Terpenylic Acid and Related Compounds from the Oxidation of α-Pinene: Implications for New Particle Formation and Growth above Forests

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Novel secondary organic aerosol (SOA) products from the monoterpene α-pinene with unique dimer-forming properties have been identified as lactone-containing terpenoic acids, i.e., terpenylic and 2-hydroxyterpenylic acid, and diaterpenylic acid acetate. The structural characterizations were based on the synthesis of reference compounds and detailed interpretation of mass spectral data. Terpenylic acid and diaterpenylic acid acetate are early oxidation products generated upon both photooxidation and ozonolysis, while 2-hydroxyterpenylic acid is an abundant SOA tracer in ambient fine aerosol that can be explained by further oxidation of terpenylic acid. Quantum chemical calculations support that noncovalent dimer formation involving double hydrogen bonding interactions between carboxyl groups of the monomers is energetically favorable.

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The molecular properties allow us to explain initial particle formation in laboratory chamber experiments and are suggested to play a role in new particle formation and growth above forests, a natural phenomenon that has fascinated scientists for more than a century.

Introduction

Blue haze is a natural phenomenon that is observed in forested regions worldwide and is due to the formation of tiny (<100 nm) secondary organic aerosol (SOA) particles from the oxidation of biogenic volatile organic compounds (BVOCs) (*1*). SOA formation from BVOCs can be simulated in laboratory chamber experiments and involves nucleation and condensation of low-volatility oxygenated compounds. On the basis of such experiments, it is assumed that new particle formation and growth above forests require oxidation products of monoterpenes such as α-/β-pinene (*2, 3*). While evidence exists for organic molecular clusters in the size range of <3 nm (*4*), the chemical structures of the nucleating particles have remained unresolved. Knowledge on the chemical composition of α-/β-pinene SOA is also crucial to gaining basic insights into atmospheric chemistry processes involved in fine aerosol formation from biogenic origin as well as for SOA source characterization.

Tentative structural proposals have been made in previous work for organic compounds that participate in new particle formation and growth. Considerable attention has been given to a high-molecular weight (MW) 358 product from α-pinene ozonolysis (*5, 6*), which was first detected by direct negative ion atmospheric pressure chemical ionization−mass spectrometry [(−)APCI-MS] and tentatively assigned to a non-covalent adduct formed in the ion source between *cis*-pinic (MW 186) and *cis*-norpinic (MW 172) acids, both major ozonolysis products (*5*). In the present study, we examined terpenoic acids from the oxidation of α-pinene with MWs of 172, 188, and 232, compounds that are present in α-pinene SOA as well as in ambient fine (PM2.5, particulate matter with aerodynamic diameter <2.5 μm) aerosol and show non-covalent dimer-forming properties upon electrospray ionization in the negative ion mode [(−)ESI]. Both the compounds with MWs of 172 and 232 have been reported in laboratory (*5, 7−10*) and field studies (*11, 12*); assignment of the compound with a MW of 172 to *cis*-norpinic acid was scrutinized (*7−9*), while for the α-pinene SOA product with a MW of 232, tentative structures were proposed (*11−13*). We demonstrate that the α-pinene-related products with MWs 172 and 188 can be assigned to the lactone-containing terpenoic acids, terpenylic and 2-hydroxyterpenylic acids, respectively, while the compound with MW of 232 corresponds to diaterpenylic acid acetate, which has recently been reported as a 1,8-cineole SOA tracer (*14*). The MW 172 α-pinene SOA product identified here as terpenylic acid is known to be formed in the early stages of SOA formation from the photooxidation and ozonolysis of α-pinene with a high yield (*5, 8*) (i.e., higher or comparable to that of *cis*-pinonic and/or *cis*-pinic acid). Interestingly, terpenylic acid was reported in the early German chemical literature as an oxidative degradation product of monoterpenoids (*15*). Using quantum chemical calculations, we show that noncovalent dimer formation is energetically favorable for terpenylic acid. Hence, it is strongly suggested that terpenylic acid and related compounds participate in new particle formation and growth above forests.

Experimental Section

Aerosol Samples. α-Pinene secondary organic aerosol (SOA) for structural characterization was obtained from photo-oxidation experiments carried out in Caltech's dual indoor 28 m³ Teflon smog chambers as reported in a previous study (*16*). A composited sample (3.8 mg) was prepared to obtain sufficient material for various types of mass spectrometric analyses from five experiments that were carried out under different conditions (Table 2 in ref *15*), i.e., H_2O_2/neutral (low-NO$_x$), H_2O_2/highly acidic (low-NO$_x$), H_2O_2/NO/neutral (intermediate-NO$_x$), HONO/neutral (high-NO$_x$), and HONO/acidic (high-NO$_x$). The sample was dissolved in 1 mL of methanol. For liquid chromatography/mass spectrometry (LC/MS) experiments a part of the sample was diluted with the same volume of water and an aliquot of 5 μL was injected. Experimental details about the α-pinene ozonolysis samples are given in Supporting Information (section S1).

Ambient aerosol samples were collected from the state forest "De Inslag", Brasschaat, during the 2007 summer period (i.e., from 5 June until 13 July) using a high-volume dichotomous sampler providing two fractions of different sizes, a fine fraction (PM$_{2.5}$, particulate matter with aerodynamic diameter <2.5 μm) and a coarse size fraction (with aerodynamic diameter >2.5 μm). Day- and night-time samples were collected. The sampling site is located in a mixed coniferous/deciduous forest about 12 km NE of Antwerp and is heavily impacted by anthropogenic activities. For the selected daytime samplings (7 and 8 June (Figure 1)) the average temperatures were 24 and 23 °C, while the average ozone concentrations were 57 and 38 ppb, respectively. A quarter of the PM$_{2.5}$ quartz fiber filter was extracted with methanol, the residue was redissolved in 150 μL of a methanol/water (1:1, v/v) mixture, and an aliquot of 3 μL (corresponding to 6.7 μg of organic carbon) was injected for LC/MS analysis. For accurate mass measurements, a pooled day-/night-time sample from 7 June (191 μg organic carbon) was used, the residue redissolved in 150 μL of a 0.1% acetic acid in methanol/0.1% acetic acid in water (1:1, v/v) solvent mixture, and an aliquot of 5 μL was injected onto the ultra performance LC/MS system.

Mass Spectrometric Analyses. *Liquid Chromatography/Mass Spectrometry.* 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 Fisher, San Jose, USA). A T3 Atlantis C18 column (3 μm; 2.1 × 150 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 elution 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 mL min^{-1}. The linear ion trap was operated under the following conditions: sheath gas flow (nitrogen), 0.75 L min^{-1}; auxiliary gas flow (nitrogen), 1.5 L min^{-1}; source voltage, −4.5 kV; capillary temperature, 350 °C; and maximum ion injection time, 200 ms. For MS^2 and MS^3 experiments, an isolation width of 2 *m/z* units and a normalized collision energy level of 35% were applied, unless mentioned otherwise. Additional information Figure 1 (i.e., normalization level): Figure 1A (BPC, 1.65 10^5; *m/z* 171 EIC, 1.24 10^5; *m/z* 187 EIC, 2.84 10^4; *m/z* 231 EIC, 1.65 10^5); Figure 1B (BPC, 1.18 10^5; *m/z* 171 EIC, 4.51 10^4; *m/z* 187 EIC, 7.30 10^4; *m/z* 231 EIC, 2.73 10^4).

High-Resolution Mass Spectrometry. Accurate mass measurements for selected α-pinene SOA samples and the ambient filter were performed with a Waters LCT Premier XT time-of-flight mass spectrometer (TOFMS) equipped with an ESI source, and interfaced to a Waters ultra performance liquid chromatography (UPLC) system. Details about the

UPLC/(−)ESI-TOFMS technique are given in ref *16*. The accurate mass data are summarized in Table S1 of Supporting Information (section S3).

Preparation of Standards. See Supporting Information (section S2).

Quantum Chemical Calculations. All calculations were performed on isolated molecules using the Gaussian 03 suite of programs (*17*) in combination with the RELAX program, which is part of the BRABO suite of programs (*18*), applying the density functional (DFT) level of theory, using the B3LYP (*19*) functional and the 6-311+G* basis set, as it is implemented in Gaussian 03. Single-point and gradient calculations were performed using Gaussian 03, while geometry steps were made using the RELAX program. Dimerization energies were corrected only for the basis set superposition error (BSSE) using the counterpoise (CP) formalism.

Results and Discussion

Characterization of Terpenylic Acid, 2-Hydroxyterpenylic Acid, and Diaterpenylic Acid Acetate in α-Pinene SOA and Fine Ambient Aerosol. Figure 1 shows liquid chromatography (LC)/(−)ESI-MS data (i.e., base peak chromatograms (BPCs) and extracted ion chromatograms (EICs)) obtained for (A) α-pinene SOA and (B) daytime PM$_{2.5}$ aerosol from a forested site. It can be seen that the compounds with MWs of 172 and 232 are major products in α-pinene SOA and are also present in the ambient sample, while the compound with a MW of 188 is abundant in the ambient sample but is only minor in α-pinene SOA. A notable feature is noncovalent dimer formation upon (−)ESI, a soft ionization technique that operates at atmospheric pressure and hence can be regarded as a screening technique for dimer-forming molecules of potential atmospheric relevance. The first-order mass spectra clearly show a signal due to the homodimer (i.e., for the MW 172 and 188 compounds [2M − H]$^-$ at *m/z* 343 and 375, respectively (Figure 1C and E, respectively), for the MW 232 compound [2M + Na − 2H]$^-$ at *m/z* 485 (Figure 1D)). In contrast, *cis*-pinic acid (MW 186), a C_9-dicarboxylic acid, did not reveal dimer formation under the same conditions, suggesting that the dimer-forming properties of the three compounds are unique.

The structural elucidations were based on MS data obtained in the (−)ESI mode and comparison of MS and LC data with synthesized reference compounds. Here, we only present MS data for the MW 172 compound; data for the compounds with MWs 232 and 188 are provided in Supporting Information (section S4). The elemental composition of the deprotonated compound with MW of 232 ($C_{10}H_{15}O_6$) and its MS and LC behaviors lead to its identification as diaterpenylic acid acetate (IUPAC name: 3-[1-(acetyloxy)-1-methylethyl]pentanedioic acid), while the MS data of the deprotonated compound with MW of 172 ($C_8H_{11}O_4$) points to a close relationship with the latter compound and leads to its assignment as terpenylic acid (IUPAC name: 2-(2,2-dimethyl-5-oxooxalan-3-yl)acetic acid). The compound with MW of 188 ($C_8H_{11}O_5$) was elucidated as 2-hydroxyterpenylic acid (IUPAC name: tetrahydro-2-hydroxymethyl-2-methyl-5-oxo-3-furylacetic acid).

(−)ESI-MS data for the α-pinene SOA product with MW of 172 are presented in Figures 1C and 2, and Scheme 1. The (−)ESI-MS and LC data agreed perfectly with those of a synthesized reference compound (results not shown). The first-order (−)ESI mass spectrum (Figure 1C) shows ions at *m/z* 171 [M − H]$^-$ and *m/z* 343 [2M − H]$^-$. The accurate masses indicated elemental compositions of $C_8H_{11}O_4$ and $C_{16}H_{23}O_8$, respectively. The ion at *m/z* 187 is due to coeluting compounds, which are attributed to *mono*-aldehydic precursors of 3-methyl-1,2,3-butanetricarboxylic acid (Supporting Information, S5). The *m/z* 343 MS^2 product ion spectrum (Figure 2A) indicates that the *m/z* 343 precursor fragments
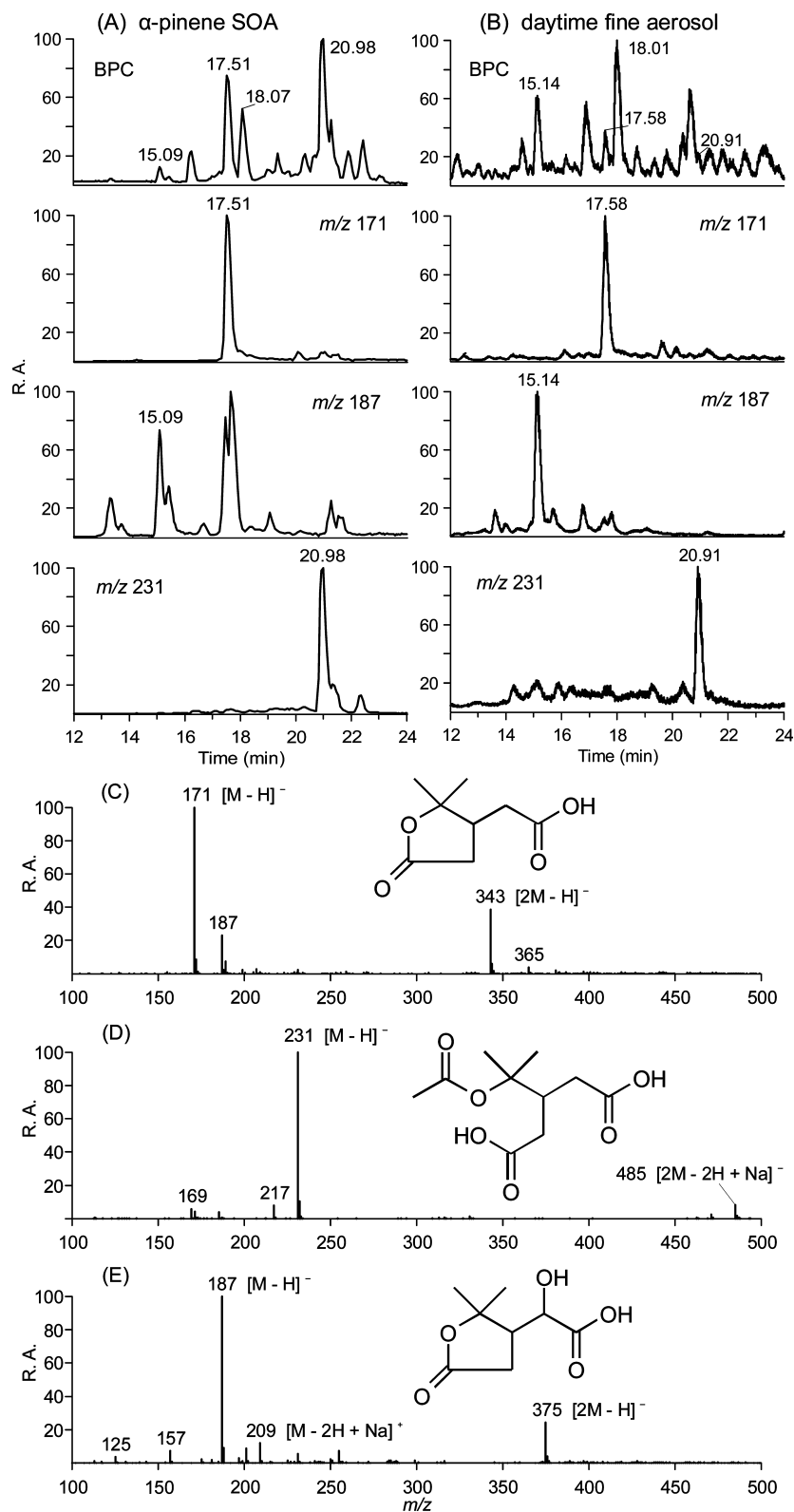
FIGURE 1. LC/(−)ESI-MS data (base peak chromatograms (BPCs) and extracted ion chromatograms (EICs)) for (A) α-pinene SOA and (B) PM$_{2.5}$ daytime aerosol from Brasschaat, Belgium, collected on a warm summer day (8 June, 2007). The major compound eluting around 18 min was identified as 3-methyl-1,2,3-butanetricarboxylic acid (*34*). First-order (−)ESI mass spectra of (C) the compound with MW 172 (α-pinene SOA) eluting at 17.51 min, (D) the compound with MW 232 (α-pinene SOA) eluting at 20.98 min, and (E) the compound with MW 188 (ambient sample) eluting at 15.14 min. The signals at *m/z* 343 (C), *m/z* 485 (D), and *m/z* 375 (E) are attributed to noncovalent homodimer formation, while the *m/z* 187 peak in C is assigned to *mono*-aldehydic precursors of 3-methyl-1,2,3-butanetricarboxylic acid. Additional information on the *m/z* 187 compounds is given in Supporting Information (section S5).

to *m/z* 171, the deprotonated monomer. Lowering of the collision energy level showed that the onset of fragmentation already occurs at a very low value (i.e., 10%), consistent with

a noncovalent adduct. It is noted that the hydrogen bonding in the carboxylic acid−carboxylate anion complex (Scheme 1) is expected to be stronger than that for the neutral system
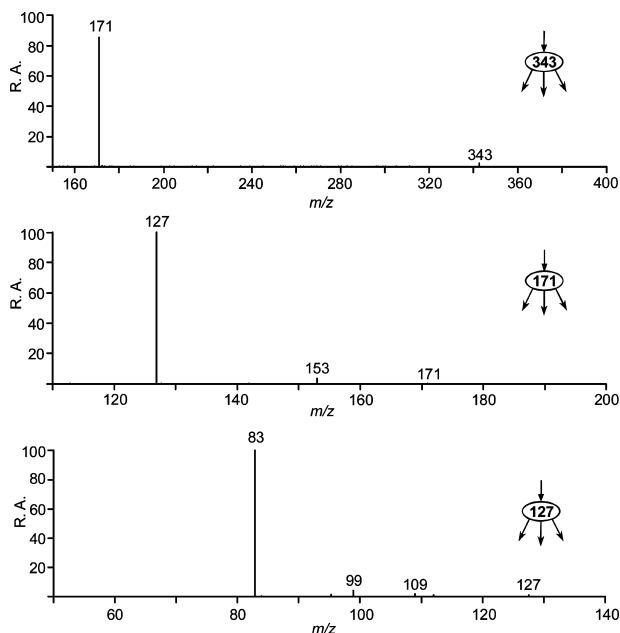
FIGURE 2. (−)ESI-MS data for the compound with MW 172 from α-pinene SOA, identified as terpenylic acid: (A) *m/z* 343 MS²; (B) *m/z* 171 MS²; and (C) *m/z* 171 → *m/z* 127 MS³.

(*20*); quantum chemical calculations indicate that the dimerization energy for the carboxylic terpenylic acid–carboxylate anion complex is −34.6 kcal mol⁻¹, which is substantially higher than that for the neutral case (−17.0 kcal mol⁻¹), implying that the (−)ESI-MS technique is a very sensitive probe for screening neutral molecules with dimer-forming properties of potential atmospheric relevance. With regard to the dimeric cluster anion [2M − H]⁻, only homodimeric species are detected here (i.e., for terpenylic acid at *m/z* 343). Unlike during LC where monomers are separated and only homodimers can be detected upon (−)ESI-MS, heterodimers could be formed when monomers are simultaneously generated as in chamber experiments and are analyzed without prior chromatography (*5*).

Formation Mechanisms for Terpenylic Acid and Diaterpenylic Acid Acetate. Scheme 2 proposes formation pathways for diaterpenylic acid acetate (DTAA) and terpenylic acid (TA) through OH radical-initiated oxidation of α-pinene, involving a hydroxyl alkyl radical intermediate (*21*). The formation of 2-hydroxyterpenylic acid can be explained by further oxidation of terpenylic acid, likely involving oxidation reactions in the particle phase. Both DTAA and TA can also be generated through O₃-initiated reactions, involving cam-pholenic aldehyde as an intermediate (Supporting Information, S3). For new particle formation and growth above forests, however, it is more likely that OH radical chemistry plays a role since events are clearly linked to photooxidation and not affected by ozone concentrations (*11*). Moreover, it could be shown in plant reaction chamber experiments where ozone was present that addition of the OH radical greatly enhanced new particle formation and growth from pine and spruce emissions, which are known to contain α-pinene as a major component (*22*).

Noncovalent Dimer-Forming Properties of Terpenylic Acid. We consider here noncovalent dimer formation from terpenylic acid, where the carboxyl group is available for double hydrogen bonding interactions. Quantum chemical calculations support that dimer formation from neutral terpenylic acid is energetically favorable; the dimerization energy is −17.0 kcal mol⁻¹, indicating that the dimeric cluster is stable in the gas phase (Figure 3). This value is comparable to the dimerization energy of acetic acid, which is known to exist as a dimer in the gas phase (*23*), and to that reported

for *cis*-pinonic acid (*24*). Noncovalent dimer formation can also be explained for diaterpenylic acid acetate, where two carboxyl groups are available for hydrogen bonding, and the second one can support interaction with additional terpenoic acids and thus contribute to particle growth. Furthermore, the lactone group in terpenylic acid may also be a target for esterification reactions and as such enable particle growth (*25*). A possible reason why diaterpenylic acid acetate (and *cis*-pinic acid) reveals a decreased (or none for *cis*-pinic acid) dimer-forming capacity compared to that of terpenylic acid under (−)ESI-MS conditions is intramolecular hydrogen bonding, preventing intermolecular interactions. A compound with noncovalent dimer-forming potential should therefore only possess one carboxyl group, and an additional functional group in the molecule should not result in strong intermolecular interactions. Like the postulated intermolecular secondary ozonides (*26–28*), noncovalent dimeric clusters of terpenylic acid and diaterpenylic acid acetate, and aldehydic precursors (Scheme 2), should have sufficiently low vapor pressure to participate in a self-nucleating process (*29*).

Implications for New Particle Formation and Growth above Forests. Large efforts have been undertaken during the past decade to correlate new particle formation and growth events with the generation of specific α-/β-pinene tracers such as *cis*-pinic or *cis*-pinonic acid, but these experiments have not been conclusive (*11*). It is suggested that terpenylic acid and diaterpenylic acid acetate correspond to oxygenated compounds from reactive biogenic emissions that have been detected above a pine plantation by proton-transfer-reaction MS (PTR-MS) and were shown to partition to the particle phase (*30*). In particular, the strong PTR-MS signals at *m/z* 155 and 173 can be readily attributed, i.e., *m/z* 173 corresponds to protonated TA, while *m/z* 155 is due to subsequent loss of water; *m/z* 173 also corresponds to the loss of acetic acid from protonated DTAA. In addition, the carbon-to-oxygen (C/O) mole ratios are 2 (TA; $C_8H_{12}O_4$) and 1.7 (DTAA; $C_{10}H_{16}O_6$), which compare quite well with the values of 1.9 for 9 nm α-pinene ozonolysis particles experimentally determined with nanoaerosol MS (*31*).
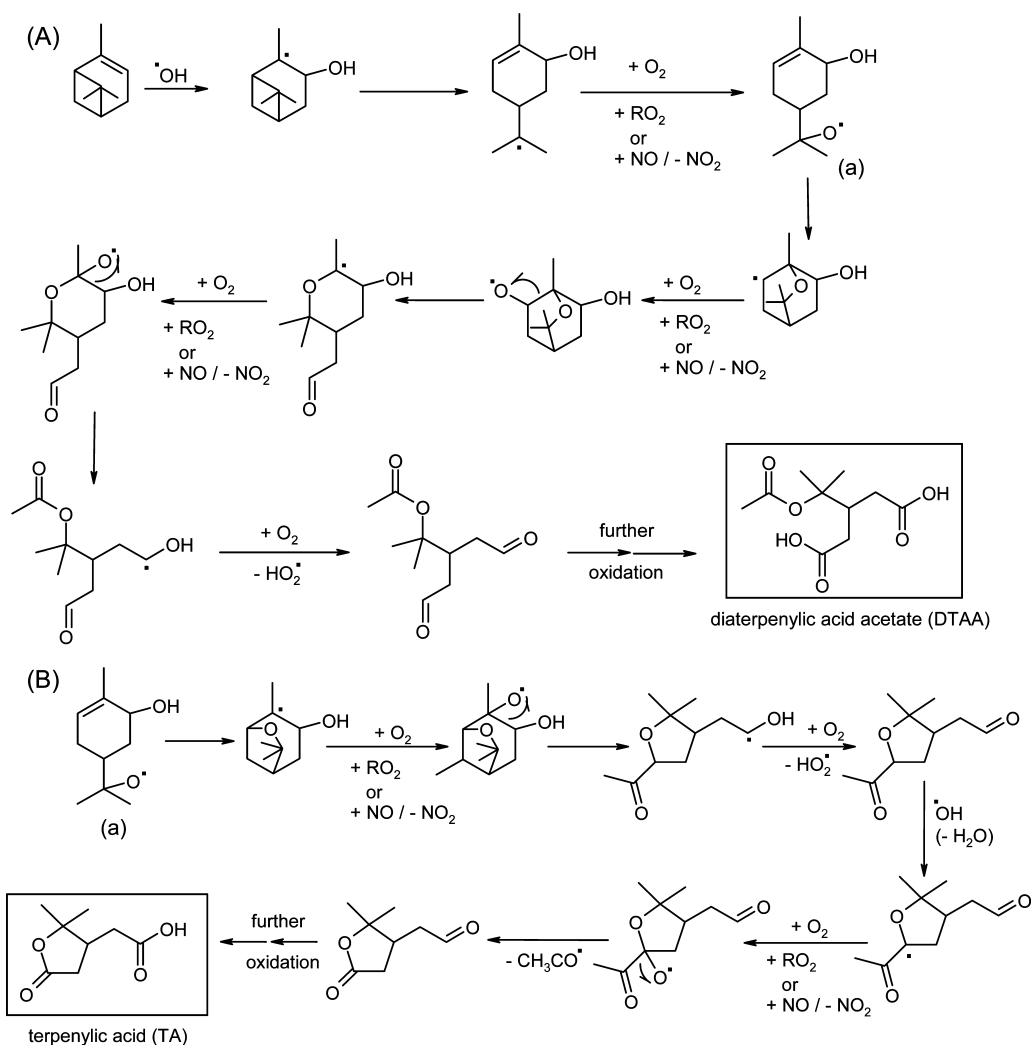
Taking into account the structure of the terpenylic acid dimer (Figure 3) where the carboxyl groups are in the central part and not exposed, we expect the cluster to have a hydrophobic character. This feature is in agreement with ambient measurements using ultrafine organic tandem differential mobility analysis that indicate that nucleation mode particles above a boreal forest have a significant organic fraction (*32*). In addition, it is worth noting that the maximum size of the dimer is 1.46 nm, which is in agreement with the observation of small-size particles, ~1.5 nm, during nucleation burst events (*4*). This suggests that organic clusters participating in these events may only comprise two or a very small number of individual molecules. Another characteristic of small (<3 nm) nucleation mode particles is that they can be detected as neutral clusters as well as positive and negative ion clusters (*4*). This feature is in agreement with the chemical nature of the terpenoic acids examined in the current study (i.e., terpenylic acid, 2-hydroxyterpenylic acid, and diaterpenylic acid acetate) since they have functionalities that can be deprotonated (i.e., a carboxyl group), leading to negative ion species, as well as functionalities that can be protonated or adducted with alkali or ammonium cations (i.e., a lactone or ester), affording positive ion species. In this respect, we noted that the latter terpenoic acids can be detected in the (+)ESI-MS mode as protonated/sodiated/ammoniated molecules (results not shown).

It has been demonstrated using a flow reactor that initial particle formation from α-pinene ozonolysis requires only a short reaction time (i.e., ≥0.4 − 6 s) (*28*). This observation can be reconciled with results from previous work (*8*) that

SCHEME 1. Proposed Fragmentation Pathways for Deprotonated Terpenylic Acid (*m/z* 171) upon Collisional Activation in the Ion Trap and the Structure of the *m/z* 343 Neutral-Anion Cluster

m/z 171   − CO₂   *m/z* 127   *m/z* 127   *m/z* 127

rearrangement

− CO₂

m/z 83

m/z 343
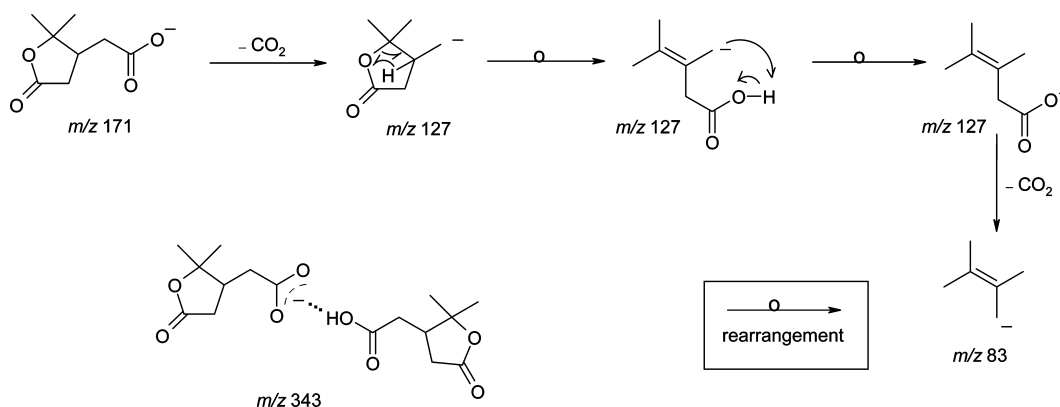
SCHEME 2. Suggested Formation Pathways for (A) Diaterpenylic Acid Acetate [Adapted with Permission from Ref *21*. Copyright 2007 Royal Society of Chemistry.] and (B) Terpenylic Acid through OH Radical-Initiated Oxidation of α-Pinene[a]

(A)

·OH   + O₂   + RO₂   or   + NO / − NO₂   (a)

+ O₂   + RO₂   or   + NO / − NO₂

+ O₂   + RO₂   or   + NO / − NO₂

+ O₂   − HO₂·

further oxidation

diaterpenylic acid acetate (DTAA)

(B)

(a)

+ O₂   + RO₂   or   + NO / − NO₂

+ O₂   − HO₂·

·OH (− H₂O)

+ O₂   + RO₂   or   + NO / − NO₂

− CH₃CO·

further oxidation

terpenylic acid (TA)

[a] 2-Hydroxyterpenylic acid can be explained by further oxidation of terpenylic acid. Pathways for the formation of diaterpenylic acid acetate and terpenylic acid through O₃-initiated reactions are given in Supporting Information (section S3).

the MW 172 α-pinene compound, identified here as terpenylic acid, is an early SOA product, and is thus consistent with a role in initial particle formation (see also Supporting Information, S3). Noncovalent dimer formation is also in agreement with the short reaction time needed for the detection of particles since subsequent to the formation of the terpenoic acids only chemical interaction and no reaction is required.

As regards to future studies, soft real-time MS techniques such as thermal desorption CI-MS (*33*) may enable
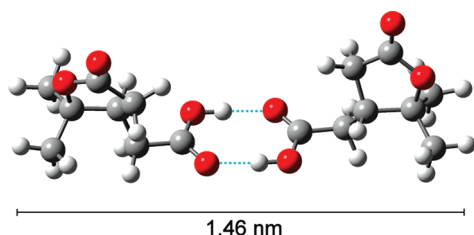
FIGURE 3. Structure of the noncovalent dimer formed through double hydrogen bonding interactions between the carboxyl groups of terpenylic acid monomers.

the specific detection of terpenylic acid and related compounds in submicrometer particles from forested regions, where α-pinene emissions are high. We have preliminary evidence that molecules with similar hydrogen bonding properties can also be generated from monoterpenes other than α-pinene (i.e., β-pinene, limonene, and Δ³-carene), but additional research is necessary to establish their chemical structures. Further experimental and theoretical work is also suggested on the formation mechanisms of terpenylic acid and related compounds, of which to date only the *di*-aldehydic precursor of diaterpenylic acid acetate has been predicted as an α-pinene SOA product in a theoretical study (*21*). It can also be anticipated that terpenylic acid and diaterpenylic acid acetate will interact with other organic or inorganic acids such as formic, acetic, and sulfuric acid, which are abundantly present in the ambient atmosphere and give rise to stable adduct formation (*23, 24*).

The findings presented here give clues about the complex atmospheric chemistry occurring in new particle formation and growth. The process of new particle formation and growth must be better understood not only because of its fundamental importance for biosphere-atmosphere interactions but also to allow its incorporation in global and regional atmospheric models. It is noteworthy that terpenylic acid, a lactone-containing terpenoic acid with unique noncovalent dimer-forming potential, is an important constituent of biogenic SOA formed over coniferous forest. Terpenylic acid, 2-hydroxyterpenylic acid, and diaterpenylic acid acetate will also serve as specific monoterpene SOA tracers for fine particulate matter characterization, a topic of great actual interest, since knowledge on aerosol sources is needed in abatement strategies.

Acknowledgments

Supporting Information Available

Experimental information on α-pinene ozonolysis samples and preparation of standards; additional results and discussion on the formation of TA and DTAA through ozonolysis and photooxidation of α-pinene; structure and mass spectrometric characterization of DTAA and 2-hydroxyterpenylic acid; and characterization of additional MW 188 compounds in α-pinene SOA. This material is available free of charge via the Internet at http://pubs.acs.org.

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