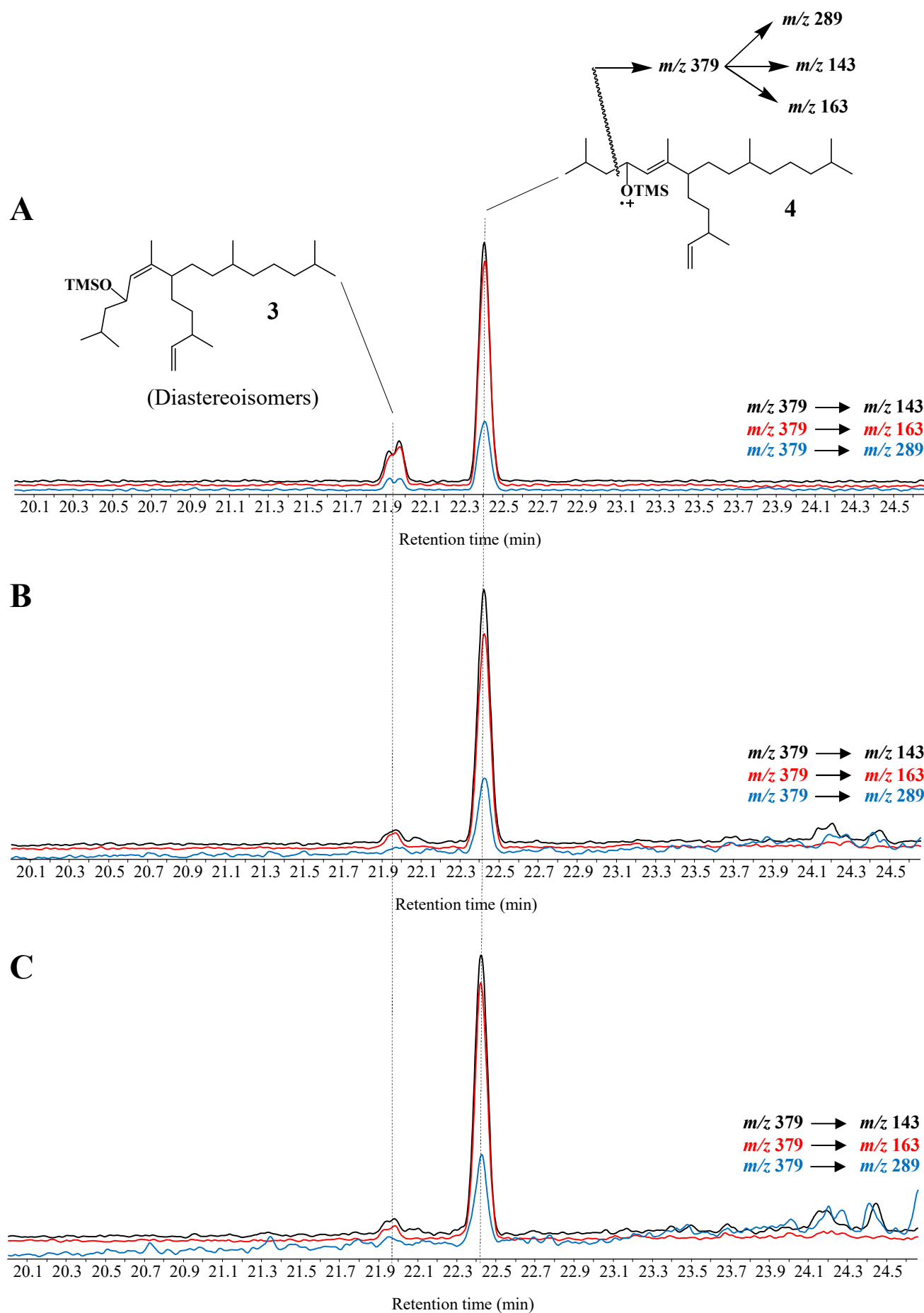
Depth (cm)	HBI 1 ($\mu\text{g g}^{-1}$)	Compound 3 (ng g^{-1})	Compound 4 (ng g^{-1})	Total (3 + 4) (ng g^{-1})	(3 + 4)/ 1 (%)
1-2	0.19	4.0	15.6	19.6	10
2-3	0.32	2.0	19.6	21.6	7
4-5	0.31	4.6	43.4	48.0	16
6-7	0.27	3.8	42.6	46.4	17
8-9	0.16	Tr*	9.6	9.6	6
10-11	0.22	16.2	41.2	57.4	26

* Traces (< LOD)

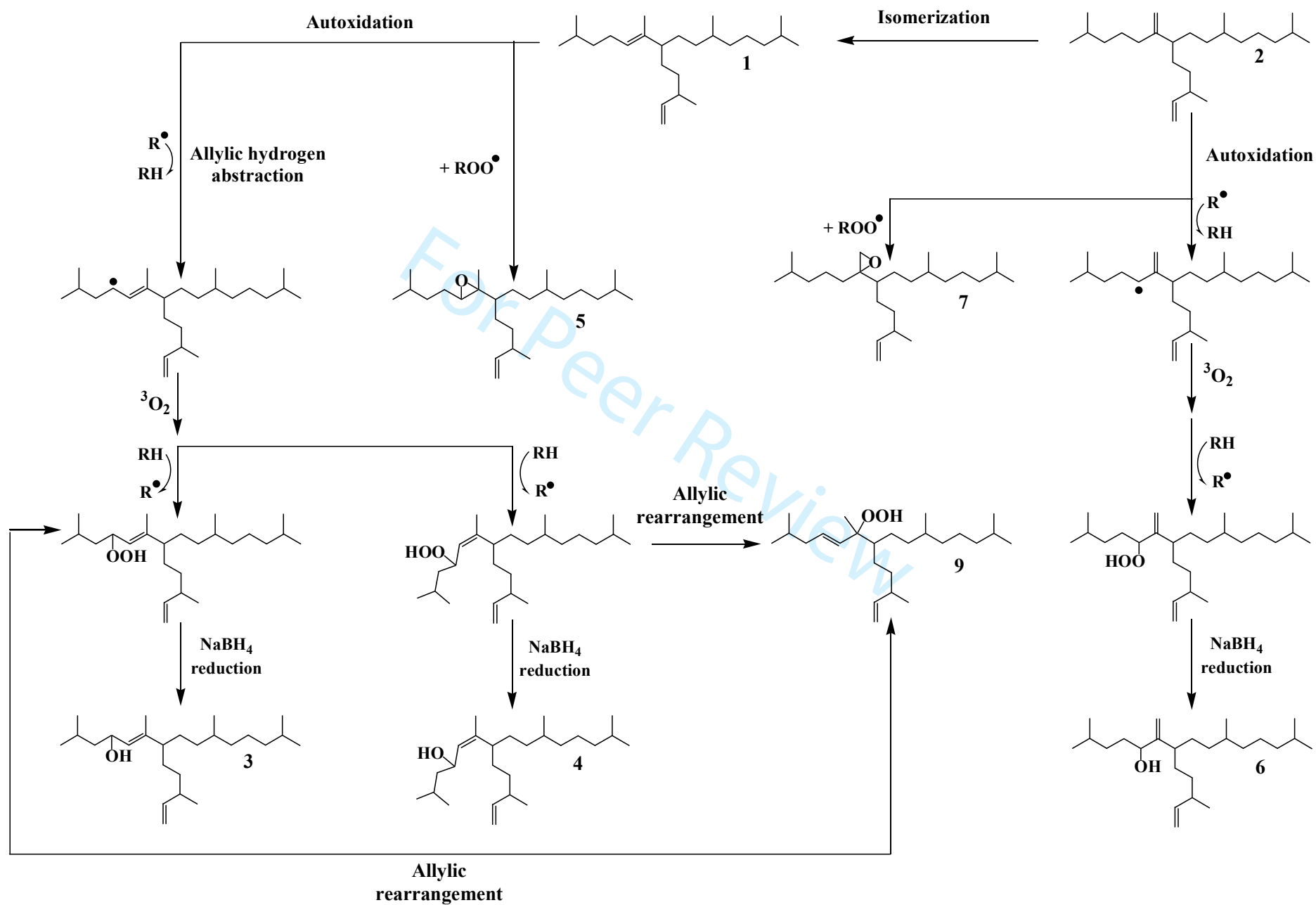
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