

1 2-Hydroxyterpenylic acid: An oxygenated marker
2 compound for α -pinene secondary organic aerosol in
3 ambient fine aerosol

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21 ABSTRACT

22 An oxygenated MW 188 compound is commonly observed in substantial abundance in
23 atmospheric aerosol samples and was proposed in previous studies as an α -pinene-related marker
24 compound which is associated with ageing processes. Owing to difficulties to produce this
25 compound in sufficient amounts in laboratory studies and the occurrence of isobaric isomers, a
26 complete assignment for individual MW 188 compounds could not be achieved in these studies.
27 Results from a comprehensive mass spectrometric analysis are presented here to corroborate the
28 proposed structure of the most abundant MW 188 compound as a 2-hydroxyterpenylic acid
29 diastereoisomer with *2R,3R* configuration. The application of collision-induced dissociation with
30 liquid chromatography/electrospray ionization – ion trap mass spectrometry in both negative and
31 positive ion modes, as well as chemical derivatization to methyl ester derivatives and analysis by
32 the latter technique and gas chromatography/electron ionization mass spectrometry, enabled a
33 comprehensive characterization of MW 188 isomers, including a detailed study of the
34 fragmentation behavior using both mass spectrometric techniques. Furthermore, a MW 188
35 positional isomer, 4-hydroxyterpenylic acid, was tentatively identified, which is also of
36 atmospheric relevance as it could be detected in ambient fine aerosol. Quantum chemical
37 calculations were performed to support the diastereoisomeric assignment of the 2-
38 hydroxyterpenylic acid isomers. Results from a time-resolved α -pinene photooxidation
39 experiment show that the 2-hydroxyterpenylic acid *2R,3R* diastereoisomer has a time profile
40 distinctly different from 3-methyl-1,2,3-butanetricarboxylic acid, a marker for oxygenated (aged)
41 secondary organic aerosol. This study presents a comprehensive chemical data set for a more
42 complete structural characterization of hydroxyterpenylic acids in ambient fine aerosol, which
43 sets the foundation to better understand the atmospheric fate of α -pinene in future studies.

44 INTRODUCTION

45 The atmospheric degradation of biogenic volatile organic compounds (BVOCs) leads to the
46 formation of multi-functionalized oxidation products. Knowledge about the corresponding
47 volatile precursor compounds and their chemical structure can help to identify sources and
48 understand the fate of BVOCs in the atmosphere. This information is also crucial to more
49 completely characterize ambient aerosols as specific oxidation products are related to certain
50 aerosol properties; for example, the hydrophilic or cloud-formation properties of ambient fine
51 aerosol can be associated with highly oxygenated secondary organic aerosol (SOA) (1). Despite
52 the relevance of highly oxygenated SOA marker compounds, only one such product, the C₈-
53 tricarboxylic acid 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA; C₈H₁₂O₆), has been
54 structurally identified in ambient aerosol so far (2, 3). MBTCA was shown to originate from
55 monoterpene oxidation and was proposed as a marker for aged α -pinene SOA. The structural
56 elucidation of MBTCA posed a considerable analytical challenge because its structure lacks the
57 α -pinene or the cyclobutane skeleton, complicating its attribution to a specific VOC precursor
58 and formulation of possible formation mechanisms. The targeted unknown MW 188 compound
59 (C₈H₁₂O₅) in the present study is another highly oxygenated compound, which is often observed
60 in ambient aerosol samples in high abundance and was recently proposed as an additional
61 suitable marker for aged biogenic SOA by Gómez-González et al. (4). In the latter study, this
62 compound was shown to be, together with MBTCA and *cis*-pinonic acid, one of the most
63 abundant monoterpene markers in PM_{2.5} filter samples collected from a forested site, Brasschaat,
64 Belgium, during a 2007 summer episode. Based on mass spectral data, indicating the presence of
65 a carboxylic and a hydroxyl group, and its relatively low retention time in reversed-phase liquid
66 chromatography (4-6), this unknown MW 188 compound represents a very hydrophilic

67 compound. Its formation was reported both from laboratory α -pinene ozonolysis (7, 8) and OH
68 radical-initiated oxidations (5, 8, 9), but was generally observed in substantially lower abundance
69 than other known α -pinene SOA markers in chamber-generated samples (10). Based on mass
70 spectral evidence, two structures have been proposed for the unknown MW 188 compound, i.e.,
71 a C₈-monohydroxycarboxylic acid structure (2-hydroxyterpenylic acid) (5), and a C₈-
72 hydroxydicarboxylic acid structure (hydroxynorpinic acid) (6). In addition, an unknown MW
73 188 compound has been tentatively assigned to norpinic peroxy acid, but no structural evidence
74 was provided (11). The MW 188 compound could not be detected by gas chromatography/mass
75 spectrometry (GC/MS) with prior trimethylsilylation in previous studies, showing a similar
76 behavior as other lactone-containing terpenoic acids, i.e., terebic and terpenylic acid (12). A
77 possible analogous structure, 2-hydroxyterpenylic acid, was proposed earlier by Claeys et al. (5),
78 mainly based on its non-covalent dimer formation properties similar to terpenylic acid, but no
79 further evidence for this structural proposal could be provided to date for various reasons,
80 including the difficulty to produce the compound from laboratory α -pinene oxidation, the
81 occurrence of several isobaric isomers, and the lack of an authentic reference compound. The
82 MW 188 compound was recently described to also form from campholenic aldehyde ozonolysis
83 (13) and based on the agreement of mass spectral data with those from ambient filter samples,
84 campholenic aldehyde ozonolysis (CAO) SOA was chosen in the present investigation to further
85 characterize the MW 188 compound. A comprehensive mass spectrometric analysis was
86 performed here, involving chemical derivatization to methyl ester derivatives and two
87 instrumental approaches: (i) liquid chromatography/electrospray ionization ion trap mass
88 spectrometry (LC/ESI-ITMS) employing both the (-) negative and (+) positive ion mode and (ii)
89 GC/MS, whereby collision-induced dissociation (CID) was applied using the capabilities of the

90 ion trap. In addition, the comparison to other lactone-containing terpenoic acid standard
91 compounds, i.e., terebic and terpenylic acid, enabled the study of specific fragmentation
92 behaviors and to support the proposed hydroxyterpenylic acid structure.
93 Furthermore, the time profile of 2-hydroxyterpenylic acid was compared with that of MBTCA,
94 an established marker for aged α -pinene SOA (2, 3), and other terpenoic acids, in a time-
95 resolved α -pinene photooxidation experiment.

96

97 MATERIAL AND METHODS

98 *Chamber aerosol*

99 Samples from CAO SOA were obtained as described by Kahnt et al. (13). Briefly, the
100 experiments were carried out in the 19 m³ TROPOS aerosol chamber at 50% relative humidity
101 (RH) and 21 °C. The initial campholenic aldehyde mixing ratio was 100 ppb and the reaction
102 was performed with about 60 ppb ozone in the presence of (NH₄)₂SO₄/H₂SO₄ seed particles. No
103 OH radical scavenger was added and the formed aerosol was sampled after about four hours of
104 reaction. The aerosol was collected on borosilicate glass fiber filter coated with fluorocarbon (47
105 mm diameter, Pallflex T60A20, Pall, NY, USA), which was stored at -22 °C before analysis.

106 Time-resolved α -pinene/NO_x/air irradiation experiments were performed in the EPA chamber in
107 the batch mode as described in detail in Jaoui et al. (14). The precursor was injected with a
108 mixing ratio of 5 ppmC in the 14.5 m³ smog chamber that was operated at 28% RH, with an
109 initial NO mixing ratio of 508 ppb. For the photooxidation study 4 light banks were used and the
110 experiment was carried out in the presence of 1 $\mu\text{g m}^{-3}$ (NH₄)₂SO₄ seed particles. This chamber
111 experiment replicates a similar experiment described previously by Claeys et al. (15). In total

112 eight filter samples were collected in this study (filters ER617 from GF1 until GF8); further
113 information is provided in Section S1 of the Supporting Information (SI).

114 A quarter of the CAO SOA filter was extracted three times using 10 mL of methanol under
115 ultrasonic agitation for 3 min. The combined extracts from the filter piece were concentrated to
116 about 1 mL at 35 °C using a rotary evaporator, were transferred afterwards to a 1 mL reaction
117 glass vial, and blown to dryness under a stream of nitrogen. The dried residue was reconstituted
118 in 250 µL methanol/water (50/50, v/v) and analyzed by LC/(–)ESI-ITMS.

119 The standards used in this study were terebic acid (purity > 98%; TCI Europe, Zwijndrecht,
120 Belgium) and terpenylic acid, which was synthesized at the Leibniz Institute of Tropospheric
121 Research (Leipzig, Germany). Both authentic standards were used to investigate the LC/MS
122 (non- and derivatized) and GC/MS (derivatized) behaviors of lactone-containing terpenoic acids.

123 *Atmospheric aerosol*

124 Pooled filter samples, which were collected during a summer field campaign from K-puszta,
125 Hungary, in 2006 were analyzed in the present study. The sampling station is situated in the
126 clearing of a mixed coniferous/deciduous forest on the Great Hungarian Plain (46°58'N, 19°35',
127 125 m above sea level) about 80 km southeast of Budapest. Details on the measurement
128 campaign can be found in Maenhaut et al. (16). The pooled filter samples were prepared as
129 described in Kahnt et al. (13).

130 *Sample derivatization procedure*

131 Diazomethane was freshly prepared using diazald (99%, Sigma-Aldrich) as a precursor
132 according to a standard procedure (17). An ethereal diazomethane solution was used to convert
133 carboxylic acids into corresponding methyl esters. Therefore, the dried filter extract from a
134 quarter part of the CAO SOA sample was reacted with 500 µL of ethereal diazomethane

135 solution. The derivatization was performed for 5 min, and, subsequently, the sample was dried
136 under a gentle stream of nitrogen, followed by reconstitution in 250 μL methanol/water (50/50,
137 v/v) for LC/ESI-ITMS analysis. The K-pushta sample was methylated using 400 μL of the
138 pooled filter extract, which was first dried, followed by the addition of 400 μL ethereal
139 diazomethane. The applied derivatization procedure was performed as described above, and,
140 afterwards, the dried sample was reconstituted in 400 μL methanol/water (50/50, v/v) for LC/MS
141 analysis. The same derivatization procedure was carried out for GC/MS analysis, except that the
142 final reconstitution solvent was 100% dichloromethane (Pesti-S grade, Biosolve, The
143 Netherlands).

144 *Chemical analysis*

145 The LC/ESI-ITMS analysis was carried out using a Surveyor Plus system (pump and
146 autosampler) (Thermo Scientific, San Jose, CA, USA) connected to an Atlantis T3 column (2.1 x
147 150 nm, 3 μm particle size, Waters, Milford, MA, USA), providing polar retention for the MW
148 188 compounds under investigation. The mobile phase consisted of (A) 50 mM ammonium
149 formate buffer with pH 3 and (B) methanol. A 65 min gradient was applied with the following
150 program: (B) was kept at 3% for 5 min, increased to 95% in 15 min and kept for 25 min,
151 followed by the reconditioning to 3% in 10 min and keeping (B) at 3% for 10 min. The samples
152 were injected using a volume of 10 μL and the flow rate was 0.2 mL min^{-1} . A linear ion trap
153 mass spectrometer (LXQ, Thermo Scientific, San Jose, CA, USA) was used as the mass analyzer
154 and both positive and negative ionization modes were employed. The mass spectrometer was
155 operated and optimized as described by Kahnt et al. (13).

156 The GC/MS analysis was performed using a TRACE GC2000 gas chromatograph and a Polaris
157 Q ion trap mass spectrometer fitted with an external electron ionization source (ThermoFinnigan,

158 San Jose, CA, USA). A deactivated silica pre-column (2 m x 0.25 mm i.d.) and a CP Sil 8CB
159 low-bleed capillary column (95% dimethyl-, 5% phenylpolysiloxane, 0.25 μm film thickness, 30
160 m x 0.25 mm i.d.) (Chrompack, Middelburg, The Netherlands) were employed for the
161 chromatographic separation using a sample injection volume of 1 μL in the splitless mode
162 (splitless time: 0.5 min) at 250 $^{\circ}\text{C}$. The carrier gas was helium with a flow rate of 1.2 mL min^{-1}
163 and the temperature of the transfer line was set to 280 $^{\circ}\text{C}$. The oven temperature program was as
164 follows: initial temperature of 100 $^{\circ}\text{C}$, which was maintained during 2 min, followed by a
165 gradient of 3 $^{\circ}\text{C min}^{-1}$ to 310 $^{\circ}\text{C}$, which was held constant for 2 min. The total GC/MS analysis
166 time was 43 min. The mass spectrometer was operated in the electron ionization (EI) mode at an
167 electron energy of 70 eV and an ion source temperature of 220 $^{\circ}\text{C}$. The full scan mode was
168 applied in the mass range of m/z 50–650. The targeted methylated compounds were characterized
169 on the basis of their EI mass spectra and MS^2 product ion spectra. For these fragmentation
170 studies the target mass isolation width was set to 2 m/z units.

171 *Quantum chemical calculations*

172 Calculations on 2-hydroxyterpenylic acid were performed using the Gaussian–09 suite of
173 programs (18) applying density functional theory (DFT) with the B3LYP functional (19) and the
174 6-311++G** basis set, as it is implemented in Gaussian–09. Geometry optimizations were
175 performed for the isolated molecules in the gas phase as well as “in solution” in methanol and
176 water applying the Polarized Continuum Model (PCM). Dimerization energies for (2*R*,3*R*) and
177 (2*S*,3*R*) 2-hydroxyterpenylic acid were corrected for the Basis Set Superposition Error (BSSE)
178 using the counterpoise method implemented in Gaussian09.

179

180 RESULTS AND DISCUSSION

181 **Characterization of MW 188 compounds using LC/ESI-ITMS analysis**

182 An overview of the studied compounds is given in Table 1, showing the structures of the
183 standard compounds terebic and terpenylic acid, and those of the proposed 2-hydroxyterpenylic
184 acid diastereoisomers with the m/z values of their deprotonated and protonated molecules as well
185 as of the protonated methyl ester derivatives. A summary of known mechanistic pathways
186 leading to 2-hydroxyterpenylic acid, involving either α -pinene ozonolysis or OH reactions, is
187 presented in Figure S2 of the SI.

188 [Table 1]

189 Figure 1 presents selected LC/MS data, extracted ion chromatograms (EICs) for m/z 187
190 corresponding to the deprotonated molecule of the targeted analytes eluting at 16.4 and 17.2 min
191 and MS data (m/z 187 MS^2 and m/z 187 \rightarrow m/z 125 MS^3 product ion spectra) present in CAO
192 SOA and ambient fine aerosol from K-puszta. Selected LC/MS data obtained for an α -pinene
193 NO_x photooxidation experiment are provided in Figure S3 of the SI. The targeted analytes at
194 16.4 and 17.2 min are assigned to 2-hydroxyterpenylic acid $2R,3R$ and $2S,3R$ diastereoisomers as
195 will be discussed in detail in this and the following two sections. In addition, it should be noted
196 that CAO (Fig. 1) and α -pinene (Fig. S3) SOA samples reveal intense m/z 187 peaks eluting
197 between 18 and 20 min and at 24.2 min; these m/z 187 compounds correspond to *mono*-
198 aldehydic forms of MBTCA [SI of (5)] and azelaic acid (6), are thus not related to 2-
199 hydroxyterpenylic acid and will therefore not be discussed here. It is worth noting that CAO
200 SOA clearly shows two MW 188 compounds in a ratio of about 1:3, of which the second-eluting
201 isomer (17.2 min) is also present at relative small abundance in the ambient sample. The product
202 ion spectra from the (-)ESI- MS^n analysis for the compound eluting at 16.4 min agreed well with

203 reported spectra in the literature (5, 6, 10, 13). This MW 188 compound was proposed earlier as
204 2-hydroxyterpenylic acid (5), an α -pinene-related marker compound originating from OH-
205 radical initiated processes; however, no diastereoisomeric assignment was made in this study.
206 The m/z 187 MS² product ion spectrum [Fig. 1(C, D)] is dominated by m/z 125, which
207 corresponds to the combined loss of a molecule water and CO₂ (62 *u*) and is in agreement with a
208 hydroxycarboxylic acid structure. Further fragmentation of m/z 125 leads to ions at m/z 107, 97
209 and 81 [Fig. 1(E, F)], which can also be explained with the proposed structure, as outlined in
210 Figure S4 of the SI. It can be noted that the MS data obtained for the MW 188 compound eluting
211 at 17.2 min [Fig. 1(G-I)] are very similar to those of the first-eluting isomer [Fig. 1(C-F)] and
212 mainly differ by the relative abundances of their product ions, which is consistent with
213 diastereoisomeric forms of 2-hydroxyterpenylic acid.

214 In order to obtain additional structural information, the targeted MW 188 compounds were also
215 analyzed with LC/ESI-ITMS in the positive ion mode and the MS data were compared with
216 those of available standard compounds, i.e., terebic and terpenylic acid. Selected MS data and
217 interpretation are provided in Figure S5 of the SI. The m/z 187 MS² data obtained for MW 188
218 compounds show the loss of two molecules of water, one molecule originating in the lactone ring
219 and a second one owing to loss of a molecule of water from the side chain containing a hydroxyl
220 group, which is in agreement with the proposed 2-hydroxyterpenylic acid structure.

221 [Figure 1]

222

223 **Characterization of methylated MW 188 compounds using LC/(+)ESI-ITMS**

224 In order to support the presence of a lactone structure in the targeted MW 188 compounds, a
225 derivatization experiment with diazomethane, a soft methylation reagent, was performed. This

226 experiment demonstrated that the targeted molecules only contain one acidic hydroxyl group as
227 they were converted to *mono*-methyl ester derivatives with a MW of 202, consistent with the
228 proposed 2-hydroxyterpenylic acid structure. Prior to derivatizing the targeted MW 188
229 compounds, the methylation reaction with diazomethane was tested with terebic and terpenylic
230 acid and it was confirmed that this procedure results in their *mono*-methyl derivatives and thus
231 does not lead to an opening of the lactone ring. Selected MS data and their interpretation are
232 provided in the SI (Figs. S6-S7).

233 Analysis of methylated extracts of CAO SOA and the ambient sample reveals signals
234 corresponding to the targeted methylated MW 188 compounds at m/z 203 and 220,
235 corresponding to the protonated forms, and the ammonium adducts, respectively (Fig. 2). The
236 latter ions were selected for further fragmentation experiments as they were more abundant than
237 the m/z 203 ions. The compounds eluting at 18.6 and 19.1 min were present in both the CAO
238 SOA and the ambient sample. The compound eluting at 19.1 min was attributed to the methyl
239 ester of the 2-hydroxyterpenylic acid 2*R*,3*R* diastereoisomer which is abundant in the ambient
240 sample, whereas that eluting at 20.5 min was assigned to the 2-hydroxyterpenylic acid 2*S*,3*R*
241 diastereoisomer which had a high signal intensity in the CAO SOA sample. The m/z 220 MS²
242 product ion spectrum [Fig. S8(E) and (G)] is dominated by m/z 203, owing to the loss of
243 ammonia and corresponding to the protonated molecule. Fragmentation of m/z 203 leads to m/z
244 185, 167, 135 and 153 [Fig. S8(H), (J), (K), (M)], which can all be explained with the proposed
245 structure, as outlined in Figure S9. It is worth noting that the MS data obtained for the
246 methylated compound eluting at 20.5 min [Fig. S8(F), (I), (L), (O)] are very similar to those
247 obtained for the earlier-eluting compound at 19.1 min, which is again consistent with
248 diastereoisomeric forms of 2-hydroxyterpenylic acid methyl ester.

249 [Figure 2]

250 The MW 202 compounds eluting at 18.6 and 19.6 min are tentatively assigned to methylated
251 4-hydroxyterpenylic acid diastereoisomers, where 4-hydroxyterpenylic acid is a positional
252 isomer of 2-hydroxyterpenylic acid. Selected MS data and interpretation are provided in Figures
253 S10 and S11 of the SI. In regard of the identification of 4-hydroxyterpenylic acid, it is worth
254 mentioning that the non-methylated form was not observed in the current study from the CAO
255 SOA sample but that a compound possibly corresponding to it has been detected in ambient fine
256 aerosol in previous studies (5, 6). Additional information is provided in Section S4 of the SI. As
257 4-hydroxyterpenylic acid could be observed in the ambient sample, it is also of atmospheric
258 relevance.

259

260 **Characterization of methylated MW 188 compounds using GC/EI-MS analysis**

261 It has been reported in a previous study that terebic and terpenylic acid could not be detected in
262 ambient samples upon GC/EI-MS with prior trimethylsilylation (12). Some possible reasons for
263 the failure to detect these lactone-containing compounds include that they are too volatile and are
264 lost in the sample preparation step, which involves concentration of the extract using rotary
265 evaporation and evaporation under a nitrogen stream, as well as their thermal instability upon
266 injection into the GC/MS instrument. Therefore, it was evaluated in the present study whether
267 methylated terebic and terpenylic acid trimethylsilyl esters, as well as methylated MW 188
268 compounds, which are expected to be slightly more polar than the first mentioned standard
269 compounds, could be detected from the methylated extracts of CAO SOA and the ambient
270 sample. Selected MS data and interpretation of the methylated terebic acid and terpenylic acid
271 standards are provided in the SI (Figs. S12, S13, and S14).

272 As shown in Figure 3, the GC/EI-MS analysis revealed two peaks for methylated
273 2-hydroxyterpenylic acid diastereoisomers in the CAO SOA sample. It is interesting to note that
274 only one of them matched with a peak from the K-puszta sample, i.e., the peak eluting at 21.1
275 min, which was detected only with low signal intensity in the ambient sample. This supports an
276 earlier proposal that lactone-containing compounds might have escaped detection upon GC/MS
277 with prior derivatization (12). The mass spectral data and possible EI fragmentation routes for
278 2-hydroxyterpenylic acid methyl ester are provided in Figures S15 and S16 of the SI. As
279 expected for an alcoholic compound, the molecular ion at m/z 202 was absent from the EI mass
280 spectrum; however, the ion at m/z 201, formed by the loss of a hydrogen radical through an α -
281 cleavage relative to the ionized hydroxyl function, is typical for alcohols. Other characteristic
282 fragment ions include m/z 169, corresponding to the loss of a molecule of water and a methyl
283 radical, and m/z 141, owing to an additional loss of CO. Both ions were selected for MS²
284 experiments and the proposed structure of 2-hydroxyterpenylic acid methyl ester could be further
285 supported (Fig. S16). It is worth noting that for the two MW 202 compounds present in CAO
286 SOA similar product ions were observed in MS² experiments [Fig S15(F-K)] with only slight
287 differences in relative abundance, consistent with diastereoisomers. Instead of m/z 127 in the m/z
288 201 isomer eluting at 21.1 min, a product ion at m/z 129 is observed for the isomer at 20.6 min
289 [Fig. S15(I)], likely owing to the addition of two hydrogen radicals to the double bond, a feature
290 that has been previously reported for compounds containing a double bond upon MS² ion trap
291 experiments (20).

292 [Figure 3]

293

294

295 **Assignment of 2-hydroxyterpenylic acid diastereoisomers**

296 Considering that 2-hydroxyterpenylic acid is formed from the oxidation of (-)- α -pinene which has
297 a $1S,5S$ configuration for its two chiral C-atoms, the stereochemistry in the resulting C-3 position
298 of the oxidation product is fixed. As shown in Table 1, also for terpenylic acid the chiral C-3
299 atom has a S configuration. However, the introduction of an OH-group at the neighboring
300 position in 2-hydroxyterpenylic acid, changes the order of priorities according to the Cahn-
301 Ingold-Prelog nomenclature (21), resulting in a $3R$ configuration for 2-hydroxyterpenylic acid.
302 The stereochemistry for the other chiral C-2 atom can be either S or R . Based on theoretical
303 considerations the major diastereoisomer in ambient fine aerosol [Fig. 1(B)] was assigned to the
304 $2R,3R$ diastereoisomer as it is more polar in comparison to the $(2S,3R)$ 2-hydroxyterpenylic acid.
305 Differences in physical and chemical properties are expected for diastereoisomers containing a
306 hydroxyl group since the spacial orientation of the OH-group can lead to a different exposition of
307 the polar group. Derived dipole moments for the R,R -form were 5.5, 7.2 and 7.3 Debye (D) in
308 the gas phase, methanol and water, respectively. In comparison to the S,R -form, which had
309 dipole moments of 4.2, 5.1 and 5.1 D in the gas phase, methanol and water, respectively, a much
310 higher polarity was hence observed for the $(2R,3R)$ 2-hydroxyterpenylic acid, explaining its
311 earlier retention time in reversed-phase chromatography [Fig. 1(A, B)]. Energy differences
312 between the diastereoisomers were negligibly small, being 0.01 and 0.02 kcal mol⁻¹ in methanol
313 and water, respectively, favoring slightly the R,R -form.

314 It has been previously observed that the major 2-hydroxyterpenylic acid diastereoisomer shows
315 non-covalent dimer formation upon (-)ESI-MS detection (5), whereas this behavior was not
316 observed for the later-eluting compound. In this regard also quantum chemical calculations were
317 performed to derive dimerization energies for the two diastereoisomers, and energies for the

318 homodimeric species (i.e., MW 376) were calculated. For the neutral case a value of -16.6 kcal
319 mol^{-1} for the $2R,3R$ and -16.5 kcal mol^{-1} for the $2S,3R$ enantiomer were obtained pointing to
320 similar dimerization probabilities for the two 2-hydroxyterpenylic acid diastereoisomers. Based
321 on the calculated dimerization energies, the formation of dimers is favored over the presence as
322 monomeric species. The values are also comparable with reported dimerization energies for the
323 terpenylic acid homodimer, i.e., -17 kcal mol^{-1} (5), implying similar importance of 2-
324 hydroxyterpenylic acid in new particle formation.

325 However, the observation that only for the ($2R,3R$) 2-hydroxyterpenylic acid a homodimer could
326 be detected after LC separation upon (-)ESI-MS detection, and not for the $2S,3R$ -form, might be
327 misleading. Owing to the much lower signal intensity of the ($2S,3R$) enantiomer, the dimeric
328 cluster anion $[\text{M-H}]^-$ m/z 375 might be not detectable under these conditions.

329

330 **Temporal evolution of the major 2-hydroxyterpenylic acid $2R,3R$ diastereoisomer**

331 The temporal evolution of the targeted MW 188 compound, which elutes at 16.4 min and is
332 attributed to the 2-hydroxyterpenylic acid $2R,3R$ diastereoisomer (Table 1), and of other known
333 oxidation products was examined in an α -pinene photooxidation experiment and is summarized
334 in Figure S1 of the SI, together with the SOA mass formation as a function of irradiation time. It
335 can be seen that the concentrations of most of the studied oxidation products were highest in the
336 sample collected at approximately 5 hours of irradiation. The most abundant compound was
337 diaterpenylic acid acetate (m/z 231), followed by terpenylic acid (m/z 171), *cis*-pinic acid (m/z
338 185), *cis*-pinonic acid (m/z 183), MBTCA (m/z 203), terebic acid (m/z 157) and the targeted MW
339 188 compound at the maximum. A further significant formation was only observed for MBTCA,
340 a known ageing compound (2, 3), whereas for terebic acid and the MW 188 compound only a

341 marginal increase was detected until the chamber experiment was stopped after 7 hours. All the
342 other oxidation products decreased after 5 hours of irradiation, although an on-going SOA mass
343 formation was observed, pointing to particle phase reactions probably also from yet non-
344 identified compounds that lead to additional aerosol growth. Although the curve shape in SOA
345 mass formation was somewhat different in comparison to a similarly designed α -pinene
346 photooxidation experiment in a previous study (15), comparable maximum SOA mass
347 concentrations were obtained in this study.

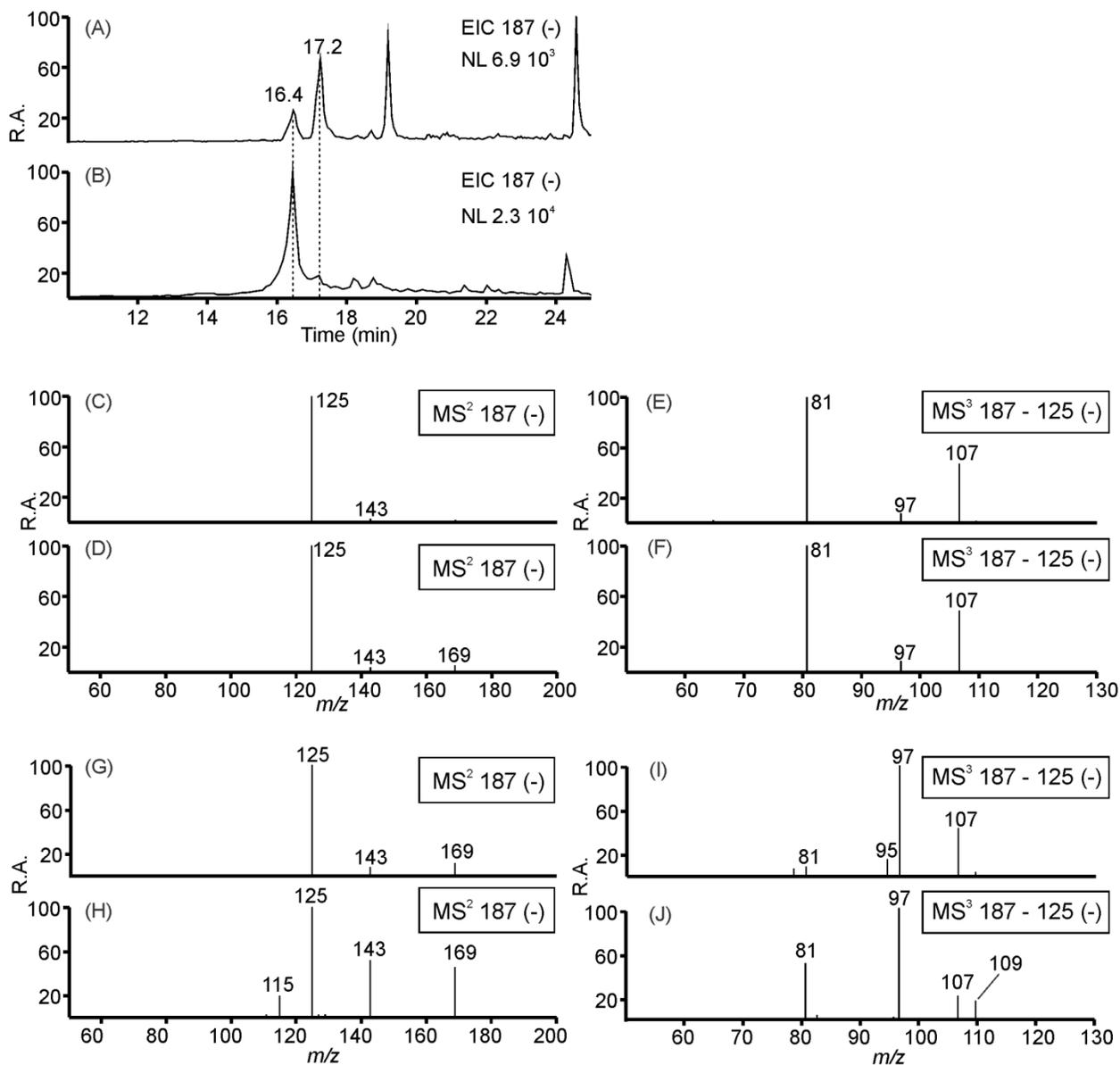
348 The product evolution shows that the 2-hydroxyterpenylic acid 2*R*,3*R* diastereoisomer has a time
349 profile distinctly different from MBTCA, consistent with different formation pathways.
350 Compared to terpenylic acid, the formation of 2-hydroxyterpenylic acid requires one additional
351 oxidation step (Fig. S2); hence, it can be regarded as a higher-generation product of the α -pinene
352 oxidation cascade. As shown in the current study, it has been detected in rural fine aerosol from
353 K-pusztta, Hungary, during a warm 2006 summer episode characterized by high solar irradiation.
354 In addition, it is worth mentioning that the 2-hydroxyterpenylic acid 2*R*,3*R* diastereoisomer has
355 been detected at concentrations that are comparable with those of MBTCA in forest fine aerosol
356 from Brasschaat, Belgium, during a warm 2007 summer episode (4). Furthermore, it has been
357 detected in tropical aerosol from the Amazon and Borneo forests, where solar radiation is at its
358 maximum (22, 23).

359

360 ATMOSPHERIC IMPLICATIONS

361 In the present study, we have characterized in detail an α -pinene oxidation product with a MW
362 of 188 that is abundantly present in ambient fine aerosol as the 2-hydroxyterpenylic acid 2*R*,3*R*
363 diastereoisomer. Other less abundant isomers were assigned to the 2-hydroxyterpenylic acid

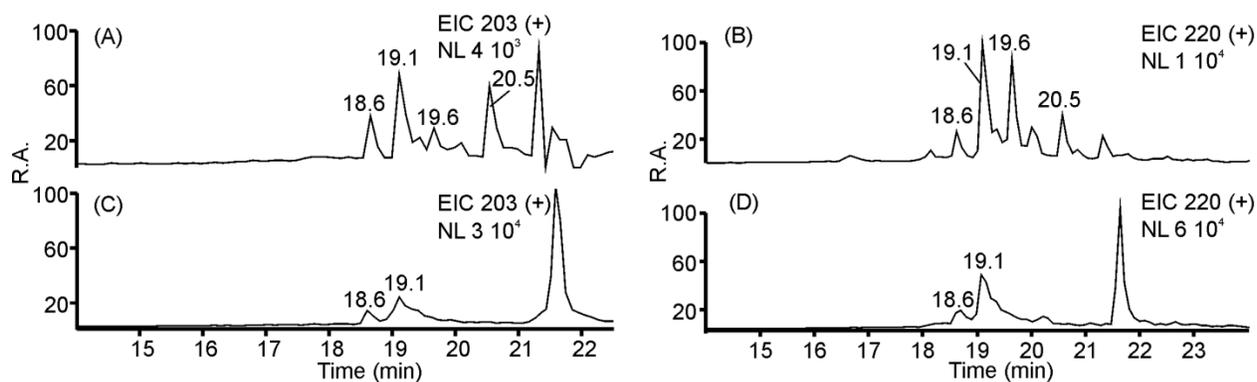
364 2*S*,3*R* diastereoisomer and 4-hydroxyterpenylic acid diastereoisomers. The time-resolved α -
365 pinene photooxidation experiment shows that the 2-hydroxyterpenylic acid 2*R*,3*R*
366 diastereoisomer has a different time profile than MBTCA, consistent with different formation
367 pathways. Furthermore, as the MW 188 compound represented only a minor oxidation product in
368 the performed chamber experiment, it is clear that crucial ambient conditions could not be met.
369 Additional research is therefore warranted to design α -pinene oxidation experiments which
370 better simulate ambient conditions. Another interesting and puzzling feature that merits further
371 exploration is that there seems to be a stereochemical control in the formation of the 2-
372 hydroxyterpenylic acid 2*R*,3*R* diastereoisomer, which shows a relative abundance that is about 5-
373 fold higher than the other diastereoisomeric 2*S*,3*R* form in ambient filter samples.
374 Terpenylic acid has been suggested to play a role in the early stages of particle formation in
375 laboratory α -pinene oxidation experiments (5) and shown to be important in small biogenic
376 particles (10-20 nm) by direct thermal desorption chemical ionization MS (24). It has also been
377 demonstrated to be incorporated into a high MW compound, i.e., a MW 358 diester consisting of
378 a terpenylic acid and a *cis*-pinic acid residue (25, 26), which is formed together with the
379 corresponding monomers upon α -pinene ozonolysis (27, 28) and has been observed in ambient
380 fine aerosol from different forested environments (25, 28-30). As 2-hydroxyterpenylic acid is a
381 higher-generation oxidation product than terpenylic acid it is logical that it is formed under
382 conditions of high solar radiation. Experiments aiming to explore the organic molecules involved
383 in new particle formation under ambient conditions by direct measurements should therefore
384 consider the sensitive detection of terpenylic acid and the related oxidation products, 2-
385 hydroxyterpenylic and terebic acid, as well as of diesters in which the latter terpenoic acids are
386 incorporated.



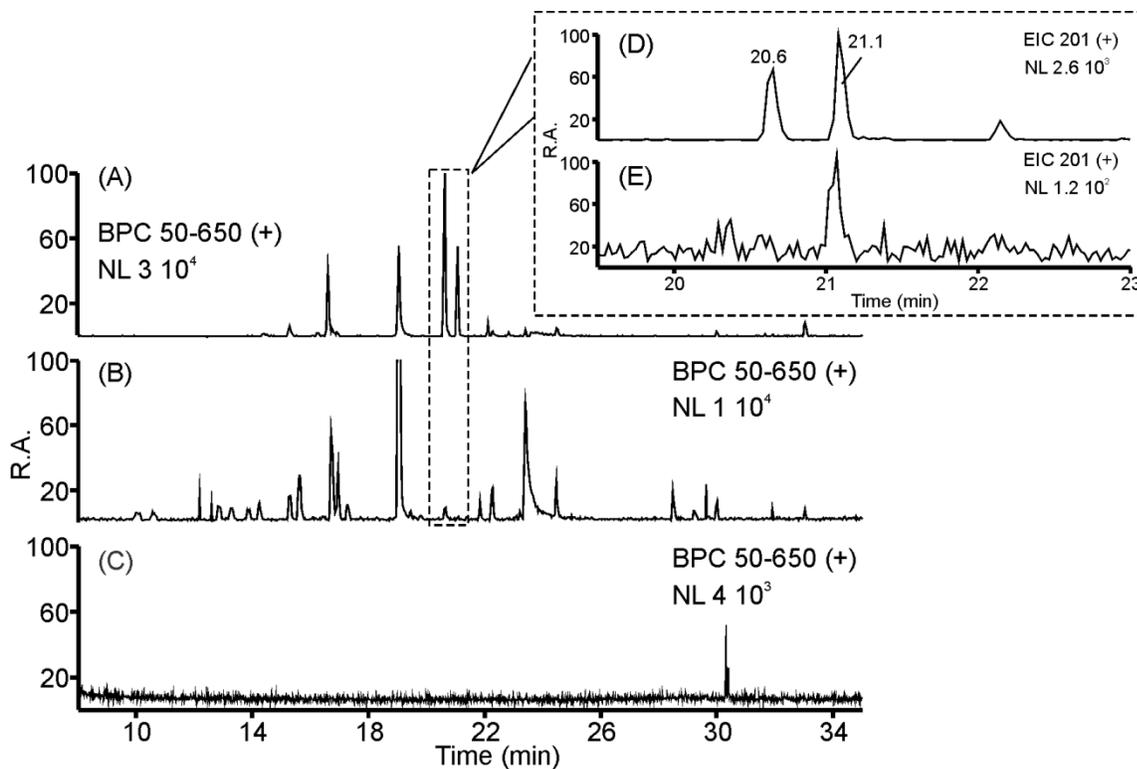
388

389 **Figure 1.** Selected LC/(-)ESI-ITMS data for the MW 188 compounds present in CAO SOA (A)
 390 and K-pusztza fine aerosol (B) showing the m/z 187 extracted ion chromatograms (EICs). (C) and
 391 (D) show m/z 187 MS^2 data, (E) and (F) m/z 187 \rightarrow m/z 125 MS^3 data for the compound eluting
 392 at 16.4 min in CAO SOA and the ambient sample, respectively, and (G) and (H) corresponding

393 m/z 187 MS² data, and (I) and (J) m/z 187 → m/z 125 MS³ data for the compound eluting at 17.2
394 min. Abbreviation: NL, normalization level.
395



397 **Figure 2.** LC/(+)ESI-MS data (EICs) for the methylated MW 188 compounds: (A) and (C) show
398 the protonated *mono*-methyl forms at m/z 203, and (B) and (D) the corresponding ammonium
399 adduct ions at m/z 220 from CAO SOA and K-pusztá fine aerosol, respectively. Abbreviation:
400 NL, normalization level.

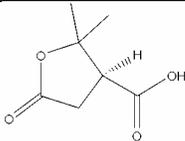
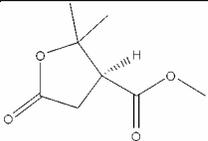
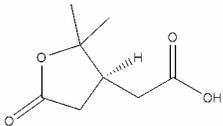
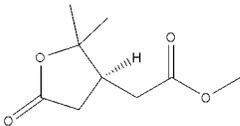
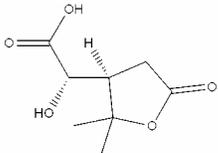
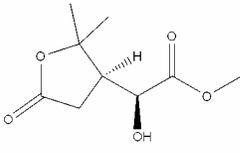
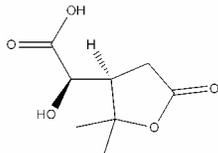
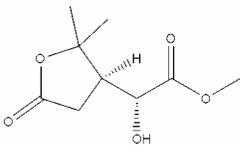


401
 402 **Figure 3.** Base Peak Chromatograms (BPCs) of methylated filter samples by GC/(+)EI-MS of
 403 (A) CAO SOA sample, (B) K-pusztza fine aerosol, and (C) the blank derivatization solution. In
 404 (D) and (E) Extracted Ion Chromatograms (EICs) of m/z 201 are shown from COA SOA and the
 405 K-pusztza fine aerosol sample that reveal methylated MW 188 compounds. Abbreviation: NL,
 406 normalization level.

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415 TABLES

416 **Table 1.** Overview of compounds investigated in the present study with the m/z values of their
 417 deprotonated and protonated molecules as well as of the protonated methyl ester derivatives.

compound	non-derivatized	methylated	
terebic acid (C ₇ H ₁₀ O ₄ , MW 158)			
	[M-H] ⁻	[M+H] ⁺	[M+H] ⁺
	m/z 157	m/z 159	m/z 173
terpenylic acid (C ₈ H ₁₂ O ₄ , MW 172)			
	[M-H] ⁻	[M+H] ⁺	[M+H] ⁺
	m/z 171	m/z 173	m/z 187
2-hydroxyterpenylic acid (C ₈ H ₁₂ O ₅ , MW 188)	 (<i>S,R</i>)-form		
	[M-H] ⁻	[M+H] ⁺	[M+H] ⁺ and [M+NH ₄] ⁺
	m/z 187	m/z 189	m/z 203 and m/z 220
	 (<i>R,R</i>)-form		

418

419

420 ASSOCIATED CONTENT

421 **Supporting Information**

422 Additional information on the time-resolved α -pinene/NO_x/air irradiation experiment,
423 supporting figures and explanation of the figures. This material is available free of charge via the
424 Internet at <http://pubs.acs.org>.

425

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432 **Notes**

433 The authors declare no competing financial interest.

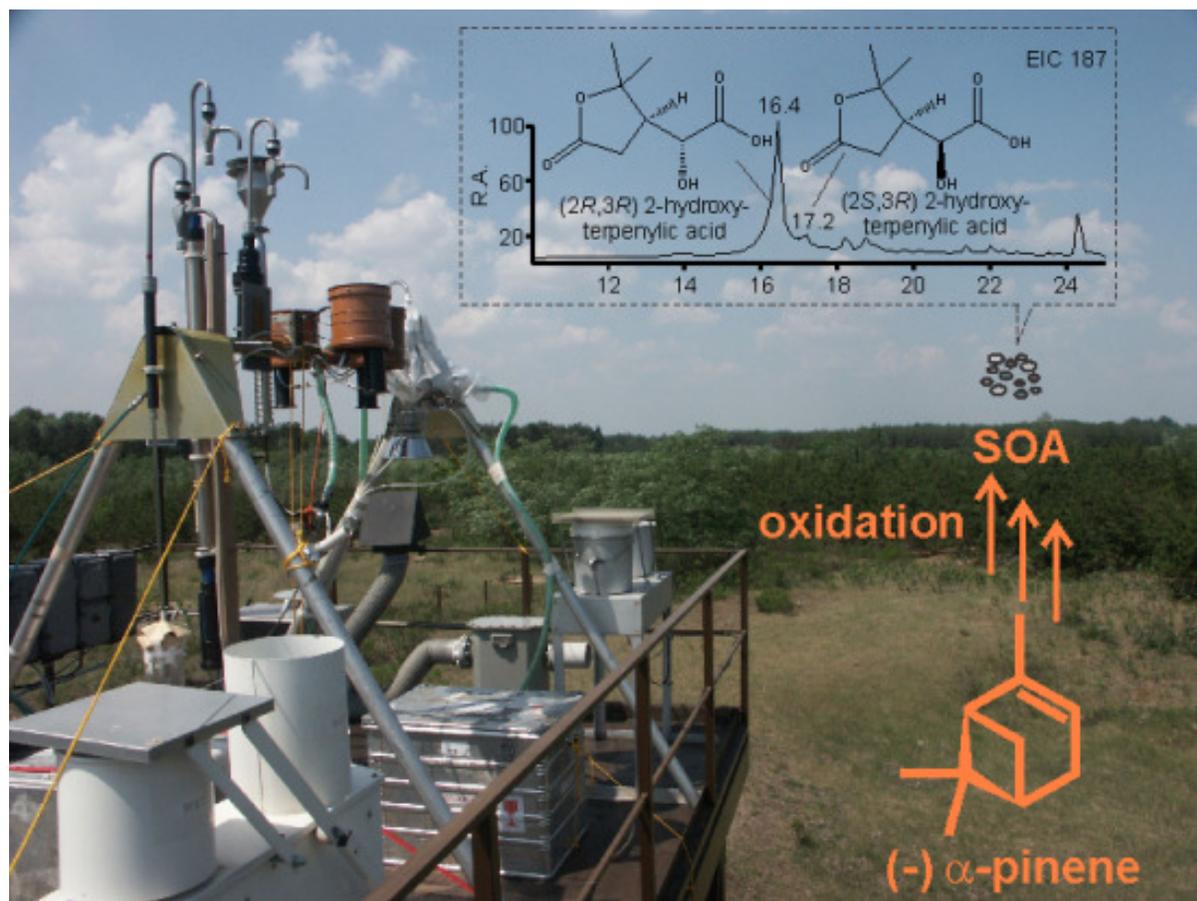
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447 procedures and approved for joint publication based on its scientific merit, technical accuracy, or
448 contribution to advancing public understanding of environmental protection. Mention of trade
449 names or commercial products does not constitute an endorsement or recommendation for use.

450 TOC GRAPHIC



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