

# Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of $\alpha$ - and $\beta$ -pinene

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**Abstract.** In the present study, we have characterized the structure of a higher-molecular weight (MW) 358  $\alpha$ - and  $\beta$ -pinene dimeric secondary organic aerosol (SOA) product that received ample attention in previous molecular characterization studies and has been elusive. Based on mass spectrometric evidence for deprotonated molecules formed by electrospray ionization in the negative ion mode and chemical considerations, it is suggested that diaterpenylic acid is a key monomeric intermediate for dimers of the ester type. It is proposed that *cis*-pinic acid is esterified with the hydroxyl-containing diaterpenylic acid, which can be explained through acid-catalyzed hydrolysis of the recently elucidated lactone-containing terpenylic acid and/or diaterpenylic acid acetate, both first-generation oxidation products. To a minor extent, higher-MW 358 and 344 diester products are formed containing other terpenoic acids as monomeric units, i.e., diaterpenylic acid instead of *cis*-pinic acid, and diaterebic acid instead of diaterpenylic acid. It is shown that the MW 358 diester and related MW 344 compounds, which can be regarded as processed SOA products, also occur in ambient fine (PM<sub>2.5</sub>) rural aerosol collected at night during the warm period of the 2006 summer field campaign

conducted at K-puszta, Hungary, a rural site with coniferous vegetation. This indicates that, under ambient conditions, the higher-MW diesters are formed in the particle phase over a longer time-scale than that required for gas-to-particle partitioning of their monomeric precursors in laboratory  $\alpha$ -/ $\beta$ -pinene ozonolysis experiments.

## 1 Introduction

The formation of higher-molecular weight (MW) products is considered as a driving force for secondary organic aerosol (SOA) formation and growth, because their formation leads to products with a substantially decreased vapor pressure that is several orders of magnitude lower than that of the precursor hydrocarbons. Higher-MW products either correspond to non-covalent dimers between monomeric carboxylic acids that are held together by hydrogen bonds (e.g., Hoffmann et al., 1998; Claeys et al., 2009) or to covalent dimers between monomeric carboxylic acids that are connected through covalent bonds, such as, esters (e.g., Hamilton et al., 2006; Szmigielski et al., 2007; Müller et al., 2008) and oligomers formed through gem-diol intermediates (e.g., Gao et al., 2004; Iinuma et al., 2004; Tolocka et al., 2004; Docherty et al., 2005) or aldol condensation reactions (e.g., Tolocka et al., 2004). These heterogeneous processes are consistent



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with the observation that sulfuric acid seed aerosol catalyzes the formation of SOA (e.g., Jang et al., 2002, 2003; Czoschke et al., 2003; Iinuma et al., 2004).

Structural proposals have been made in previous work for higher-MW SOA products that participate in new particle formation and growth, including dimers and oligomers. The structural elucidation at the molecular level of such compounds is a complex and analytically challenging task as it is only readily feasible if the structures of the composing monomers are known. Conversely, lack of knowledge about the monomeric units has severely hampered structural characterization efforts of higher-MW di- and oligomeric compounds in previous studies.

Considerable attention has been given in previous work to a higher-MW 358 SOA product from  $\alpha$ -pinene ozonolysis (Hoffmann et al., 1998; Gao et al., 2004; Iinuma et al., 2004), which was first detected by direct negative ion atmospheric pressure chemical ionization – mass spectrometry and tentatively assigned to a stable adduct between *cis*-pinic (MW 186) and *cis*-norpinic acid (MW 172), both ozonolysis products (Hoffmann et al., 1998). It was shown in the latter study that the MW 358 compound remained intact upon reversed-phase liquid chromatography; however, a straightforward explanation for the formation of a stable dimer between *cis*-pinic and *cis*-norpinic acid was not presented. Following this initial study by Hoffmann et al. (1998), other tentative structures have been proposed for higher-MW  $\alpha$ -pinene ozonolysis products (Gao et al., 2004; Iinuma et al., 2004; Docherty et al., 2005). Gao et al. (2004) attributed the MW 358  $\alpha$ -pinene ozonolysis product to a dehydration product formed between the gem-diol forms of two norpinonic acid molecules. Iinuma et al. (2004) reported MW 354 and 370 dimeric products from the ozonolysis of  $\alpha$ -pinene that were enhanced in acidic conditions and tentatively assigned the products to reaction products between the gem-diol of pinonaldehyde and pinonaldehyde, and of pinonaldehyde and hydroxypinonaldehyde, respectively. Docherty et al. (2005) proposed peroxydicarboxylic acid dimers for the structure of higher-MW SOA products from the ozonolysis of  $\alpha$ -pinene in which peroxydicarboxylic acid and the gem-diol of a keto or aldehydic compound are connected via a peroxy bridge. Furthermore, the MW 358 product was detected as a major tracer in other  $\alpha$ -pinene as well as  $\beta$ -pinene ozonolysis SOA characterization studies (Iinuma et al., 2007; Müller et al., 2008). In addition, Tolocka et al. (2004) characterized dimers in  $\alpha$ -pinene ozonolysis SOA and suggested that the dimers were most likely formed by aldol and/or gem-diol formation. Müller et al. (2008) reported the presence of abundant MW 358 and 368 products upon  $\alpha$ -pinene ozonolysis and provided evidence for esterification of *cis*-pinic acid with hydroxyl-containing terpenoic acids as a major formation pathway; the MW 370 product was attributed to a diester formed between *cis*-pinic acid and 10-hydroxypinonic acid but the structure of the MW 358 product remained unresolved. In a more recent study by Müller et al. (2009),

the structure of the MW 358 dimer was readdressed and proposed to contain a *cis*-pinic acid residue and a hydroperoxy-hemiacetal or peroxyhemiacetal function, thus involving peroxyradical chemistry. From all these studies it appears that the structure of the MW 358 dimeric product formed upon  $\alpha$ -/ $\beta$ -pinene ozonolysis has been elusive.

Esterification together with anhydride formation were shown to be important routes for dimer formation from the ozonolysis of cyclohexene (Hamilton et al., 2006). In addition, esterification was shown to operate in the formation of di-, tri-, and tetramers in  $\alpha$ -pinene ozonolysis based on direct mass spectrometric analysis of complex SOA mixtures and accurate mass measurements that revealed repetitive structures and changes in O:C ratios (Reinhardt et al., 2007). Esterification of small hydroxycarboxylic acids such as hydroxyacrylic, glycolic, lactic, and 2-methylglyceric acid was also found to be a route resulting in isoprene SOA formation (Altieri et al., 2006, 2008; Surratt et al., 2006; Szmigielski et al., 2007; Perri et al., 2009). Furthermore, theoretical calculations by Barsanti and Pankow (2006) show that esterification is a thermodynamically favorable route for SOA formation under atmospheric conditions.

In the present study, we address the structure of a relatively abundant MW 358 compound and related weak MW 344 and 358 compounds that are formed upon  $\alpha$ - and  $\beta$ -pinene ozonolysis and are also present in ambient fine (PM<sub>2.5</sub>, particulate matter with aerodynamic diameter <2.5  $\mu$ m) rural continental aerosol. We propose that diaterpenylic acid, a hydrolysis product of terpenylic acid (MW 172) and/or diaterpenylic acid acetate (MW 232), recently reported  $\alpha$ -pinene SOA tracers formed upon both photooxidation and ozonolysis (Claeys et al., 2009), serves together with *cis*-pinic acid as a monomeric building unit for the higher-MW 358 diester products.

## 2 Experimental

### 2.1 Aerosol samples

$\alpha$ - and  $\beta$ -pinene SOA for structural characterization was obtained from ozonolysis experiments carried out in the 19 m<sup>3</sup> IfT smog chamber. Briefly, the ozonolysis of  $\alpha$ - and  $\beta$ -pinene was carried out in the presence of acidic seed particles, which were generated by nebulizing a 0.03/0.06 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> solution. The relative humidity and temperature of the chamber were approximately 50% and 23 °C for all experiments. The initial concentrations of  $\alpha$ -pinene and ozone were 100 ppb and 72 ppb, respectively. For  $\beta$ -pinene ozonolysis, the initial concentrations were 300 ppb for  $\beta$ -pinene and 108 ppb for ozone. No OH scavenger was used in these chamber experiments. Aerosol samples were collected on a 47 mm PTFE filter (Pall, Fiberfilm) and a volume of 2 m<sup>3</sup> of the gaseous reaction mixture was sampled. The filter samples were extracted with methanol (3  $\times$  20 mL),

and the combined methanol extracts were concentrated by rotary evaporation to about 1 mL. Subsequently, the concentrated extracts were filtered over a Teflon filter (0.45  $\mu\text{m}$ ), then further evaporated under a nitrogen stream and reconstituted in 200  $\mu\text{L}$  methanol. For liquid chromatography/mass spectrometry (LC/MS) analysis a part of the samples was diluted with the same volume of water and an aliquot of 5  $\mu\text{L}$  was injected. With regard to extraction with methanol, it was verified that this procedure could be applied in the present work. Using a dicarboxylic acid as a model substance (i.e., 1,4-cyclohexanedicarboxylic acid, Sigma-Aldrich, 100 ng), we have examined in prior tests whether extraction with methanol and further sample workup under our conditions (i.e., solvent removal) results in artifacts such as methyl ester formation; the results show that the mono-ester of 1,4-cyclohexanedicarboxylic acid was formed with a yield of less than 5%. Since the present study was mainly qualitative, possible artifact methyl ester formation due to extraction with methanol was not considered.

The ambient aerosol samples used in this work were collected from K-pusztá, Hungary, during the BIOSOL (Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols) campaign between 22 May and 29 June 2006. Information about the site and the sampling campaign is given in the supplement (Sect. 1). Day- and night-time samples were collected using a high-volume dichotomous sampler providing two size fractions, a fine ( $\text{PM}_{2.5}$ ) and a coarse size fraction (with aerodynamic diameter  $>2.5 \mu\text{m}$ ). A quarter or one eighth (depending on the organic carbon amount) of the  $\text{PM}_{2.5}$  quartz fiber filter was extracted with methanol ( $3 \times 20 \text{ mL}$ ), the residue was redissolved in 150  $\mu\text{L}$  of a methanol:water (1:1, v/v) mixture, and an aliquot of 5  $\mu\text{L}$  (corresponding to 5.6  $\mu\text{g}$  organic carbon in the case of the selected nighttime sample of 19 June, Fig. 2) was injected for LC/MS analysis.

## 2.2 Chemicals

The terpenoic acid standards used in this work were: *cis*-pinic acid (purity  $>98\%$ ; Sigma-Aldrich, St. Louis, MI, USA) and terebic acid (purity  $>98\%$ ; TCI Europe, Zwijndrecht, Belgium). Terpenylic acid and diaterpenylic acid acetate were available from previous studies (Claeys et al., 2009; Iinuma et al., 2009).

## 2.3 LC/MS analysis

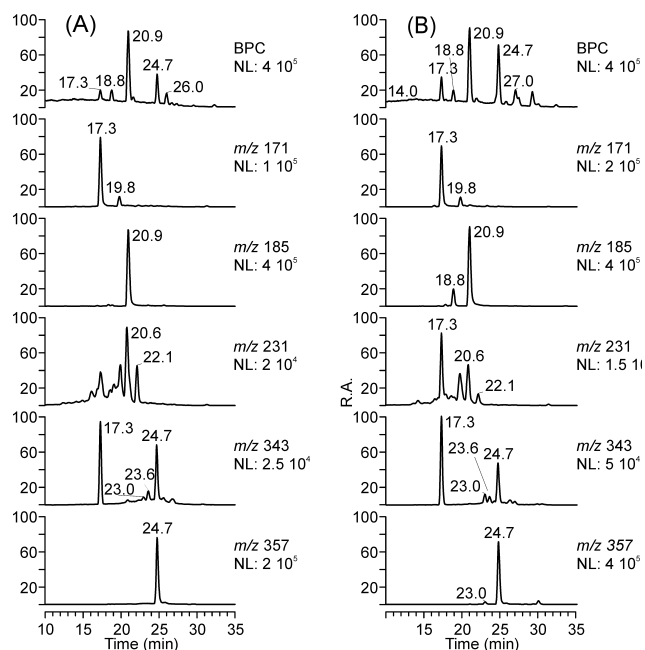
The LC/MS system comprised a Surveyor Plus system (pump and autosampler), a linear ion trap mass spectrometer (LXQ) equipped with an electrospray ionization (ESI) source, and a data system using Xcalibur version 2.0 software (Thermo Scientific, San Jose, USA). A T3 Atlantis C18 column (3  $\mu\text{m}$ ;  $2.1 \times 150 \text{ mm}$ ) (Waters, Milford, USA) was employed. The mobile phases consisted of acetic acid 0.1% (v/v) (A) and methanol (B). The applied 80-min gradient elu-

tion program was as follows: the concentration of eluent B was kept at 3% for 2 min, then increased to 90% in 18 min, kept at 90% for 43 min, then decreased to 3% in 5 min, and kept at 3% for 12 min. The flow rate was  $0.2 \text{ mL min}^{-1}$ . The linear ion trap was operated under the following conditions: sheath gas flow (nitrogen),  $0.75 \text{ L min}^{-1}$ ; auxiliary gas flow (nitrogen),  $1.5 \text{ L min}^{-1}$ ; source voltage,  $-4.5 \text{ kV}$ ; capillary temperature,  $350 \text{ }^\circ\text{C}$ ; and maximum ion injection time, 200 ms. For  $\text{MS}^n$  ( $n = 2, 3$  and 4) experiments, an isolation width of 2  $m/z$  units and a normalized collision energy level of 35% were applied.

## 3 Results and discussion

### 3.1 Structural characterization of MW 172, 186, and 232 terpenoic acids

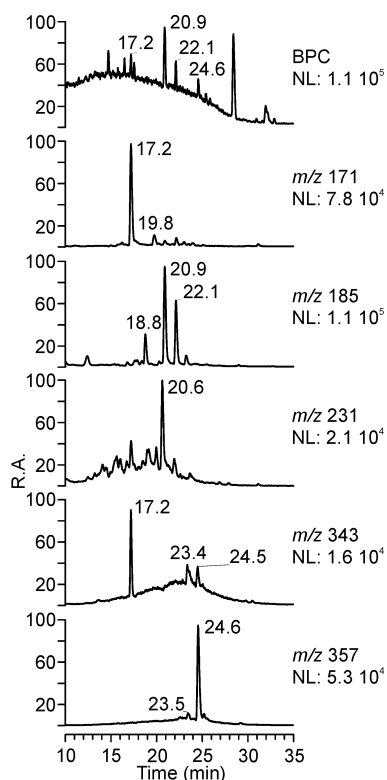
In this section we deal with the structural characterization of terpenoic acids that serve as monomeric precursors to the dimeric MW 344 and 358 compounds, which will be addressed in the next sections, as well as with the structural characterization of some weak monomeric/isobaric compounds (i.e., compounds with the same elemental composition but a different structure, either a compound with a positional isomeric structure or a non-isomeric compound with different functional groups). Figure 1a and b present chromatographic data (base peak chromatograms – BPCs – and extracted ion chromatograms – EICs) for SOA from the ozonolysis of  $\alpha$ - and  $\beta$ -pinene, respectively, while Fig. 2 presents chromatographic data for a nighttime  $\text{PM}_{2.5}$  aerosol sample from K-pusztá. It can be seen that the chromatographic data for  $\alpha$ - and  $\beta$ -pinene SOA are rather similar. The major peak on the  $m/z$  171 EICs with RT 17.3 min is assigned to the lactone-containing terpenylic acid, a novel terpenoic acid which has only been recently reported (Claeys et al., 2009), based on comparison of its chromatographic and mass spectrometric behaviors with that of a synthesized reference compound. It is noted that terpenylic acid is an isobaric compound of *cis*-norpinic acid (i.e., a non-isomeric product with the same elemental composition but different functional groups). For comparison reasons (see next section), (–)ESI-MS data for terpenylic acid are presented in Fig. 3a and Scheme 1a. It is noted that the product ions at  $m/z$  127 and 83 are also characteristic for diaterpenylic acid acetate (Claeys et al., 2009) and are also expected to be formed from diaterpenylic acid, produced through hydrolysis of terpenylic acid and diaterpenylic acid acetate (see below). (–)ESI-MS data for diaterpenylic acid acetate are presented in Fig. 3b and Scheme 1b. It can be seen in Fig. 2 that there is also a minor peak on the  $m/z$  171 EIC with RT 19.8 min; this peak is attributed to *cis*-norpinic acid based on detailed interpretation of the (–)ESI-MS data and comparison with LC/MS data reported in the literature (Glasius et al., 2000; Warnke et al., 2006). (–)ESI-MS data for the latter MW 172 compound



**Fig. 1.** LC/MS chromatographic data (base peak chromatograms – BPCs – and extracted ion chromatograms – EICs) for (A)  $\alpha$ -pinene and (B)  $\beta$ -pinene ozonolysis SOA. Abbreviation: NL, normalization level. EICs are presented for  $m/z$  171 (terpenylic acid and isobaric compounds)  $m/z$  185 (*cis*-pinic acid and isobaric compounds),  $m/z$  231 (diaterpenylic acid acetate and isobaric compounds),  $m/z$  343 (MW 344 non-covalent and covalent dimeric compounds) and  $m/z$  357 (MW 358 dimeric compounds).

are given in the supplement (Sect. 2: Fig. S1, Scheme S1). It is likely that in previous work terpenylic acid has often been misassigned to *cis*-norpinic acid, owing to the fact that the mass spectrometric fragmentation of terpenylic acid shows a double loss of 44 u ( $\text{CO}_2$ ), indicating the presence of two carboxyl groups and thus rather misleading.

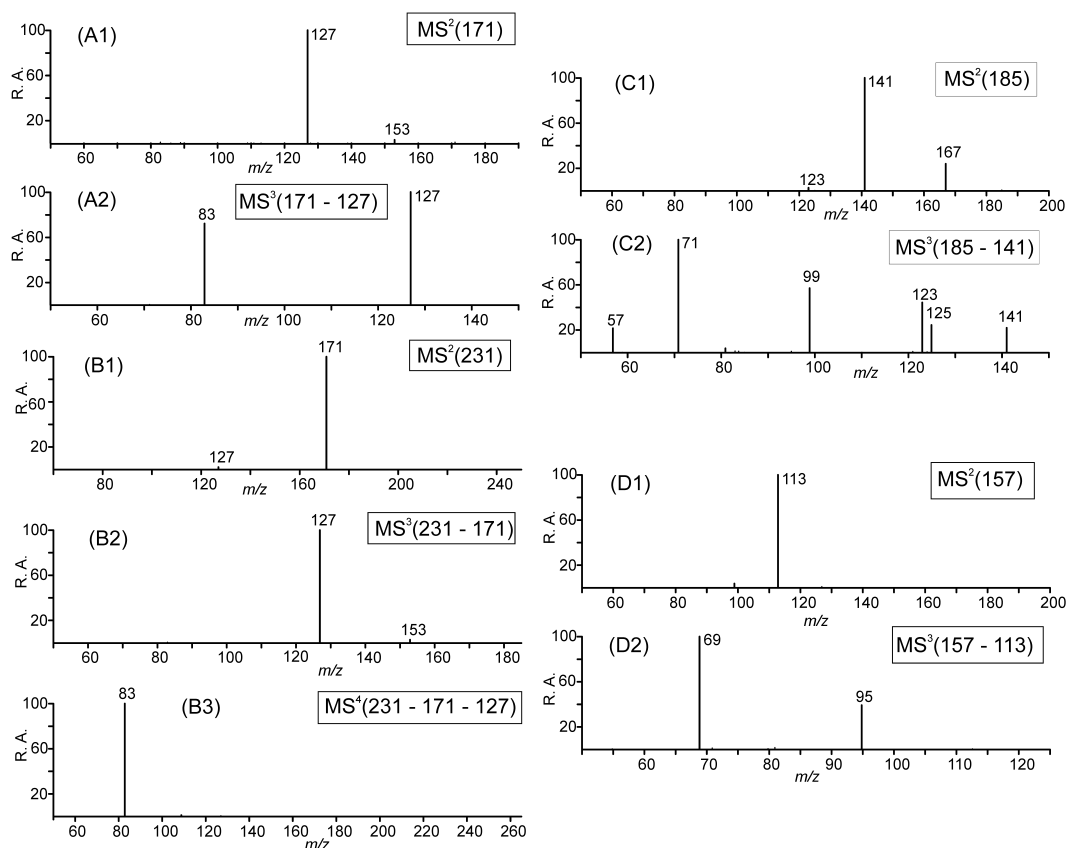
The  $m/z$  185 EIC obtained for  $\alpha$ - and  $\beta$ -pinene ozonolysis SOA (Fig. 1) shows a prominent peak at RT 20.9 min, which is assigned to *cis*-pinic acid, known to be formed through both ozonolysis and OH radical-initiated reactions (e.g., Yu et al., 1999; Glasius et al., 2000; Larsen et al., 2001; Winterhalter et al., 2003; Ng et al., 2007). For comparison reasons (see next section), (–)ESI-MS data for *cis*-pinic acid are presented in Fig. 3c and Scheme 1c. The second  $m/z$  185 compound present in  $\beta$ -pinene ozonolysis SOA at RT 18.8 min corresponds to a new and specific  $\beta$ -pinene SOA tracer, which is tentatively identified as a homolog of terpenylic acid, i.e., homoterpenylic acid, based on detailed interpretation of (–)ESI-MS data. (–)ESI-MS data for homoterpenylic acid are presented in Fig. 4 and Scheme 2. Comparison of the MS data obtained for *cis*-pinic acid (Fig. 3c, Scheme 1c) and homoterpenylic acid (Fig. 4, Scheme 2) show that the isobaric compounds can be differentiated on the basis of the  $m/z$  185  $\rightarrow$   $m/z$  141  $\text{MS}^3$  product ion spectrum; in the case



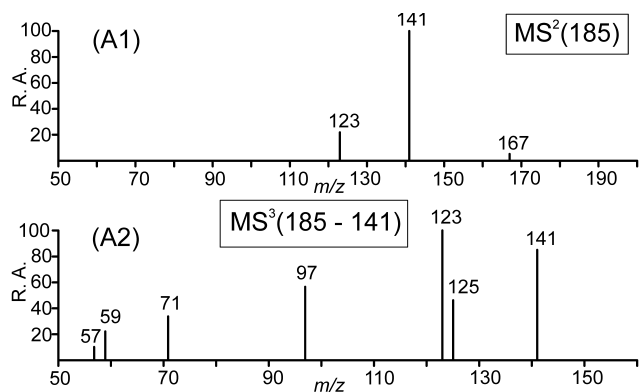
**Fig. 2.** LC/MS chromatographic data (BPC and EICs) for fine ambient aerosol ( $\text{PM}_{2.5}$ ) from K-puszt, Hungary, collected during the night of 19 June 2006 of the warm period of the 2006 summer field campaign. The peak at RT 22.1 min (not discussed in the main text) on the  $m/z$  185 EIC is tentatively assigned to *cis*-caronic acid, a positional isomer of *cis*-pinic acid, based on comparison of its chromatographic properties with literature data (Larsen et al., 2001).

of *cis*-pinic acid fragmentation of  $m/z$  141 results in  $m/z$  99 through loss of 42 u (propene), while in the case of homoterpenylic acid  $m/z$  141 produces  $m/z$  97 through loss of 44 u ( $\text{CO}_2$ ). It can also be seen that the relative abundance of  $m/z$  123 in the  $m/z$  185  $\text{MS}^2$  product ion spectrum is the highest in the case of homoterpenylic acid (i.e., 20% vs. 2% for *cis*-pinic acid). A possible formation pathway of homoterpenylic acid involving reaction of  $\beta$ -pinene with OH radicals (which are also generated in the ozonolysis experiments since no OH scavenger was used), similar to that proposed for terpenylic acid (Claeys et al., 2009), is provided in the supplement (Sect. 3: Scheme S2).

The  $m/z$  231 EIC contains four distinct peaks; the first two peaks with RTs 17.3 and 19.8 min are interpreted as non-covalent adducts formed between acetic acid (present in the LC eluent) and the MW 172 compounds (i.e., terpenylic and *cis*-norpinic acid), while the last two peaks with RTs 20.6 and 22.1 min correspond to isobaric MW 232 compounds. Of these, the peak with RT 20.6 min is assigned to diaterpenylic acid acetate, which has recently been reported as a SOA tracer for the photooxidation of 1,8-cineole (Inuma et al.,



**Fig. 3.** (–)ESI-MS data for authentic reference compounds of (A) terpenylic acid, (B) diaterpenylic acid acetate, (C) *cis*-pinic acid, and (D) terebic acid.



**Fig. 4.** (–)ESI-MS data for the SOA product formed upon ozonolysis of  $\beta$ -pinene with RT 18.8 min (Fig. 1B), tentatively assigned to homoterpenylic acid.

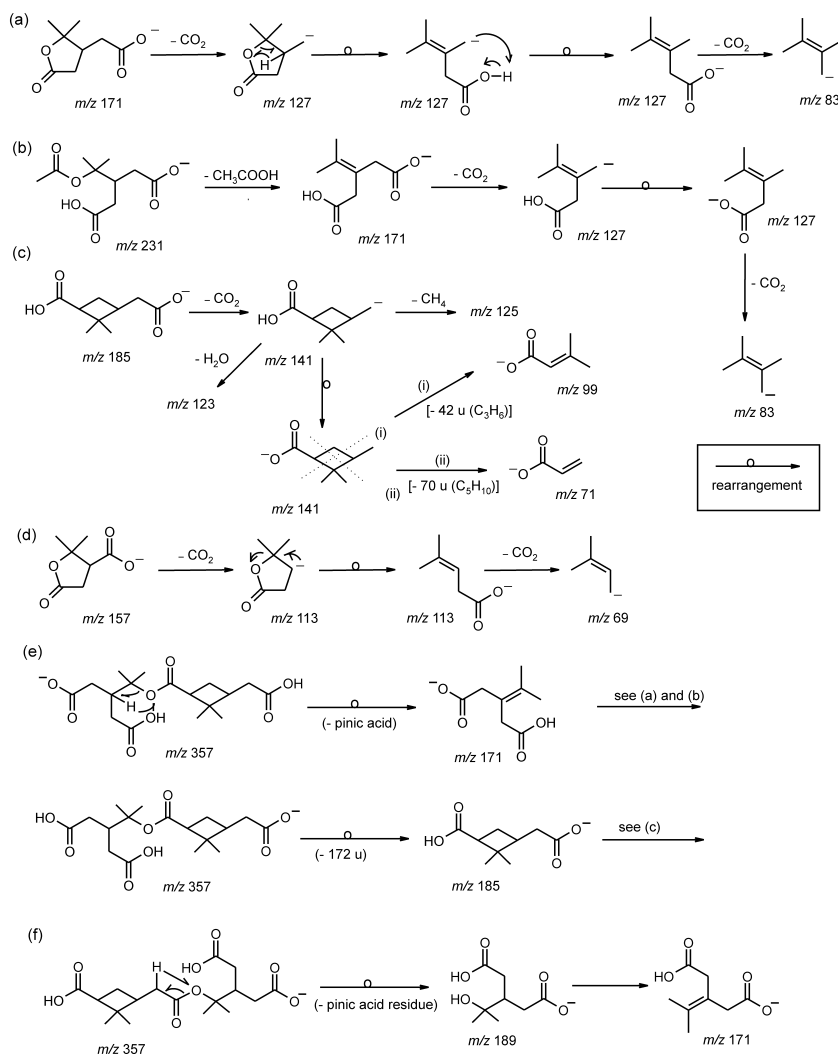
2009) and for the photooxidation and ozonolysis of  $\alpha$ -pinene (Claeys et al., 2009). The last eluting *m/z* 231 compound with RT 22.1 min corresponds to an isobaric compound of diaterpenylic acid acetate, a new compound which still remains to be elucidated. In this respect, it has been reported by Iinuma et al. (2004, 2005) that three isomers of a MW 232

compound are detected in  $\alpha$ -pinene ozonolysis SOA using capillary electrophoresis/(–)ESI-MS. (–)ESI-MS data for the isobaric MW 232 compound with RT 22.1 min are given in the supplement (Sect. 4: Fig. S2).

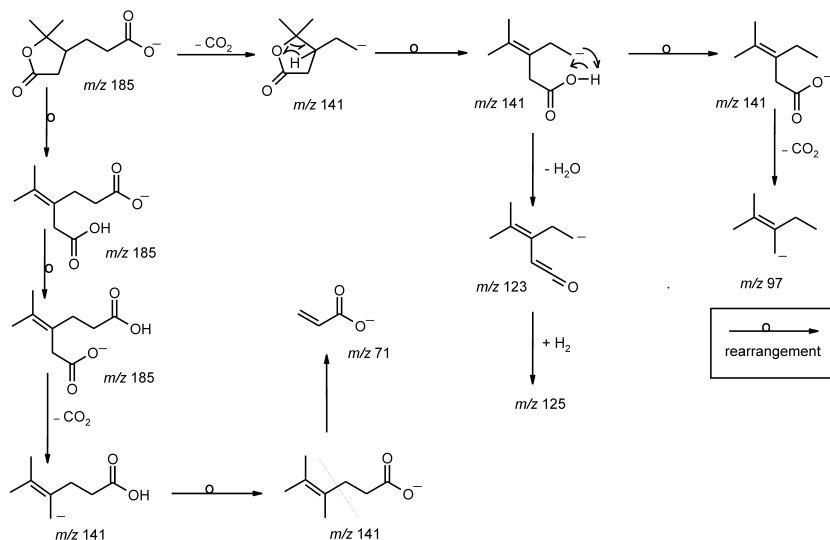
Comparison of the chromatographic data for  $\alpha$ - and  $\beta$ -pinene SOA and ambient samples from K-pusztas shows the presence of all the terpenoic acids mentioned above in all samples. The data obtained for a nighttime sample of the warm period of the campaign are illustrated in Fig. 2. It is noted that the relatively abundant MW 358 compound (*m/z* 357) is only detected in the nighttime samplings of the warm period. Hence, an effort was done to structurally characterize the MW 358 compound and related weak MW 358 and 344 compounds.

### 3.2 Structural characterization of MW 358 dimeric compounds

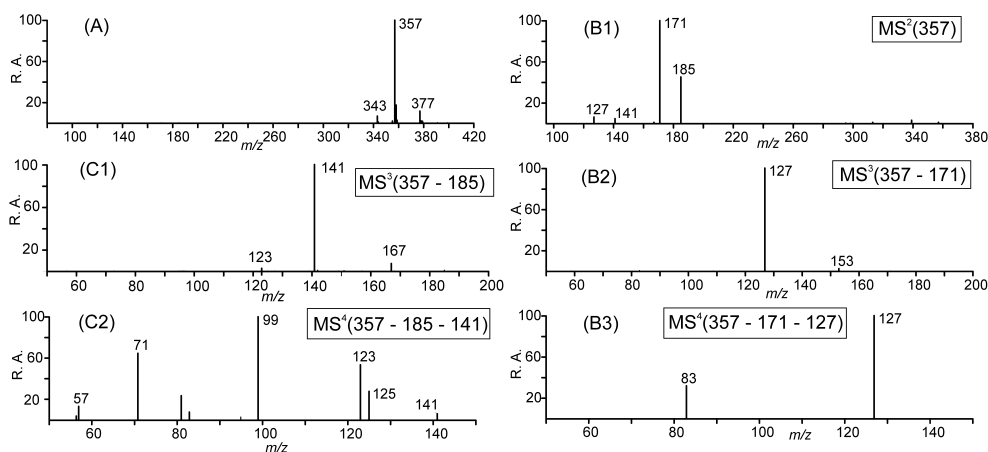
Figure 5 presents the (–)ESI-MS data for the relatively abundant MW 358 compound that can be detected at RT 24.7 min in  $\alpha$ -pinene ozonolysis SOA. Exactly the same product ion data were obtained for the MW 358 compound in the ambient nighttime sample (supplement; Sect. 5: Fig. S3), while some differences were observed for the relatively abundant



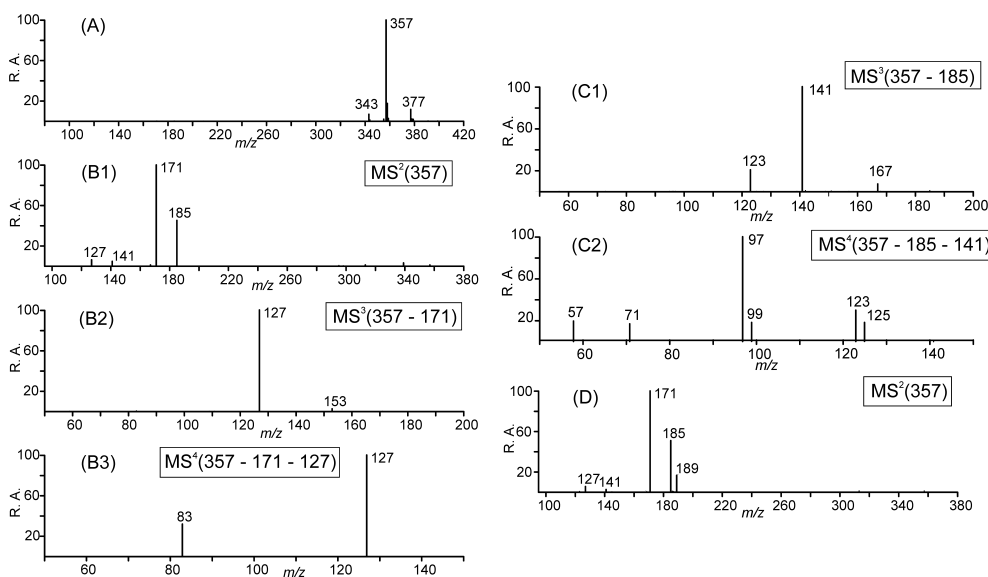
**Scheme 1.** Proposed (–)ESI-MS fragmentation pathways for deprotonated (a) terpenylic acid, (b) diaterpenylic acid acetate, (c) *cis*-pinonic acid, (d) terebic acid, and the (e) relatively abundant and (f) weak MW 358 compounds.



**Scheme 2.** Proposed (–)ESI-MS fragmentation pathways for deprotonated homoterpenylic acid.



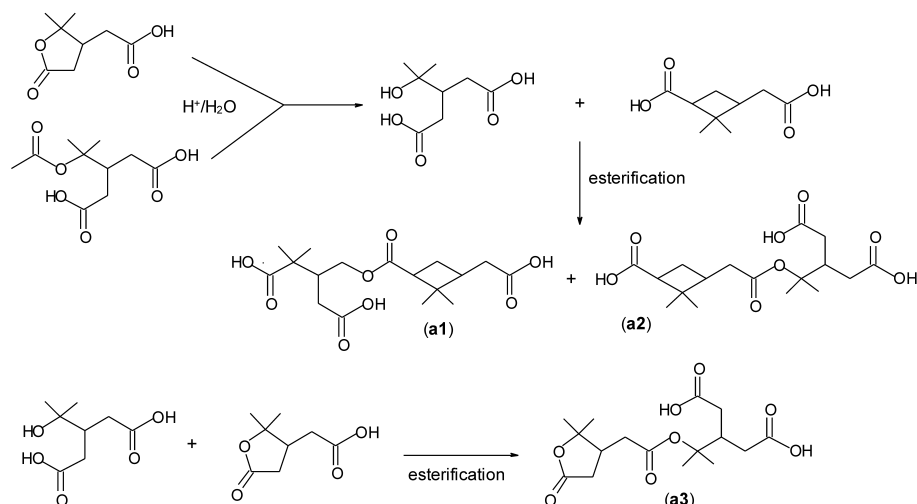
**Fig. 5.** (–)ESI-MS data for the relatively abundant MW 358 compound (RT 24.7 min; Fig. 1A) present in  $\alpha$ -pinene ozonolysis SOA, assigned to a covalent dimer of the ester type: (A) first-order mass spectrum; (B1)  $m/z$  357  $MS^2$  spectrum; (B2) and (B3)  $m/z$  357  $\rightarrow$   $m/z$  171  $MS^n$  ( $n = 3, 4$ ) spectra; and, (C1) and (C2)  $m/z$  357  $\rightarrow$   $m/z$  185  $MS^n$  ( $n = 3, 4$ ) spectra.



**Fig. 6.** (–)ESI-MS data for the relatively abundant MW 358 compound (RT 24.7 min; Fig. 1B) present in  $\beta$ -pinene ozonolysis SOA, assigned to a covalent dimer of the ester type: (A) first-order mass spectrum; (B1)  $m/z$  357  $MS^2$  spectrum; (B2) and (B3)  $m/z$  357  $\rightarrow$   $m/z$  171  $MS^n$  ( $n = 3, 4$ ) spectra; and, (C1) and (C2)  $m/z$  357  $\rightarrow$   $m/z$  185  $MS^n$  ( $n = 3, 4$ ) spectra. (D)  $m/z$  357  $MS^2$  spectrum for the weak MW 358 compound at RT 23.0 min (Fig. 1B).

MW 358 compound in  $\beta$ -pinene ozonolysis SOA (Fig. 6) (see below). The relatively abundant higher-MW 358 compound in  $\alpha$ -pinene ozonolysis SOA is assigned to a covalent dimer of the ester type containing diaterpenylic acid and *cis*-pinic acid as monomeric building units, based on mass spectral considerations. The first-order mass spectrum (Fig. 5a) shows in addition to the deprotonated molecule  $[M-H]^-$  ( $m/z$  357) an ion at  $m/z$  377 which could not be assigned and an ion at  $m/z$  343 due to co-elution of a homologous MW 344 species (see below). The  $m/z$  357  $MS^2$  spectrum (Fig. 5b1) shows two abundant product ions at  $m/z$  185 and 171, of which  $m/z$  185 upon further fragmentation reveals a pattern (Fig. 5c) comparable to that observed for deprotonated *cis*-

pinic acid (Fig. 3c). Further fragmentation of  $m/z$  171 reveals a pattern (Fig. 5b) similar to that observed for deprotonated terpenylic acid and for further fragmentation ( $MS^2$ ) of  $m/z$  171 formed through loss of acetic acid from deprotonated diaterpenylic acid acetate (Fig. 3b). It is noted that there are differences in the relative abundances of the product ions, a feature that can be explained by a different internal energy of the first- ( $MS^2$ ) and second-generation ( $MS^3$ ) precursor ions. Precursor ions with a higher internal energy will namely result in more extensive fragmentation upon  $MS^2$  or  $MS^3$  collisional activation experiments. Although (–)ESI-MS data are not available for diaterpenylic acid, which is proposed to serve as an intermediate in dimer formation (see



**Scheme 3.** Proposed formation mechanism for the MW 358 and 344 compounds related to terpenylic acid and diaterpenylic acid acetate.

below), it is expected to result in  $m/z$  171 through loss of a molecule of water from the deprotonated molecule (similar to the loss of acetic acid from protonated diaterpenylic acid acetate).

The formation of the MW 358 compound can be explained by esterification of *cis*-pinic acid with diaterpenylic acid, which can be generated as an intermediate by acid-catalyzed hydrolysis of terpenylic acid and/or diaterpenylic acid acetate (Scheme 3). In this respect, it has recently been demonstrated that esterification is an important route to the formation of higher-MW products in  $\alpha$ -pinene ozonolysis SOA and that *cis*-pinic acid is a key monomeric unit (Müller et al., 2008).

Since *cis*-pinic acid contains two carboxyl groups, two isomeric diester structures are possible. In order to determine which positional isomeric structure belongs to the relatively abundant MW 358 compound, we also recorded data for the weak MW 358 compound present in  $\beta$ -pinene ozonolysis SOA at RT 23.0 min (Fig. 1b). Selected (–)ESI-MS data (i.e., the  $m/z$  357  $MS^2$  spectrum) for the weak MW 358 compound are given in Fig. 6d. The higher-order  $MS^n$  spectra were consistent with diaterpenylic and *cis*-pinic monomeric units (not shown). Compared to the  $m/z$  357  $MS^2$  spectrum of the relatively abundant MW 358 compound (Fig. 5b1) it can be seen that the spectrum for the weak isomer (Fig. 6d) contains an additional product ion at  $m/z$  189. The latter ion is explained by a neutral loss of 188 u corresponding to *cis*-pinic acid, which can only readily occur in the isomer where the ester linkage is at the carboxylmethyl side (Scheme 3). On the basis of these considerations structures a1 and a2 are tentatively attributed to the relatively abundant and weak MW 358 compounds, respectively. A possible explanation for the favorable ester formation at the carboxyl (attached to the dimethylcyclobutane ring) instead of the carboxylmethyl side of *cis*-pinic acid is that there is a lower conformational flexibility at this side, facilitating ester formation.

With respect to differences observed between the relatively abundant MW 358 diester in  $\alpha$ - and  $\beta$ -pinene ozonolysis SOA, it can be seen that the  $m/z$  357  $\rightarrow$   $m/z$  185  $\rightarrow$   $m/z$  141  $MS^4$  product ion spectrum in the case of  $\beta$ -pinene shows an additional  $m/z$  97 product ion (Fig. 6c2), which is typical for homoterpenylic acid (Fig. 4). It can also be noted that the  $m/z$  357  $\rightarrow$   $m/z$  185  $MS^3$  product ion spectrum (Fig. 6c1) is more similar to the  $m/z$  185  $MS^2$  spectrum of homoterpenylic acid (i.e., the relative abundance of  $m/z$  123 is 20%). Hence, it cannot be ruled out that the relatively abundant MW 358 diester in  $\beta$ -ozonolysis SOA contains a major contribution from a dimer formed between diaterpenylic and homoterpenylic acid.

### 3.3 Structural characterization of MW 344 dimeric compounds

The  $m/z$  343 EICs obtained for  $\alpha$ - and  $\beta$ -pinene ozonolysis SOA (Fig. 1) show two major peaks with RTs 17.3 and 24.7 min. The first one is attributed to strong non-covalent dimer formation of terpenylic acid upon (–)ESI-MS, a phenomenon that has been addressed in detail in Claeys et al. (2009) and has been attributed to the presence of one free carboxylic acid group that does not participate in intramolecular hydrogen bonding interactions. It is worth noting that such type of dimer formation is not observed for *cis*-norpinic acid (RT 19.8 min), consistent with the strong non-covalent dimer-forming properties of terpenylic acid. The second major  $m/z$  343 compound is due to a MW 344 compound that co-elutes with the relatively abundant MW 358 compound (Fig. 5a). (–)ESI-MS data are presented in the supplement (Sect. 6: Fig. S4). This MW 344 compound is attributed to a homolog of the relatively abundant MW 358 compound, which can be explained by reaction between diaterpenylic acid, a homolog of diaterpenylic acid, and *cis*-pinic acid. A close inspection of the (–)ESI-MS data indeed reveals that the



precursor of diaterebic acid, terebic acid, is detected at  $m/z$  157 (RT 15.8 min) with an abundance of about 21%, 13.9%, and 85% of that of terpenylic acid for  $\alpha$ - and  $\beta$ -pinene SOA, and the ambient sample, respectively. (–)ESI-MS data for terebic acid are presented in Fig. 3d and Scheme 1d. Terebic acid can be regarded as a processed derivative of terpenylic acid; its possible formation route through further reaction of terpenylic acid with OH radicals (aging) is presented in the supplement (Sect. 7: Scheme S3). Similar to terpenylic acid, terebic acid was found to exhibit strong non-covalent dimer-forming properties in (–)ESI-MS (not shown). Furthermore, this MW 344 compound could also be detected in the ambient samples of the warm period of the 2006 summer field campaign conducted at K-pusztá (not shown).

It can also be seen that the  $m/z$  343 EICs for  $\alpha$ - and  $\beta$ -pinene ozonolysis SOA (Fig. 1) show minor signals at RTs 23.0 and 23.6 min. The data obtained for the peak at RT 23.0 min were similar to those for the major peak at RT 24.7 min (not shown); on the basis of these data this minor peak is attributed to a homolog of the weak MW 358 compound (i.e., the dimer where the diaterebic acid residue is at the carboxymethyl side of *cis*-pinic acid). The weak MW 344 compound eluting at RT 23.6 min is assigned to a dimer of the ester type containing solely terpenylic and diaterebic acid units (Scheme 3; structure a3). (–)ESI-MS data for the latter compound are presented in the supplement (Sect. 8: Fig. S5). Similar data were also recorded for the ambient samples of the warm period of the 2006 summer field campaign conducted at K-pusztá (not shown).

In addition, we evaluated whether the higher-MW 368 product reported by Müller et al. (2008), which corresponds to a diester formed between *cis*-pinic acid and 10-hydroxypinonic acid, was present in our samples. We also compared its abundance with that of the relatively abundant 358 compound. The MW 368 compound could be detected at RT 25.9 min for  $\alpha$ - and  $\beta$ -pinene ozonolysis SOA, and the ambient sample, with an abundance of about 54%, 1.5%, and 54% of that of the relatively abundant MW 358 compound, respectively. Furthermore, we evaluated whether higher-MW dimers (MW 372) formed between *cis*-pinic acid and the hydrolysis product of homoterpenylic acid (i.e., dihomoterpenylic acid) could be detected in  $\beta$ -pinene ozonolysis SOA and the ambient samples considering that homoterpenylic acid is present in these samples, but no evidence could be found for them.

#### 4 Conclusions

The results of this study are consistent with terpenylic acid and related terpenoic acids (i.e., diaterebic acid and terebic acid) serving together with *cis*-pinic acid as monomeric precursors for a relatively abundant MW 358 dimeric compound as well as for structurally related weak MW 358 and 344 compounds in  $\alpha$ -/ $\beta$ -pinene ozonolysis

SOA. Our study is in line with previous studies (Hamilton et al., 2006; Müller et al., 2008) that provided evidence for esterification being an important route to dimer formation in ozonolysis SOA. Moreover, our study demonstrates that esterification reactions are important to generate higher-MW compounds in ambient aerosol. It is shown that the dimeric  $\alpha$ -/ $\beta$ -pinene SOA tracers with MWs 358 and 344 could only be detected in the nighttime samplings of the warm period of the 2006 K-pusztá summer field campaign. This suggests that their formation in the ambient atmosphere occurs at a relatively high temperature (daily maximum temperature  $>24$  °C) and a long time-scale. This behavior contrasts with the fast formation of the MW 358 diester in  $\alpha$ - and  $\beta$ -pinene ozonolysis experiments, where it is formed concurrently with the corresponding monomeric precursors (Hoffmann et al., 1998; Müller et al., 2008; Gao et al., 2010). A possible reason for this discrepancy could be related to the observation that *cis*-pinic acid, a monomeric building unit of the higher-MW dimers, shows a strong diel variation at the K-pusztá forest site and is only present at substantial concentrations in ambient fine nighttime aerosol (Kourtchev et al., 2009). Further work is warranted to define the ambient conditions under which the monoterpene SOA diester products are formed, and to assess their occurrence in other forested environments and their usefulness as SOA tracers.

#### Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/10/9383/2010/acp-10-9383-2010-supplement.pdf>.

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