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## 2-Hydroxyterpenylic Acid: An Oxygenated Marker Compound for $\alpha$ -Pinene Secondary Organic Aerosol in Ambient Fine Aerosol

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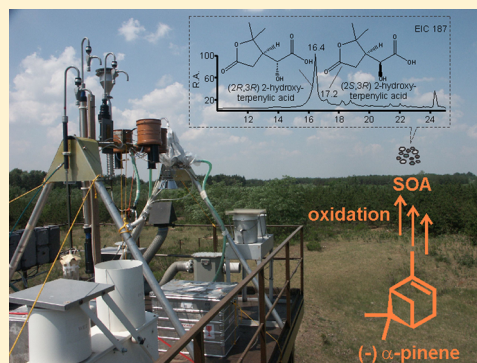
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### S Supporting Information

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



## INTRODUCTION

The atmospheric degradation of biogenic volatile organic compounds (BVOCs) leads to the formation of multifunctionalized oxidation products. Knowledge about the corresponding volatile precursor compounds and their chemical structure can help to identify sources and understand the fate of BVOCs in the atmosphere. This information is also crucial to more completely characterize ambient aerosols as specific oxidation products are related to certain aerosol properties; for example, the hydrophilic or cloud-formation properties of ambient fine aerosol can be associated with highly oxygenated secondary organic aerosol (SOA).<sup>1</sup> Despite the relevance of highly oxygenated SOA marker compounds, only one such product, the C<sub>8</sub>-tricarboxylic acid 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA; C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>), has been structurally identified in ambient aerosol so far.<sup>2,3</sup> MBTCA was shown to originate from monoterpene oxidation and was proposed as a marker for aged  $\alpha$ -pinene SOA. The structural elucidation of MBTCA posed a considerable analytical challenge because its structure lacks the  $\alpha$ -pinene or the cyclobutane skeleton, complicating its attribution to a specific VOC precursor and formulation of possible formation mechanisms. The targeted unknown MW 188 compound (C<sub>8</sub>H<sub>12</sub>O<sub>5</sub>) in the present study

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is another highly oxygenated compound, which is often observed in ambient aerosol samples in high abundance and was recently proposed as an additional suitable marker for aged biogenic SOA by Gómez-González et al.<sup>4</sup> In the latter study, this compound was shown to be, together with MBTCA and *cis*-pinonic acid, one of the most abundant monoterpene markers in PM<sub>2.5</sub> filter samples collected from a forested site, Brasschaat, Belgium, during a 2007 summer episode. Based on mass spectral data, indicating the presence of a carboxylic and a hydroxyl group, and its relatively low retention time in reversed-phase liquid chromatography,<sup>4–6</sup> this unknown MW 188 compound represents a very hydrophilic compound. Its formation was reported both from laboratory  $\alpha$ -pinene ozonolysis<sup>7,8</sup> and OH radical-initiated oxidations<sup>5,8,9</sup> but was generally observed in substantially lower abundance than other known  $\alpha$ -pinene SOA markers in chamber-generated samples.<sup>10</sup> Based on mass spectral evidence, two structures have been proposed for the unknown MW 188 compound, i.e., a C<sub>8</sub>-monohydroxycarboxylic acid structure (2-hydroxyterpenylic acid)<sup>5</sup> and a C<sub>8</sub>-hydroxydicarboxylic acid structure (hydroxynorpinic acid).<sup>6</sup> In addition, an unknown MW 188 compound has been tentatively assigned to norpinic peroxy acid, but no structural evidence was provided.<sup>11</sup> The MW 188 compound could not be detected by gas chromatography/mass spectrometry (GC/MS) with prior trimethylsilylation in previous studies, showing a similar behavior as other lactone-containing terpenoic acids, i.e., terebic and terpenylic acid.<sup>12</sup> A possible analogous structure, 2-hydroxyterpenylic acid, was proposed earlier by Claeys et al.,<sup>5</sup> mainly based on its noncovalent dimer formation properties similar to those of terpenylic acid, but no further evidence for this structural proposal could be provided to date for various reasons, including the difficulty in producing the compound from laboratory  $\alpha$ -pinene oxidation, the occurrence of several isobaric isomers, and the lack of an authentic reference compound. The MW 188 compound was recently described to also form from campholenic aldehyde ozonolysis,<sup>13</sup> and based on the agreement of mass spectral data with those from ambient filter samples, campholenic aldehyde ozonolysis (CAO) SOA was chosen in the present investigation to further characterize the MW 188 compound. A comprehensive mass spectrometric analysis was performed here, involving chemical derivatization to methyl ester derivatives and two instrumental approaches: (i) liquid chromatography/electrospray ionization ion trap mass spectrometry (LC/ESI-ITMS) employing both the (–) negative and (+) positive ion mode and (ii) GC/MS, whereby collision-induced dissociation (CID) was applied using the capabilities of the ion trap. In addition, the comparison to other lactone-containing terpenoic acid standard compounds, i.e., terebic and terpenylic acid, enabled the study of specific fragmentation behaviors and to support the proposed hydroxyterpenylic acid structure.

Furthermore, the time profile of 2-hydroxyterpenylic acid was compared with that of MBTCA, an established marker for aged  $\alpha$ -pinene SOA,<sup>2,3</sup> and other terpenoic acids, in a time-resolved  $\alpha$ -pinene photooxidation experiment.

## MATERIALS AND METHODS

**Chamber Aerosol.** Samples from CAO SOA were obtained as described by Kahnt et al.<sup>13</sup> Briefly, the experiments were carried out in the 19 m<sup>3</sup> TROPOS aerosol chamber at 50% relative humidity (RH) and 21 °C. The initial campholenic aldehyde mixing ratio was 100 ppb, and the reaction was performed with about 60 ppb ozone in the presence of

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> seed particles. No OH radical scavenger was added, and the formed aerosol was sampled after about 4 h of reaction. The aerosol was collected on a borosilicate glass fiber filter coated with fluorocarbon (47 mm diameter, Pallflex T60A20, Pall, NY, USA), which was stored at –22 °C before analysis.

Time-resolved  $\alpha$ -pinene/NO<sub>x</sub>/air irradiation experiments were performed in the EPA chamber in the batch mode as described in detail in Jaoui et al.<sup>14</sup> The precursor was injected with a mixing ratio of 5 ppmC in the 14.5 m<sup>3</sup> smog chamber that was operated at 28% RH, with an initial NO mixing ratio of 508 ppb. For the photooxidation study 4 light banks were used and the experiment was carried out in the presence of 1  $\mu$ g m<sup>–3</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> seed particles. This chamber experiment replicates a similar experiment described previously by Claeys et al.<sup>15</sup> In total eight filter samples were collected in this study (filters ER617 from GF1 until GF8); further information is provided in Section S1 of the Supporting Information (SI).

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

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

**Atmospheric Aerosol.** Pooled filter samples, which were collected during a summer field campaign from K-puszt, Hungary, in 2006 were analyzed in the present study. The sampling station is situated in the clearing of a mixed coniferous/deciduous forest on the Great Hungarian Plain (46°58'N, 19°35'E, 136 m above sea level) about 80 km southeast of Budapest. Details on the measurement campaign can be found in Maenhaut et al.<sup>16</sup> The pooled filter samples were prepared as described in Kahnt et al.<sup>13</sup>

**Sample Derivatization Procedure.** Diazomethane was freshly prepared using diazald (99%, Sigma-Aldrich) as a precursor according to a standard procedure.<sup>17</sup> An ethereal diazomethane solution was used to convert carboxylic acids into corresponding methyl esters. Therefore, the dried filter extract from a quarter part of the CAO SOA sample was reacted with 500  $\mu$ L of ethereal diazomethane solution. The derivatization was performed for 5 min, and subsequently, the sample was dried under a gentle stream of nitrogen, followed by reconstitution in 250  $\mu$ L methanol/water (50/50, v/v) for LC/ESI-ITMS analysis. The K-puszt sample was methylated using 400  $\mu$ L of the pooled filter extract, which was first dried, followed by the addition of 400  $\mu$ L of ethereal diazomethane. The applied derivatization procedure was performed as described above, and afterward, the dried sample was reconstituted in 400  $\mu$ L methanol/water (50/50, v/v) for LC/MS analysis. The same derivatization procedure was carried out for GC/MS analysis, except that the final reconstitution solvent was 100% dichloromethane (Pesti-S grade, Biosolve, The Netherlands).

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

The GC/MS analysis was performed using a TRACE GC2000 gas chromatograph and a Polaris Q ion trap mass spectrometer fitted with an external electron ionization source (ThermoFinnigan, San Jose, CA, USA). A deactivated silica precolumn ( $2 \text{ m} \times 0.25 \text{ mm i.d.}$ ) and a CP Sil 8CB low-bleed capillary column (95% dimethyl-, 5% phenylpolysiloxane,  $0.25 \mu\text{m}$  film thickness,  $30 \text{ m} \times 0.25 \text{ mm i.d.}$ ) (Chrompack, Middelburg, The Netherlands) were employed for the chromatographic separation using a sample injection volume of  $1 \mu\text{L}$  in the splitless mode (splitless time,  $0.5 \text{ min}$ ) at  $250^\circ\text{C}$ . The carrier gas was helium with a flow rate of  $1.2 \text{ mL min}^{-1}$ , and the temperature of the transfer line was set to  $280^\circ\text{C}$ . The oven temperature program was as follows: initial temperature of  $100^\circ\text{C}$ , which was maintained during 2 min, followed by a 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 time was 43 min. The mass spectrometer was operated in the electron ionization (EI) mode at an electron energy of 70 eV and an ion source temperature of  $220^\circ\text{C}$ . The full scan mode was applied in the mass range of  $m/z$  50–650. The targeted methylated compounds were characterized on the basis of their EI mass spectra and  $\text{MS}^2$  product ion spectra. For these fragmentation studies the target mass isolation width was set to 2  $m/z$  units.

**Quantum Chemical Calculations.** Calculations on 2-hydroxyterpenylic acid were performed using the Gaussian09 suite of programs<sup>18</sup> applying density functional theory (DFT) with the B3LYP functional<sup>19</sup> and the 6-311++G\*\* basis set, as it is implemented in Gaussian09. Geometry optimizations were performed for the isolated molecules in the gas phase as well as “in solution” in methanol and water applying the polarized continuum model (PCM). Dimerization energies for (2R,3R)- and (2S,3R)-2-hydroxyterpenylic acid were corrected for the basis set superposition error (BSSE) using the counterpoise method implemented in Gaussian09.

## RESULTS AND DISCUSSION

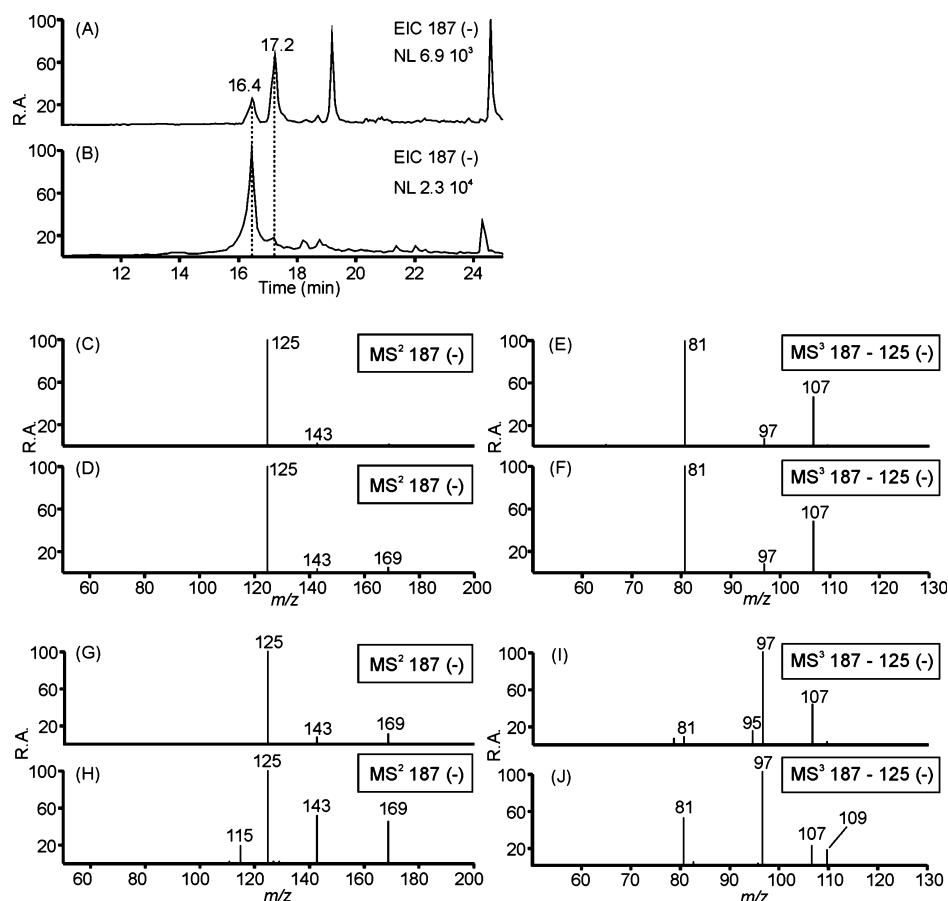
**Characterization of MW 188 Compounds Using LC/ESI-ITMS analysis.** An overview of the studied compounds is given in Table 1, showing the structures of the standard compounds terebic and terpenylic acid and those of the proposed 2-hydroxyterpenylic acid diastereoisomers with the  $m/z$  values of their deprotonated and protonated molecules as well as of the protonated methyl ester derivatives. A summary of known mechanistic pathways leading to 2-hydroxyterpenylic acid, involving either  $\alpha$ -pinene ozonolysis or OH reactions, is presented in Figure S2 of the SI.

**Table 1. Overview of Compounds Investigated in the Present Study with the  $m/z$  Values of Their Deprotonated and Protonated Molecules As Well As of the Protonated Methyl Ester Derivatives**

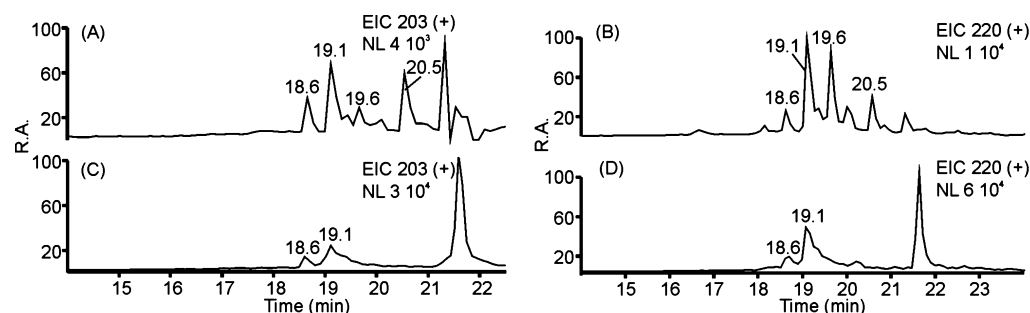
compound	non-derivatized	methylated	
terebic acid (C <sub>7</sub> H <sub>10</sub> O <sub>4</sub> , MW 158)	 [M-H] <sup>-</sup> <i>m/z</i> 157	 [M+H] <sup>+</sup> <i>m/z</i> 159	 [M+H] <sup>+</sup> <i>m/z</i> 173
terpenylic acid (C <sub>8</sub> H <sub>12</sub> O <sub>4</sub> , MW 172)	 [M-H] <sup>-</sup>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

Figure 1 presents selected LC/MS data, extracted ion chromatograms (EICs) for  $m/z$  187 corresponding to the deprotonated molecule of the targeted analytes eluting at 16.4 and 17.2 min, and MS data ( $m/z$  187  $\text{MS}^2$  and  $m/z$  187  $\rightarrow$   $m/z$  125  $\text{MS}^3$  product ion spectra) present in CAO SOA and ambient fine aerosol from K-puszt. Selected LC/MS data obtained for an  $\alpha$ -pinene  $\text{NO}_x$  photooxidation experiment are provided in Figure S3 of the SI. The targeted analytes at 16.4 and 17.2 min are assigned to 2-hydroxyterpenylic acid 2R,3R and 2S,3R diastereoisomers as will be discussed in detail in this and the following two sections. In addition, it should be noted that CAO (Figure 1) and  $\alpha$ -pinene (Figure S3 of the SI) SOA samples reveal intense  $m/z$  187 peaks eluting between 18 and 20 min and at 24.2 min; these  $m/z$  187 compounds correspond to mono-aldehydic forms of MBTCA [SI of ref 5] and azelaic acid,<sup>6</sup> are thus not related to 2-hydroxyterpenylic acid, and will therefore not be discussed here. It is worth noting that CAO SOA clearly shows two MW 188 compounds in a ratio of about 1:3, of which the second-eluting isomer (17.2 min) is also present at relative small abundance in the ambient sample. The product ion spectra from the (–)ESI- $\text{MS}^n$  analysis for the compound eluting at 16.4 min agreed well with reported spectra in the literature.<sup>5,6,10,13</sup> This MW 188 compound was proposed earlier as 2-hydroxyterpenylic acid,<sup>5</sup> an  $\alpha$ -pinene-related marker compound originating from OH radical-initiated processes; however, no diastereoisomeric assignment was made in the latter study. The  $m/z$  187  $\text{MS}^2$  product ion spectrum (Figure 1C,D) is dominated by  $m/z$  125, which corresponds to the combined loss of a molecule water and  $\text{CO}_2$  ( $62 \text{ u}$ ) and is in





**Figure 1.** Selected LC/(-)ESI-ITMS data for the MW 188 compounds present in CAO SOA (A) and K-puszt fine aerosol (B) showing the  $m/z$  187 extracted ion chromatograms (EICs). (C and D)  $m/z$  187  $MS^2$  data and (E and F)  $m/z$  187  $\rightarrow$   $m/z$  125  $MS^3$  data for the compound eluting at 16.4 min in CAO SOA and the ambient sample, respectively. (G and H) Corresponding  $m/z$  187  $MS^2$  data and (I and J)  $m/z$  187  $\rightarrow$   $m/z$  125  $MS^3$  data for the compound eluting at 17.2 min. Abbreviation: NL, normalization level.



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

agreement with a hydroxycarboxylic acid structure. Further fragmentation of  $m/z$  125 leads to ions at  $m/z$  107, 97, and 81 (Figure 1E,F), which can also be explained with the proposed structure, as outlined in Figure S4 of the SI. It can be noted that the MS data obtained for the MW 188 compound eluting at 17.2 min (Figure 1G–I) are very similar to those of the first-eluting isomer (Figure 1C–F) and mainly differ by the relative abundances of their product ions, which is consistent with diastereoisomeric forms of 2-hydroxyterpenylic acid.

In order to obtain additional structural information, the targeted MW 188 compounds were also analyzed with LC/ESI-ITMS in the positive ion mode and the MS data were

compared with those of available standard compounds, i.e., terebic and terpenylic acid. Selected MS data and interpretation are provided in Figure S5 of the SI. The  $m/z$  187  $MS^2$  data obtained for MW 188 compounds show the loss of two molecules of water, one molecule originating in the lactone ring and a second one owing to loss of a molecule of water from the side chain containing a hydroxyl group, which is in agreement with the proposed 2-hydroxyterpenylic acid structure.

**Characterization of Methylated MW 188 Compounds Using LC/(+)ESI-ITMS.** In order to support the presence of a lactone structure in the targeted MW 188 compounds, a derivatization experiment with diazomethane, a soft methyl-

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

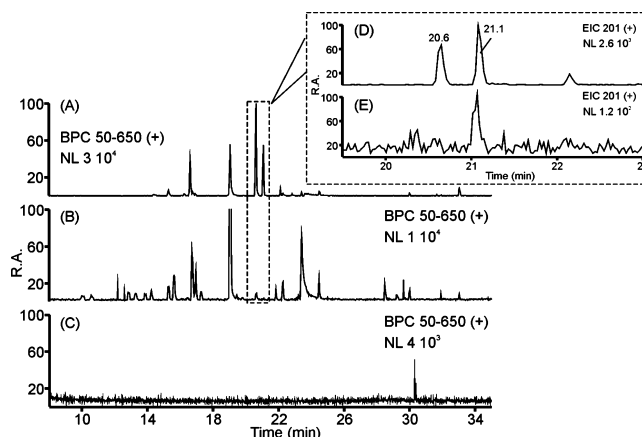
Analysis of methylated extracts of CAO SOA and the ambient sample reveals signals corresponding to the targeted methylated MW 188 compounds at  $m/z$  203 and 220, corresponding to the protonated forms and the ammonium adducts, respectively (Figure 2). The latter ions were selected for further fragmentation experiments as they were more abundant than the  $m/z$  203 ions. The compounds eluting at 18.6 and 19.1 min were present in both the CAO SOA and the ambient sample. The compound eluting at 19.1 min was attributed to the methyl ester of the 2-hydroxyterpenylic acid 2R,3R diastereoisomer, which is abundant in the ambient sample, whereas that eluting at 20.5 min was assigned to the 2-hydroxyterpenylic acid 2S,3R diastereoisomer, which had a high signal intensity in the CAO SOA sample. The  $m/z$  220 MS<sup>2</sup> product ion spectrum (Figure S8E,G in the SI) is dominated by  $m/z$  203, owing to the loss of ammonia and corresponding to the protonated molecule. Fragmentation of  $m/z$  203 leads to  $m/z$  185, 167, 135, and 153 (Figure S8H,J,K,M in the SI), which can all be explained with the proposed structure, as outlined in Figure S9 in the SI. It is worth noting that the MS data obtained for the methylated compound eluting at 20.5 min (Figure S8F,I,L,O in the SI) are very similar to those obtained for the earlier-eluting compound at 19.1 min, which is again consistent with diastereoisomeric forms of 2-hydroxyterpenylic acid methyl ester.

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

**Characterization of Methylated MW 188 Compounds Using GC/EI-MS Analysis.** It has been reported in a previous study that terebic and terpenylic acid could not be detected in ambient samples upon GC/EI-MS with prior trimethylsilylation.<sup>12</sup> Some possible reasons for the failure to detect these lactone-containing compounds include that they are too volatile and are lost in the sample preparation step, which involves concentration of the extract using rotary evaporation and evaporation under a nitrogen stream, as well as their thermal instability upon injection into the GC/MS instrument. Therefore, it was evaluated in the present study whether methylated terebic and terpenylic acid trimethylsilyl esters, as well as methylated MW 188 compounds, which are expected to be slightly more polar than the first mentioned standard

compounds, could be detected from the methylated extracts of CAO SOA and the ambient sample. Selected MS data and interpretation of the methylated terebic acid and terpenylic acid standards are provided in the SI (Figures S12, S13, and S14).

As shown in Figure 3, the GC/EI-MS analysis revealed two peaks for methylated 2-hydroxyterpenylic acid diastereoisomers



**Figure 3.** Base peak chromatograms (BPCs) of methylated filter samples by GC/(+)EI-MS of (A) CAO SOA sample, (B) K-pusztá fine aerosol, and (C) the blank derivatization solution. (D and E) Extracted ion chromatograms (EICs) of  $m/z$  201 are shown from CAO SOA and the K-pusztá fine aerosol sample that reveal methylated MW 188 compounds. Abbreviation: NL, normalization level.

in the CAO SOA sample. It is interesting to note that only one of them matched with a peak from the K-pusztá sample, i.e., the peak eluting at 21.1 min, which was detected only with low signal intensity in the ambient sample. This supports an earlier proposal that lactone-containing compounds might have escaped detection upon GC/MS with prior derivatization.<sup>12</sup> The mass spectral data and possible EI fragmentation routes for 2-hydroxyterpenylic acid methyl ester are provided in Figures S15 and S16 of the SI. As expected for an alcoholic compound, the molecular ion at  $m/z$  202 was absent from the EI mass spectrum; however, the ion at  $m/z$  201, formed by the loss of a hydrogen radical through an  $\alpha$ -cleavage relative to the ionized hydroxyl function, is typical for alcohols. Other characteristic fragment ions include  $m/z$  169, corresponding to the loss of a molecule of water and a methyl radical, and  $m/z$  141, owing to an additional loss of CO. Both ions were selected for MS<sup>2</sup> experiments, and the proposed structure of 2-hydroxyterpenylic acid methyl ester could be further supported (Figure S16 in the SI). It is worth noting that for the two MW 202 compounds present in CAO SOA similar product ions were observed in MS<sup>2</sup> experiments (Figure S15F–K in the SI) with only slight differences in relative abundance, consistent with diastereoisomers. Instead of  $m/z$  127 in the  $m/z$  201 isomer eluting at 21.1 min, a product ion at  $m/z$  129 is observed for the isomer at 20.6 min (Figure S15I in the SI), likely owing to the addition of two hydrogen radicals to the double bond, a feature that has been previously reported for compounds containing a double bond upon MS<sup>2</sup> ion trap experiments.<sup>20</sup>

**Assignment of 2-Hydroxyterpenylic Acid Diastereoisomers.** Considering that 2-hydroxyterpenylic acid is formed from the oxidation of (–)- $\alpha$ -pinene, which has a 1S,5S configuration for its two chiral C atoms, the stereochemistry in the resulting C-3 position of the oxidation product is fixed. As shown in Table 1, also for terpenylic acid the chiral

C-3 atom has a *S* configuration. However, the introduction of an OH-group at the neighboring position in 2-hydroxyterpenylic acid changes the order of priorities according to the Cahn–Ingold–Prelog nomenclature,<sup>21</sup> resulting in a 3*R* configuration for 2-hydroxyterpenylic acid. The stereochemistry for the other chiral C-2 atom can be either *S* or *R*. Based on theoretical considerations, the major diastereoisomer in ambient fine aerosol (Figure 1B) was assigned to the 2*R*,3*R* diastereoisomer as it is more polar in comparison to the (2*S*,3*R*)-2-hydroxyterpenylic acid. Differences in physical and chemical properties are expected for diastereoisomers containing a hydroxyl group since the spacial orientation of the OH-group can lead to a different exposition of the polar group. Derived dipole moments for the *R,R* form were 5.5, 7.2, and 7.3 D in the gas phase, methanol, and water, respectively. In comparison to the *S,R* form, which had dipole moments of 4.2, 5.1, and 5.1 D in the gas phase, methanol, and water, respectively, a much higher polarity was hence observed for the (2*R*,3*R*)-2-hydroxyterpenylic acid, explaining its earlier retention time in reversed-phase chromatography (Figure 1A,B). Energy differences between the diastereoisomers were negligibly small, being 0.01 and 0.02 kcal mol<sup>-1</sup> in methanol and water, respectively, favoring slightly the *R,R* form.

It has been previously observed that the major 2-hydroxyterpenylic acid diastereoisomer shows noncovalent dimer formation upon (–)ESI-MS detection,<sup>5</sup> whereas this behavior was not observed for the later-eluting compound. In this regard also quantum chemical calculations were performed to derive dimerization energies for the two diastereoisomers, and energies for the homodimeric species (i.e., MW 376) were calculated. For the neutral case a value of –16.6 kcal mol<sup>-1</sup> for the 2*R*,3*R* and –16.5 kcal mol<sup>-1</sup> for the 2*S*,3*R* enantiomer were obtained, pointing to similar dimerization probabilities for the two 2-hydroxyterpenylic acid diastereoisomers. Based on the calculated dimerization energies, the formation of dimers is favored over the presence as monomeric species. The values are also comparable with reported dimerization energies for the terpenylic acid homodimer, i.e., –17 kcal mol<sup>-1</sup>,<sup>5</sup> implying similar importance of 2-hydroxyterpenylic acid in new particle formation.

However, the observation that only for the (2*R*,3*R*)-2-hydroxyterpenylic acid could a homodimer be detected after LC separation upon (–)ESI-MS detection, and not for the 2*S*,3*R* form, might be misleading. Owing to the much lower signal intensity of the 2*S*,3*R* enantiomer, the dimeric cluster anion [M – H]<sup>–</sup> *m/z* 375 might be not detectable under these conditions.

**Temporal Evolution of the Major 2-Hydroxyterpenylic Acid 2*R*,3*R* Diastereoisomer.** The temporal evolution of the targeted MW 188 compound, which elutes at 16.4 min and is attributed to the 2-hydroxyterpenylic acid 2*R*,3*R* diastereoisomer (Table 1), and of other known oxidation products was examined in an  $\alpha$ -pinene photooxidation experiment and is summarized in Figure S1 of the SI, together with the SOA mass formation as a function of irradiation time. It can be seen that the concentrations of most of the studied oxidation products were highest in the sample collected at approximately 5 h of irradiation. The most abundant compound was diaterpenylic acid acetate (*m/z* 231), followed by terpenylic acid (*m/z* 171), *cis*-pinic acid (*m/z* 185), *cis*-pinonic acid (*m/z* 183), MBTCA (*m/z* 203), terebic acid (*m/z* 157), and the targeted MW 188 compound at the maximum. A further significant formation was observed only for MBTCA, a known aging compound,<sup>2,3</sup>

whereas for terebic acid and the MW 188 compound only a marginal increase was detected until the chamber experiment was stopped after 7 h. All of the other oxidation products decreased after 5 h of irradiation, although an ongoing SOA mass formation was observed, pointing to particle phase reactions probably also from yet nonidentified compounds that lead to additional aerosol growth. Although the curve shape in SOA mass formation was somewhat different in comparison to a similarly designed  $\alpha$ -pinene photooxidation experiment in a previous study,<sup>15</sup> comparable maximum SOA mass concentrations were obtained in this study.

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

## ■ ATMOSPHERIC IMPLICATIONS

In the present study, we have characterized in detail an  $\alpha$ -pinene oxidation product with a MW of 188 that is abundantly present in ambient fine aerosol as the 2-hydroxyterpenylic acid 2*R*,3*R* diastereoisomer. Other less abundant isomers were assigned to the 2-hydroxyterpenylic acid 2*S*,3*R* diastereoisomer and 4-hydroxyterpenylic acid diastereoisomers. The time-resolved  $\alpha$ -pinene photooxidation experiment shows that the 2-hydroxyterpenylic acid 2*R*,3*R* diastereoisomer has a time profile different than that of MBTCA, consistent with different formation pathways. Furthermore, as the MW 188 compound represented only a minor oxidation product in the performed chamber experiment, it is clear that crucial ambient conditions could not be met. Additional research is therefore warranted to design  $\alpha$ -pinene oxidation experiments that better simulate ambient conditions. Another interesting and puzzling feature that merits further exploration is that there seems to be a stereochemical control in the formation of the 2-hydroxyterpenylic acid 2*R*,3*R* diastereoisomer, which shows a relative abundance that is about 5-fold higher than the other diastereoisomeric 2*S*,3*R* form in ambient filter samples.

Terpenylic acid has been suggested to play a role in the early stages of particle formation in laboratory  $\alpha$ -pinene oxidation experiments<sup>5</sup> and shown to be important in small biogenic particles (10–20 nm) by direct thermal desorption chemical ionization MS.<sup>24</sup> It has also been demonstrated to be incorporated into a high MW compound, i.e., a MW 358 diester consisting of a terpenylic acid and a *cis*-pinic acid residue,<sup>25,26</sup> which is formed together with the corresponding monomers upon  $\alpha$ -pinene ozonolysis<sup>27,28</sup> and has been observed in ambient fine aerosol from different forested environments.<sup>25,28–30</sup> As 2-hydroxyterpenylic acid is a higher-generation oxidation product than terpenylic acid, it is logical that it is formed under conditions of high solar radiation.



Experiments aiming to explore the organic molecules involved in new particle formation under ambient conditions by direct measurements should therefore consider the sensitive detection of terpenylic acid and the related oxidation products, 2-hydroxyterpenylic and terebic acid, as well as of diesters in which the latter terpenoic acids are incorporated.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional information on the time-resolved  $\alpha$ -pinene/NO<sub>x</sub>/air irradiation experiment, supporting figures, and explanation of the figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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