

Supporting Information:

Terpenylic acid and related compounds from the oxidation of α -pinene: Implications for new particle formation and growth above forests

Magda Claeys,^{1*} Yoshiteru Iinuma,² Rafal Szmigielski,¹ Jason D. Surratt,³ Frank Blockhuys,⁴ Christian Van Alsenoy,⁴ Olaf Böge,² Berko Sierau,^{2†} Yadian Gómez-González,¹ Reinhilde Vermeylen,¹ Pieter Van der Veken,¹ Mona Shahgholi,³ Arthur W. H. Chan,⁵ Hartmut Herrmann,² John H. Seinfeld,^{5,6} and Willy Maenhaut⁷

Departments of ¹Pharmaceutical Sciences and ⁴Chemistry, University of Antwerp, BE-2610 Antwerp, Belgium.

²Leibniz-Institut für Troposphärenforschung (IfT), D-04318 Leipzig, Germany.

Departments of ³Chemistry, ⁵Chemical Engineering, and ⁶Environmental Science and Engineering, California Institute of Technology (Caltech), Pasadena, CA 91125, USA.

⁷Department of Analytical Chemistry, Institute for Nuclear Sciences, Ghent University, BE-9000 Gent, Belgium.

[†]Present address: Eidgenössische Technische Hochschule Zürich, Institute for Atmospheric and Climate Science, Universitätstrasse 16, CH-8092 Zürich, Switzerland.

*e-mail: magda.claeys@ua.ac.be

Summary

There are 9 pages in this Supporting Information, including 1 table, 4 figures, 5 schemes, and 10 references.

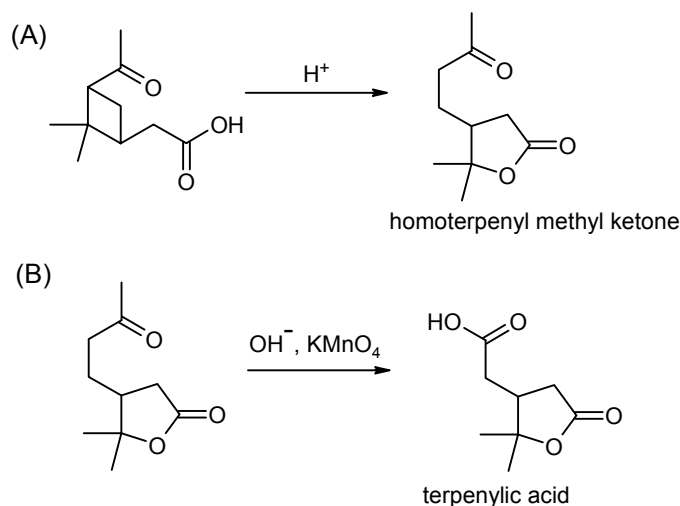
S1. Aerosol samples

The α -pinene SOA samples used for the time course analysis (Fig. S1) were obtained from an ozonolysis experiment carried out at the IfT in the 9 m³ Teflon smog chamber (S1). Briefly, α -pinene ozonolysis was performed in the presence of acidic seed particles (0.03 M (NH₄)₂SO₄/H₂SO₄). No OH scavenger was used in this experiment. The relative humidity and temperature of the chamber were around 50% and 23 °C. The initial concentrations of α -pinene, ozone, and seed particles were 100 ppb, 60 ppb, and 20,000 cm⁻³, respectively. A more detailed description of the experimental procedure is given in (S1). Samples were collected using a condensation-growth and impaction system (C-GIS). Details about the C-GIS sampling system are reported in a previous study (S2).

S2. Preparation of standards

Terpenylic acid was prepared from homoterpenyl methyl ketone as reported by Baeyer (S3) (Scheme S1). 5 g of *cis*-pinonic acid (Aldrich, *cis*-3-acetyl-2,2-dimethylcyclobutaneacetic acid) was dissolved in 60 g of H₂SO₄ (50%) at 100 °C and left for 30 min, resulting in a brown mixture with yellow-green fluorescence. Subsequently, 150 mL of water was added to the mixture, the mixture was further saturated with (NH₄)₂SO₄ and the organic phase was extracted with CHCl₃. The resulting extract was dried over Na₂SO₄, the solvent was evaporated to yield homoterpenyl methyl ketone, and the product was re-crystallized from water. In a subsequent step, homoterpenyl methyl ketone was oxidized as reported by Wallach (S4) (Scheme S1). 3 g of homoterpenyl methyl ketone was dissolved in a 0.93 M KOH solution (60 ml), and 300 mL of 0.158 M KMnO₄ solution was added to the solution within 20 min. After filtration of the brown precipitate, the solution was acidified with 10% H₂SO₄ and repeatedly extracted with diethyl ether. The extract was dried over Na₂SO₄ and the solvent was evaporated to yield terpenylic acid.

The preparation of diaterpenylic acid acetate is given in the supporting information of Iinuma et al. (S5).



Scheme S1. Synthesis of terpenylic acid: (A) rearrangement of *cis*-pinonic acid to homoterpenyl methyl ketone; and (B) oxidation of homoterpenyl methyl ketone to terpenylic acid.

S3. Formation of terpenylic acid and diaterpenylic acid acetate through ozonolysis and photooxidation of α -pinene

The α -pinene SOA tracers terpenylic acid and diaterpenylic acid acetate are formed in both ozonolysis (*S1*) and photooxidation experiments (*S6*). As mentioned in the main text, a composited α -pinene SOA sample was used from five different experiments under low-, intermediate-, and high- NO_x conditions. Inspection of UPLC/(-)ESI-TOFMS data obtained within a previous study (*S7*) for the individual samples confirmed that the terpenoic acids are present in all cases (Table S1).

Figure S1 shows the time courses of terpenylic acid, diaterpenylic acid acetate, and other known terpenoic acids (i.e., *cis*-pinic acid, *cis*-norpinonic acid, hydroxypinonic acid) during an ozonolysis experiment, where no OH scavenger was used. It is noted that terpenylic acid and diaterpenylic acid acetate show a similar time course and were together with *cis*-norpinonic acid the first products that could be detected. Inspection of time courses of α -pinene SOA products available in the literature (*S8*) for different types of experiments (i.e., photosmog, H_2O_2 photolysis, and ozonolysis) and conditions (i.e., seeded and non-seeded) confirm that the MW 172 α -pinene SOA compound, identified here as terpenylic acid, is formed during the early stages of particle formation. More specifically, its relative abundance was the highest in an ozonolysis (non-seeded) and photosmog (seeded) experiment, while MW 188 products showed the highest relative abundance in a H_2O_2 photolysis (seeded) experiment.

Possible pathways leading to diaterpenylic acid acetate and terpenylic acid through O_3 -initiated reactions and the ester decomposition channel (*S9*) involving campholenic aldehyde as an intermediate are presented in Scheme S2. In this respect, we have experimental evidence that campholenic aldehyde serves as a precursor for diaterpenylic acid acetate and terpenylic acid (results not shown). Comparison of SOA product distributions in ozonolysis experiments with and without OH scavenger indicate that the OH scavenger only has a minor effect and that terpenylic acid is also formed in the presence of OH scavenger (*S1*).

Table S1. Accurate mass data obtained for the selected α -pinene SOA and ambient fine aerosol samples.

| α -pinene SOA experiment / ambient sample | MW | RT (min) | Molecular ion species | Measured mass | Error (mDa) | Elemental composition |
|--|------|--------------------|-------------------------|---------------|---|--|
| H ₂ O ₂ /neutral Date: 5/8/2007 | 172 | 5.61 | [M-H] ⁻ | 171.0654 | -0.3 | C ₈ H ₁₁ O ₄ |
| | | | [2M-H] ⁻ | 343.1399 | 0.6 | C ₁₆ H ₂₃ O ₈ |
| | | | [2M-2H+Na] ⁻ | 365.1207 | -0.5 | C ₁₆ H ₂₂ O ₈ Na |
| | 232 | 6.80 | [M-H] ⁻ | 231.0885 | 1.6 | C ₁₀ H ₁₅ O ₆ |
| | | | [M-H] ⁻ | 187.0615 | 0.9 | C ₈ H ₁₁ O ₅ |
| H ₂ O ₂ /highly acidic Date: 6/7/2007 | 172 | 5.62 | [M-H] ⁻ | 171.0649 | -0.8 | C ₈ H ₁₁ O ₄ |
| | | | [2M-H] ⁻ | 343.1395 | 0.2 | C ₁₆ H ₂₃ O ₈ |
| | | | [2M-2H+Na] ⁻ | 365.1224 | 1.2 | C ₁₆ H ₂₂ O ₈ Na |
| | 232 | 6.82 | [M-H] ⁻ | 231.0879 | 1.0 | C ₁₀ H ₁₅ O ₆ |
| | | | [2M-H] ⁻ | 463.1866 | 5.0 | C ₂₀ H ₃₁ O ₁₂ |
| | | | [2M-2H+Na] ⁻ | 485.1623 | -1.2 | C ₂₀ H ₃₀ O ₁₂ Na |
| | 188 | 4.82 | [M-H] ⁻ | 187.0602 | -0.4 | C ₈ H ₁₁ O ₅ |
| | | | [2M-H] ⁻ | 375.1308 | 1.7 | C ₁₆ H ₂₃ O ₁₀ |
| | | | | | | |
| H ₂ O ₂ /NO/neutral Date: 5/2/2007 | 172 | 5.60 | [M-H] ⁻ | 171.0658 | 0.1 | C ₈ H ₁₁ O ₄ |
| | | | [2M-H] ⁻ | 343.1410 | 1.7 | C ₁₆ H ₂₃ O ₈ |
| | | | [2M-2H+Na] ⁻ | 365.1227 | 1.5 | C ₁₆ H ₂₂ O ₈ Na |
| | 232 | 6.80 | [M-H] ⁻ | 231.0856 | -1.3 | C ₁₀ H ₁₅ O ₆ |
| | | | [2M-H] ⁻ | 463.1806 | -1.0 | C ₂₀ H ₃₁ O ₁₂ |
| | | | [2M-2H+Na] ⁻ | 485.1601 | -3.4 | C ₂₀ H ₃₀ O ₁₂ Na |
| | 188 | 4.82 | [M-H] ⁻ | 187.0606 | 0.0 | C ₈ H ₁₁ O ₅ |
| | | | | 187.0606 | 0.0 | C ₈ H ₁₁ O ₅ |
| | | | | | | |
| HONO/neutral Date: 4/30/2007 | 172 | 5.60 | [M-H] ⁻ | 171.0658 | 0.1 | C ₈ H ₁₁ O ₄ |
| | | | [2M-H] ⁻ | 343.1403 | 1.0 | C ₁₆ H ₂₃ O ₈ |
| | | | [2M-2H+Na] ⁻ | 365.1220 | 0.8 | C ₁₆ H ₂₂ O ₈ Na |
| | 232 | 6.80 | [M-H] ⁻ | 231.0874 | 0.5 | C ₁₀ H ₁₅ O ₆ |
| | | | [2M-H] ⁻ | 463.1817 | 0.1 | C ₂₀ H ₃₁ O ₁₂ |
| | | | [2M-2H+Na] ⁻ | 485.1651 | 1.6 | C ₂₀ H ₃₀ O ₁₂ Na |
| | 188 | 4.82 | [M-H] ⁻ | 187.0590 | -1.6 | C ₈ H ₁₁ O ₅ |
| | | | [M-H] ⁻ | 187.0606 | 0.0 | C ₈ H ₁₁ O ₅ |
| | | | | | | |
| HONO/acidic Date: 5/10/2007 | 172 | 5.62 | [M-H] ⁻ | 171.0658 | 0.1 | C ₈ H ₁₁ O ₄ |
| | | | [2M-H] ⁻ | 343.1403 | 1.0 | C ₁₆ H ₂₃ O ₈ |
| | | | [2M-2H+Na] ⁻ | 365.1217 | 0.5 | C ₁₆ H ₂₂ O ₈ Na |
| | 232 | 6.83 | [M-H] ⁻ | 231.0873 | 0.4 | C ₁₀ H ₁₅ O ₆ |
| | | | [2M-H] ⁻ | 463.1824 | 0.8 | C ₂₀ H ₃₁ O ₁₂ |
| | | | [2M-2H+Na] ⁻ | 485.1642 | 0.7 | C ₂₀ H ₃₀ O ₁₂ Na |
| | 188 | 4.82 | [M-H] ⁻ | 187.0606 | -0.1 | C ₈ H ₁₁ O ₅ |
| | | | [2M-H] ⁻ | 375.1301 | 1.0 | C ₁₆ H ₂₃ O ₁₀ |
| | | | [M-H] ⁻ | 187.0607 | 0.1 | C ₈ H ₁₁ O ₅ |
| PM _{2.5} Brasschaat (7 June 2007) | 172 | 5.64 | [M-H] ⁻ | 171.0657 | 0.0 | C ₈ H ₁₁ O ₄ |
| | | | [2M-H] ⁻ | 343.1319 | -7.2 | C ₁₆ H ₂₃ O ₈ |
| | 232 | 6.88 | [M-H] ⁻ | 231.0869 | 0.0 | C ₁₀ H ₁₅ O ₆ |
| | | | [2M-H] ⁻ | 463.1854 | 3.8 | C ₂₀ H ₃₁ O ₁₂ |
| | 188 | 4.81 | [M-H] ⁻ | 187.0615 | 0.9 | C ₈ H ₁₁ O ₅ |
| | | | [2M-H] ⁻ | 375.1308 | 1.7 | C ₁₆ H ₂₃ O ₁₀ |
| | 5.61 | [M-H] ⁻ | 187.0593 | -1.3 | C ₈ H ₁₁ O ₅ | |

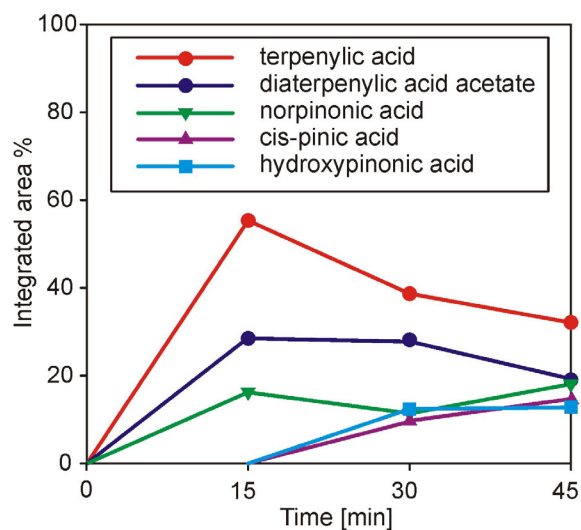
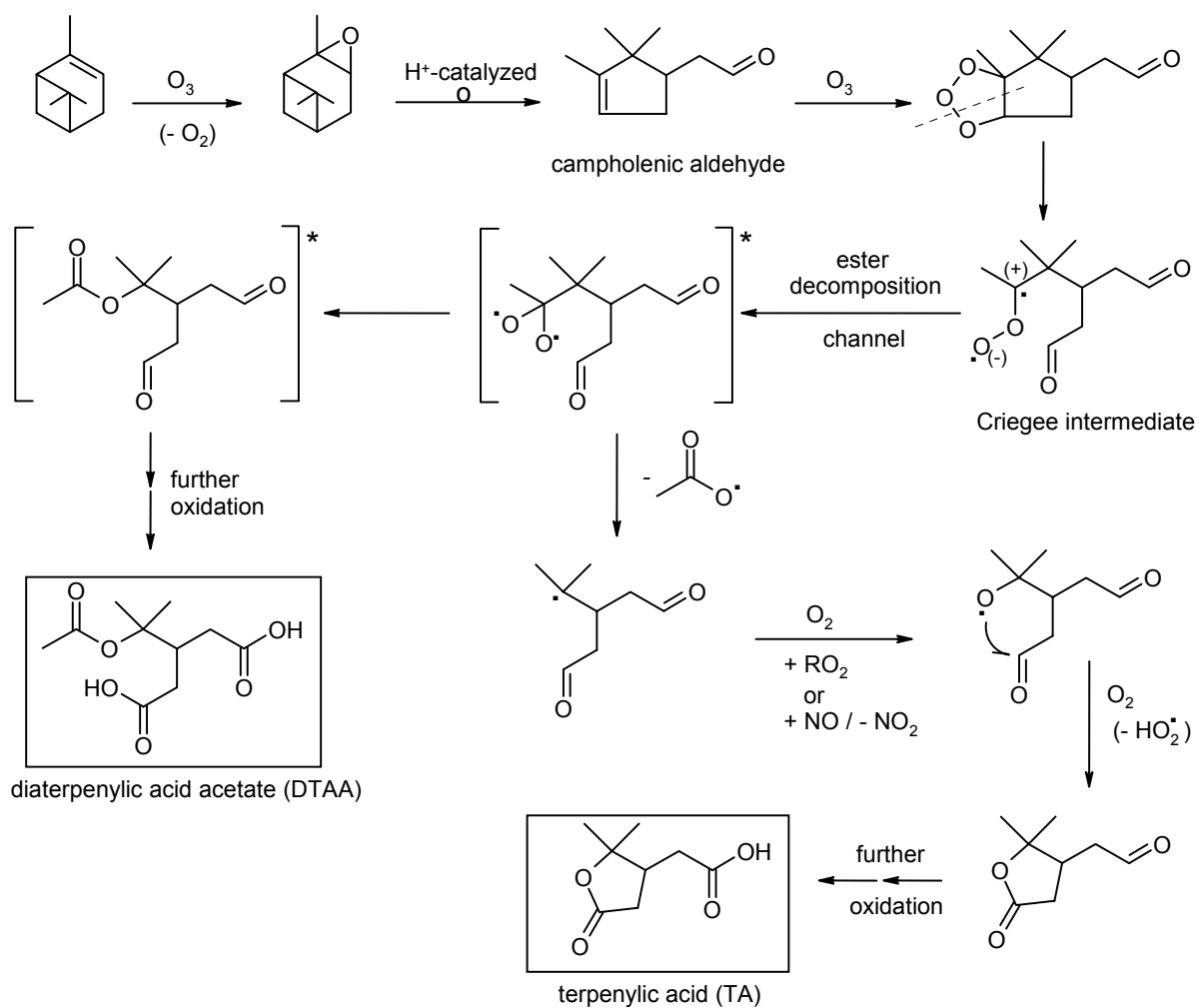


Figure S1. Time courses of α -pinene SOA products during an ozonolysis experiment where no OH scavenger was used.



Scheme S2. Pathways leading to diaterpenylic acid acetate and terpenylic acid through O_3 -initiated reactions, involving campholenic aldehyde as an intermediate.

S4. Structure and mass spectrometric characterization of diaterpenylic acid acetate and 2-hydroxyterpenylic acid

On the basis of interpretation of (–)ESI-MSⁿ data and comparison of MS and LC data with reference compounds, the MW 232 compound is identified as diaterpenylic acid acetate {IUPAC name: 3-[1-(acetyloxy)-1-methylethyl]pentanedionic acid}, while the MW 188 compound was elucidated as 2-hydroxyterpenylic acid [IUPAC name: 2-hydroxy-2-(2,2-dimethyl-5-oxooxalan-3-yl)acetic acid] based on detailed interpretation of (–)ESI-MSⁿ data.

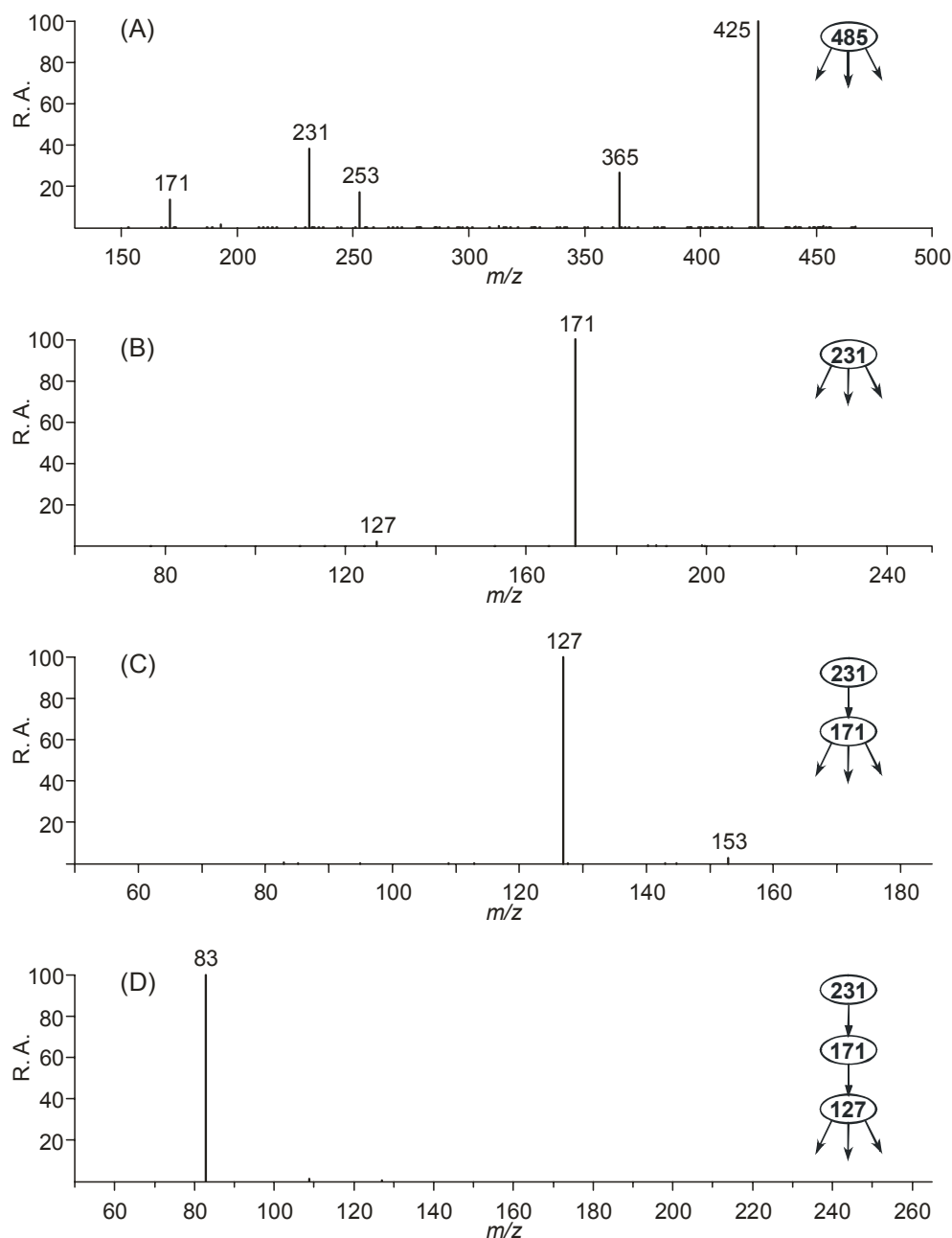
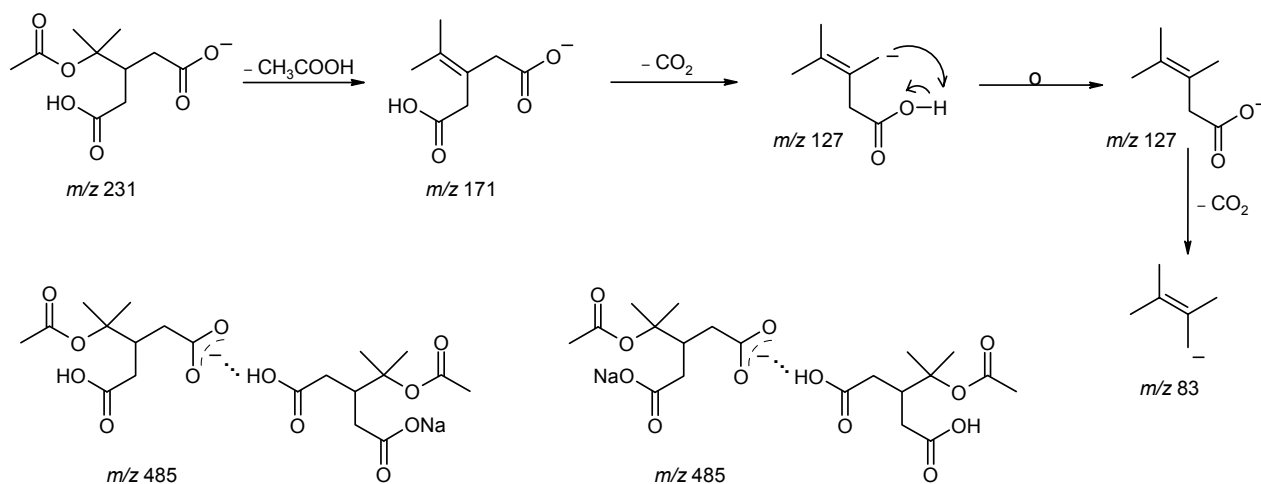


Figure S2. (–)ESI-MS data for the MW 232 product from α -pinene SOA, identified as diaterpenylic acid acetate: (A) m/z 485 MS²; (B) m/z 231 MS²; (C) m/z 231 \rightarrow m/z 171 MS³; and (D) m/z 231 \rightarrow m/z 171 \rightarrow m/z 127 MS⁴.



Scheme S3. Fragmentation pathways for deprotonated diaterpenylic acid acetate (m/z 231) upon collisional activation in the ion trap; possible structures for the m/z 485 neutral-anion cluster.

MW 232 α -SOA product

(–)ESI-MS data for diaterpenylic acid acetate are presented in Figures 1D and S2, and Scheme S3. The (–)ESI-MS and LC data matched perfectly with those of a synthesized reference compound (results not shown). Inspection of individual α -pinene SOA samples (Table S1) showed that the MW 232 compound was most efficiently formed under high- NO_x (HONO) conditions. The first-order (–)ESI mass spectrum contains ions at m/z 231 [$M - \text{H}$] $^-$ and m/z 485 [$2M - 2\text{H} + \text{Na}$] $^-$ (Fig. 1D). The accurate masses indicated elemental compositions of $\text{C}_{10}\text{H}_{11}\text{O}_4$ and $\text{C}_{16}\text{H}_{22}\text{O}_8\text{Na}$ for m/z 231 and 485, respectively. The m/z 485 MS^2 product ion spectrum (Fig. S2A) contains ions at m/z 425 (loss of acetic acid), m/z 365 (loss of two molecules of acetic acid), m/z 253 (loss of a terpenylic acid molecule), m/z 231 (loss of Na-containing terpenylic acid), and m/z 171 (further fragmentation of m/z 231 through loss of acetic acid). The m/z 231 MS^2 product ion spectrum (Fig. S2B) shows an ion at m/z 171, corresponding to the loss of acetic acid (60 u), while the m/z 231 \rightarrow m/z 171 MS^3 product spectrum (Fig. S2C) reveals a base peak at m/z 127, due to loss of CO_2 (44 u). It is worth noting that this spectrum is quite similar to the m/z 171 MS^2 product ion spectrum obtained for terpenylic acid (Fig. 2B), as could be expected considering the structural relationship, while the m/z 231 \rightarrow m/z 171 \rightarrow m/z 127 MS^4 spectrum matches the m/z 171 \rightarrow m/z 127 MS^3 spectrum (Fig. 2C).

MW 188 compound from ambient aerosol

In addition to terpenylic acid and diaterpenylic acid acetate, the ambient sample (Fig. 1B) contains a MW 188 (m/z 187) compound eluting at RT 15.14 min with similar dimer-forming properties as terpenylic acid; it can be seen that this compound is only a minor compound (RT 15.09 min) in the α -pinene SOA sample (Fig. 1A). The (–)ESI-MS data for the MW 188 compound are presented in Figure S3 and Scheme S4. Based on the fragmentation characteristics in (–)ESI-MS and the [$M - \text{H}$] $^-$ elemental composition ($\text{C}_8\text{H}_{11}\text{O}_5$), the MW 188 compound is assigned to 2-hydroxyterpenylic acid. The formation of this compound can be explained by further oxidation of terpenylic acid, likely involving oxidation reactions in the particle phase.

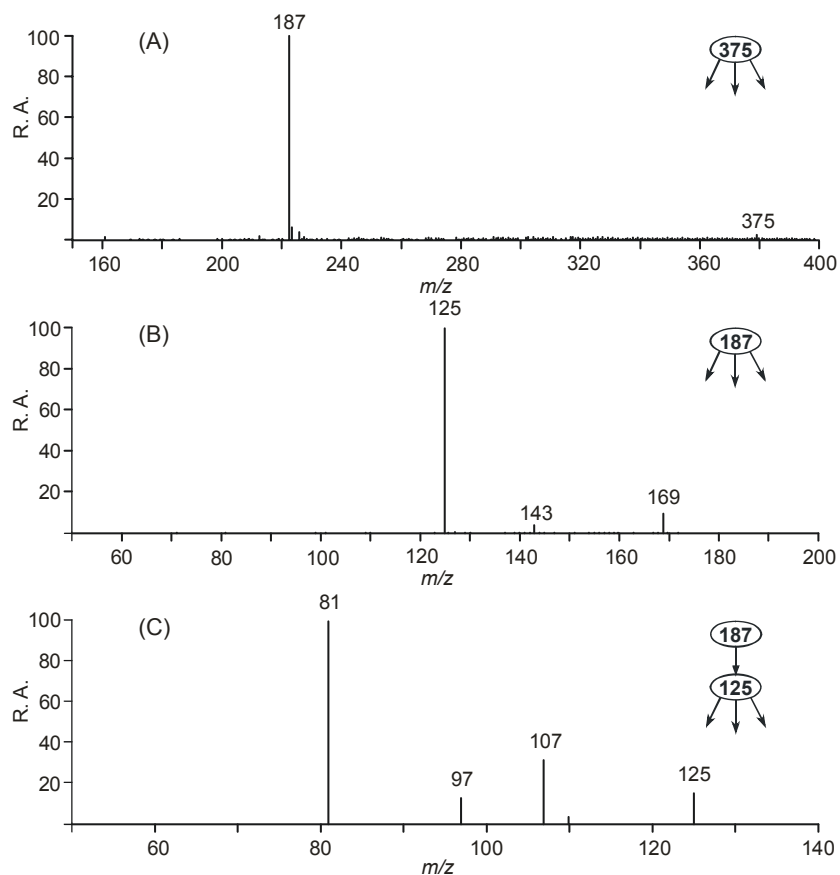
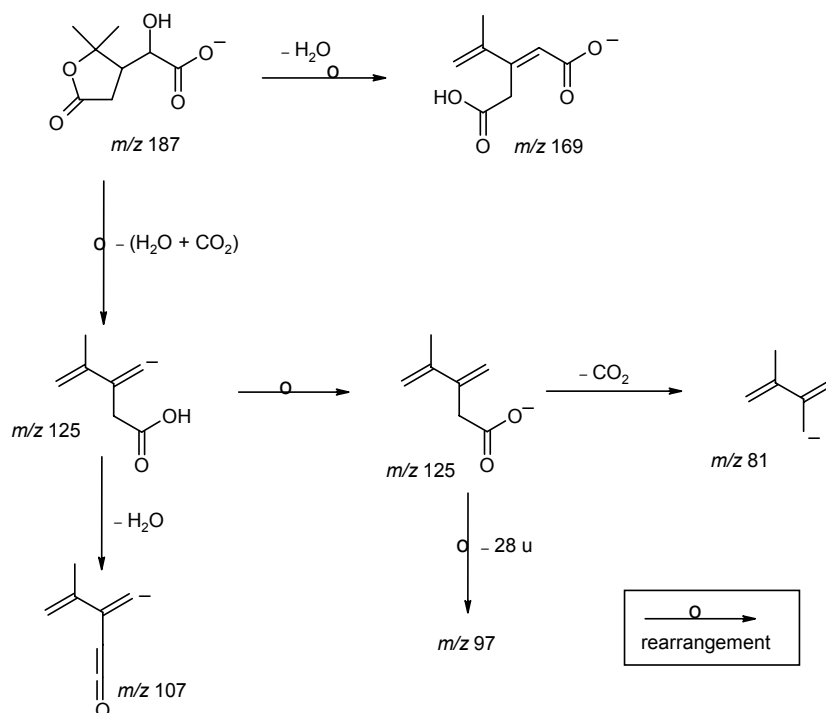


Figure S3. (-)ESI-MS data for the MW 188 compound eluting at RT 15.14 min in the ambient sample (Fig. 1B): (A) m/z 375 MS^2 ; (B) m/z 187 MS^2 ; and (C) m/z 187 \rightarrow m/z 125 MS^3 .



Scheme S4. Fragmentation of the m/z 187 compound in the ambient sample (RT 15.14 min), identified as 2-hydroxyterpenylic acid, upon collisional activation in the ion trap.

S5. Characterization of additional MW 188 compounds in α -pinene SOA

Figures 1A and C indicate that two partially resolved MW188 compounds (at around RT 17.5 min) co-elute with the MW 172 compound, i.e., terpenylic acid, in the α -pinene SOA sample. The corresponding m/z 187 MS^2 product ion spectrum is presented in Figure S4. Taking into account the fragmentation behavior (Scheme S5) and the elemental composition ($C_8H_{11}O_5$), these compounds are tentatively assigned to isomeric *mono*-aldehydic precursors of 3-methyl-1,2,3-butanetricarboxylic acid (MW 204), which has recently been structurally elucidated (S10). Furthermore, inspection of individual α -pinene SOA samples (Table S1) showed that the MW 188 compounds are only formed under intermediate- (H_2O_2/NO) and high- NO_x (HONO) conditions as well as ambient conditions. This result is consistent with the proposed mechanism for formation of 3-methyl-1,2,3-butanetricarboxylic acid, which requires the participation of NO (S10).

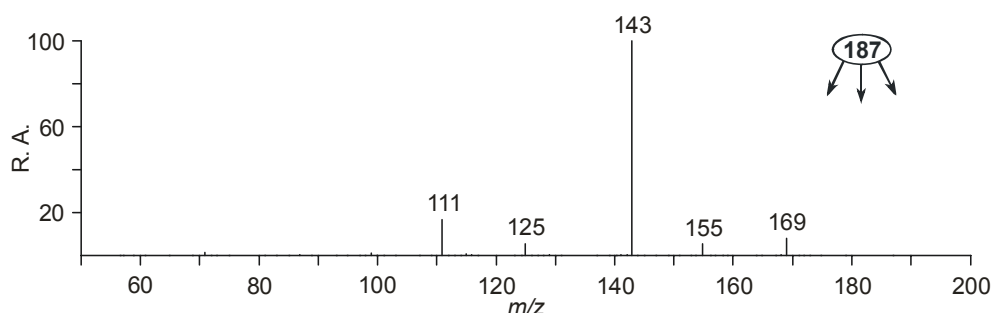
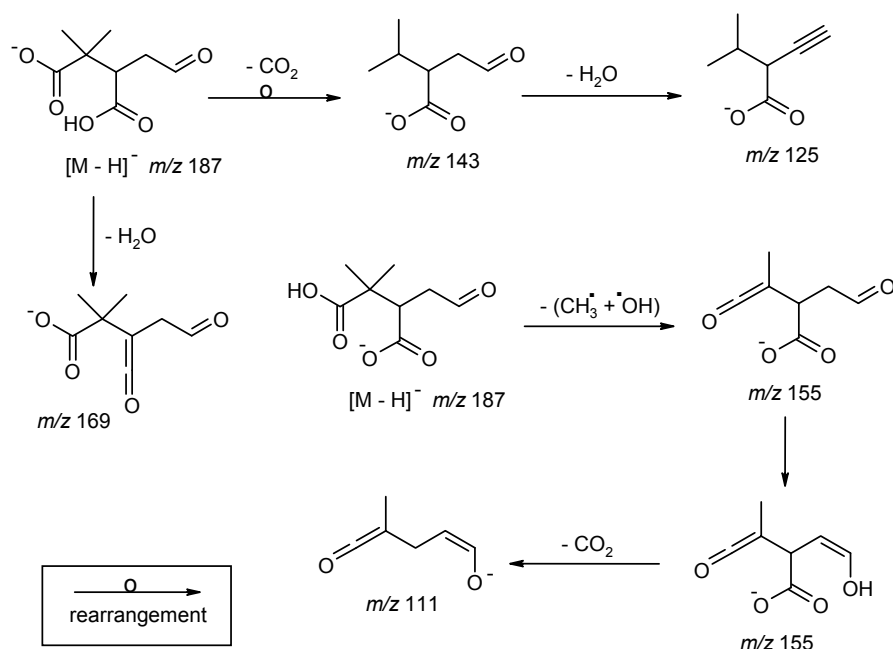


Figure S4. MS^2 (m/z 187) product ion spectrum for positional isomeric compounds corresponding to *mono*-aldehydic precursors of 3-methyl-1,2,3-butanetricarboxylic acid and closely eluting at around 17.5 min in α -pinene SOA.



Scheme S5. Fragmentation of m/z 187 compounds (RT around 17.5 min) in α -pinene SOA. The fragmentation behavior can be explained with two positional isomers, the one shown and another where the positions of the aldehyde group and the inner carboxyl group are reversed (pathways not shown).

Literature Cited

- (S1) Iinuma, Y.; Böge, O.; Miao, Y.; Sierau, B.; Gnauk, T.; Hermann, H. Laboratory studies on secondary organic aerosol formation from terpenes. *Faraday Discuss.* **2005**, *130*, 279–294.
- (S2) Sierau, B.; Stratmann, F.; Pelzing, M.; Neusüss, C.; Hoffmann, D.; Wilck, M. A condensation-growth and impaction method for rapid off-line chemical-characterization of organic submicrometer atmospheric aerosol particles. *J. Aerosol Sci.* **2003**, *34*, 225–242.
- (S3) Baeyer, A. Ortsbestimmungen in der Terpenreihe. *Ber. Dt. Chem. Ges.* **1896**, *29*, 326–329.
- (S4) Wallach, O. Zur Kenntniss der Terpene und der ätherischen Oele. *Liebigs Ann. Chem.* **1893**, *277*, 105–154.
- (S5) Iinuma, Y.; Böge, O.; Keywood, M.; Gnauk, T.; Herrmann, H. Diaterebic acid acetate and diaterpenylic acid acetate: Atmospheric tracers for secondary organic aerosol formation from 1,8-cineole oxidation. *Environ. Sci. Technol.* **2009**, *43*, 280–285; supporting information available at <http://www.acs.com>.
- (S6) Ng, N. L.; Chhabra, P. S.; Chan, A. W. H.; Surratt, J. D.; Kroll, J. H.; Kwan, A. J.; McCabe, D. C.; Wennberg, P. O.; Sorooshian, A.; Murphy, S. M.; Dalleska, N. F.; Flagan, R. C.; Seinfeld, J. H. Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes. *Atmos. Chem. Phys.* **2007**, *7*, 5159–5174.
- (S7) Surratt, J. D.; Gómez-González, Y.; Chan, A. W. H.; Vermeylen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E. O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Maenhaut, W.; Claeys, M.; Flagan, R. C.; Seinfeld, J. H. Organosulfate formation in biogenic secondary organic aerosol. *J. Phys. Chem. A* **2008**, *112*, 8345–8378.
- (S8) Winterhalter, R.; Van Dingenen, R.; Larsen, B. R.; Jensen, N. R.; Hjorth, J. LC-MS analysis of aerosol particles from the oxidation of α -pinene by ozone and OH-radicals. *Atmos. Chem. Phys. Discuss.* **2003**, *3*, 1–39.
- (S9) Finlayson-Pitts, B.J.; Pitts Jr., J. N. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*; Academic Press: San Diego, 2000; pp. 196–201.
- (S10) Szmigielski, R.; Surratt, J. D.; Gómez-González, Y.; Van der Veken, P.; Kourtchev, I.; Vermeylen, R.; Blockhuys, F.; Jaoui, M.; Kleindienst, T. E.; Lewandowski, M.; Offenberg, J. H.; Edney, E. O.; Seinfeld, J. H.; Maenhaut, W.; Claeys, M. 3-methyl-1,2,3-butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol. *Geophys. Res. Lett.* **2007**, *34*, L24811, doi:10.1029/2007GL031338.