Supplement for:

Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of α- and β-pinene

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1. The K-puszta sampling site and 2006 BIOSOL summer field campaign

K-puszta is a rural measurement site located on the Great Hungarian Plain (46°58´N, 19°35´E, 125 m a.s.l.), 15 km northwest from the nearest town Kecskemét, and 80 km southeast from Budapest. The surroundings of the measurement site are dominated by mixed forest (62% coniferous, 28% deciduous) and grassland (10%). The site is characterized by intensive solar radiation during summer. The BIOSOL (Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols) campaign took place from 24 May to 29 June 2006. Maenhaut et al. (2008) studied the composition of atmospheric particulate matter during the BIOSOL campaign and observed that the campaign time could be divided into two periods: from the start of the campaign until 11 June 2006 when it was unusually cold with daily maximum temperatures between 12 and 23 °C, and from 12 June 2006 onward when the temperatures were considerably higher with daily maxima ranging from 24 to 36 °C. During the cold period the air masses came mainly from the northwest over the North Sea or the Atlantic Ocean whereas after 12 June 2006, i.e., during the warm period, the air masses were continental.

2. Mass spectral characterization of *cis*-norpinic acid

(–)ESI-MS data for the MW 172 compound eluting at RT 19.8 min (Figs. 1 and 2), which 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), are presented in Figure S1 and Scheme S1.

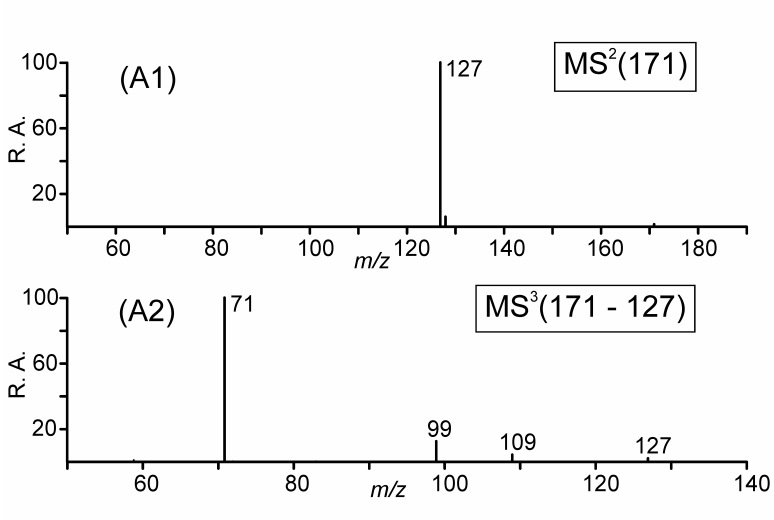
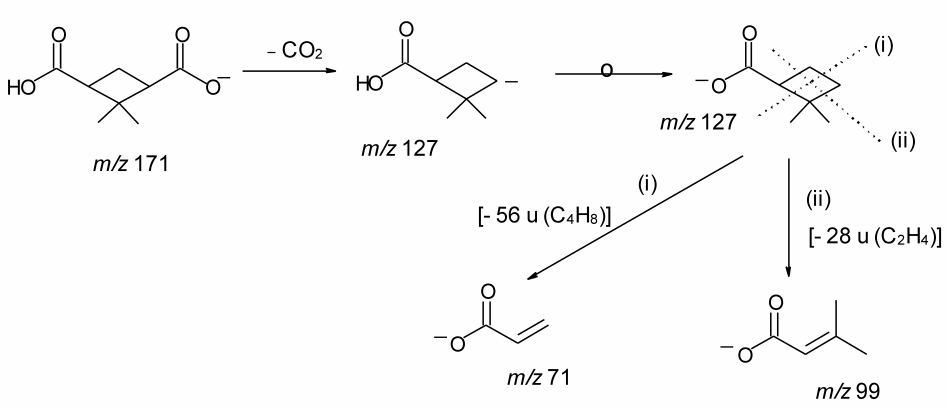


Figure S1: (–)ESI-MS^n (n = 2, 3) data for the minor MW 172 compound attributed to *cis*-norpinic acid.



Scheme S1: Proposed fragmentation pathways for deprotonated *cis*-norpinic acid.

3. Mass spectral characterization of homoterpenylic acid, a specific β-pinene SOA tracer, and possible formation pathway from β-pinene

(–)ESI-MS data obtained for the MW 186 compound present in β-pinene SOA and tentatively assigned to homoterpenylic acid based on interpretation of (-)ESI-MS data are presented in Figure S2. Proposed fragmentation pathways are given in Scheme S2. The formation of terpenylic acid and diaterpenylic acid from α-pinene have been explained in previous work through both OH radical- and ozone-initiated reactions (Claeys et al., 2009); however, in the case of β-pinene we were only able to explain the formation of homoterpenylic acid through OH radical-initiated reactions (Scheme S3). We therefore suggest that the OH radical pathway is more likely to operate under ozone-initiated reactions, where no OH scavenger is used, as well as under ambient conditions. An additional question that arises is the formation of terpenylic acid and diaterpenylic acid acetate from β-pinene. A simple but possible explanation is that there is a fast OH

radical-initiated isomerization of β-pinene to α-pinene, prior to OH radical attack on the double bond.

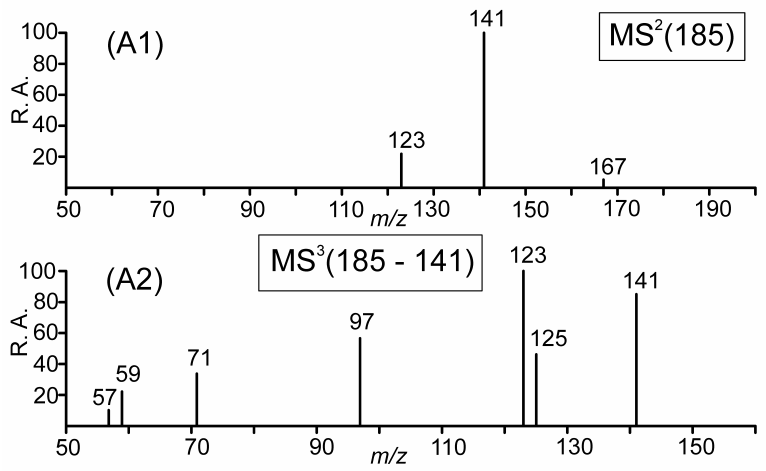
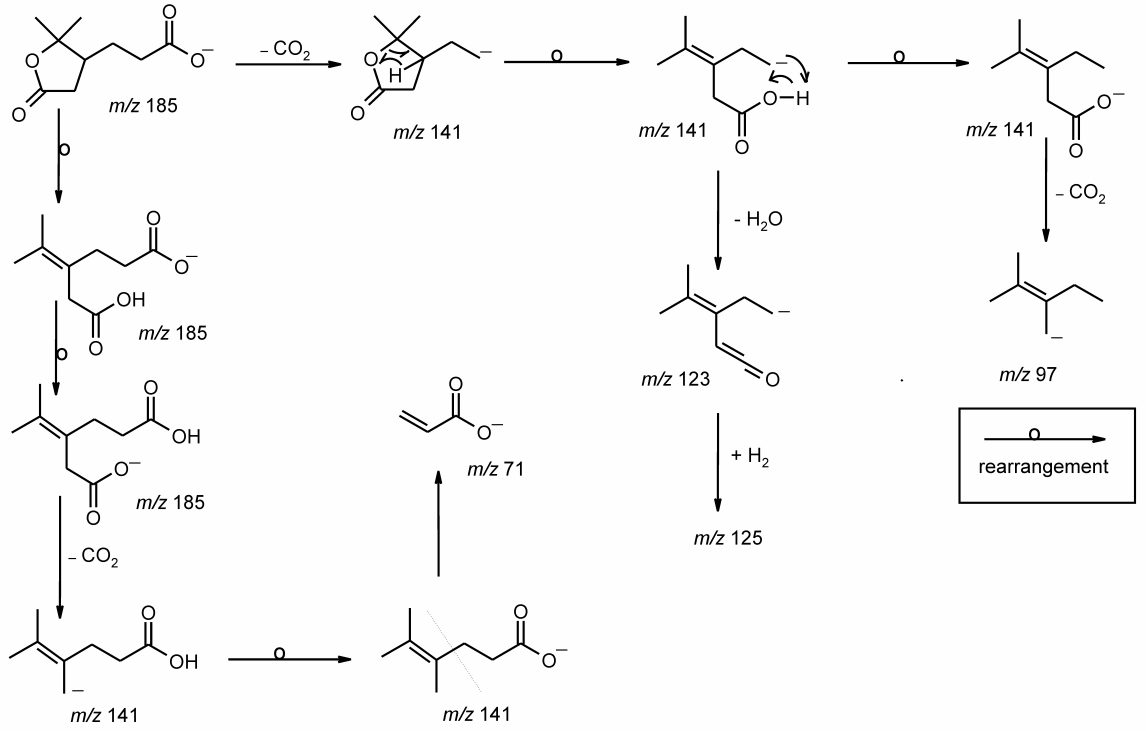
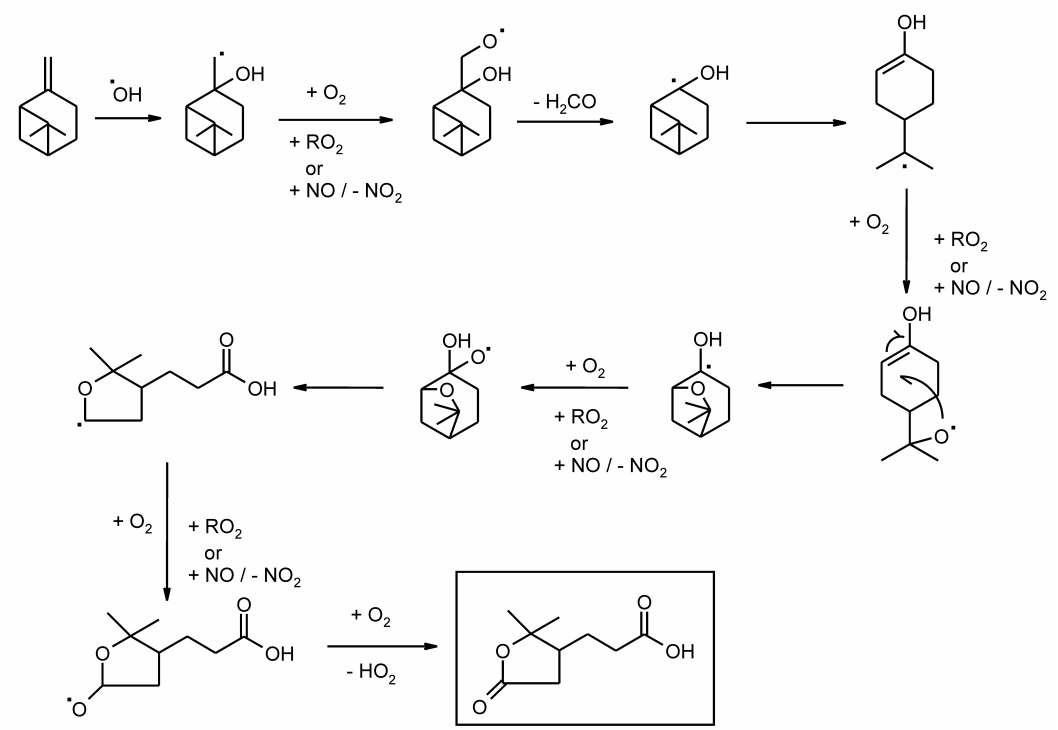


Figure S2: (–)ESI-MS^n (n = 2, 3) data obtained for the MW 186 compound present in β-pinene SOA and tentatively assigned to homoterpenylic acid.



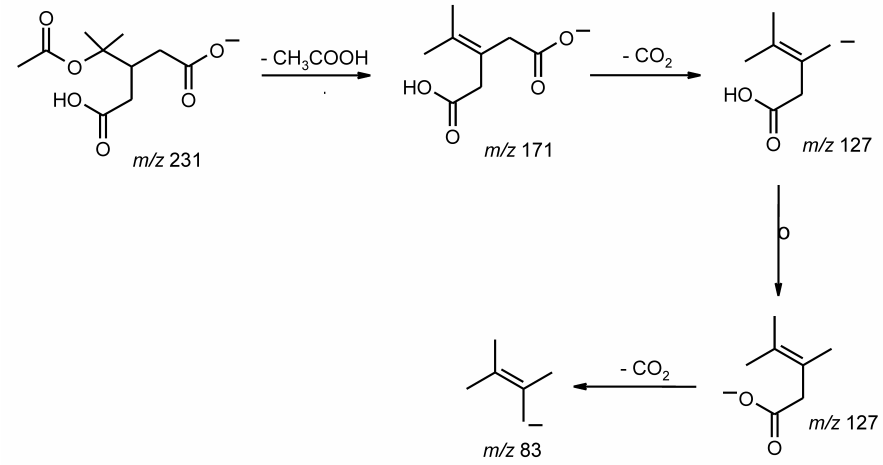
Scheme S2: Proposed fragmentation pathways for deprotonated homoterpenylic acid.



Scheme S3: Pathway leading to the formation of homoterpenylic acid from β-pinene through OH radical-initiated reactions.

4. Mass spectral characterization of diaterpenylic acid acetate and an isomeric MW 232 product

(–)ESI-MS data obtained for synthesized diaterpenylic acid acetate and for the isomeric MW 232 product with RT 22.1 min present in α-pinene SOA (Fig. 1) are presented in Figures S3 and S4, respectively. Proposed fragmentation pathways for deprotonated diaterpenylic acid acetate are given in Scheme S4.



Scheme S4: Proposed fragmentation pathways for deprotonated diaterpenylic acid acetate.

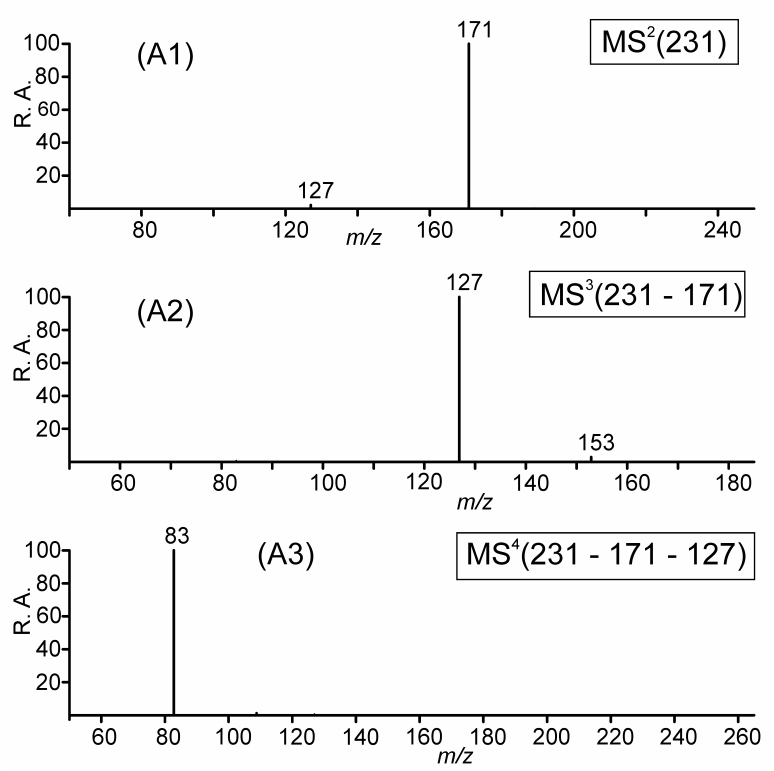


Figure S3: (–)ESI-MS^n (n = 2 - 4) data obtained for deprotonated diaterpenylic acid acetate.

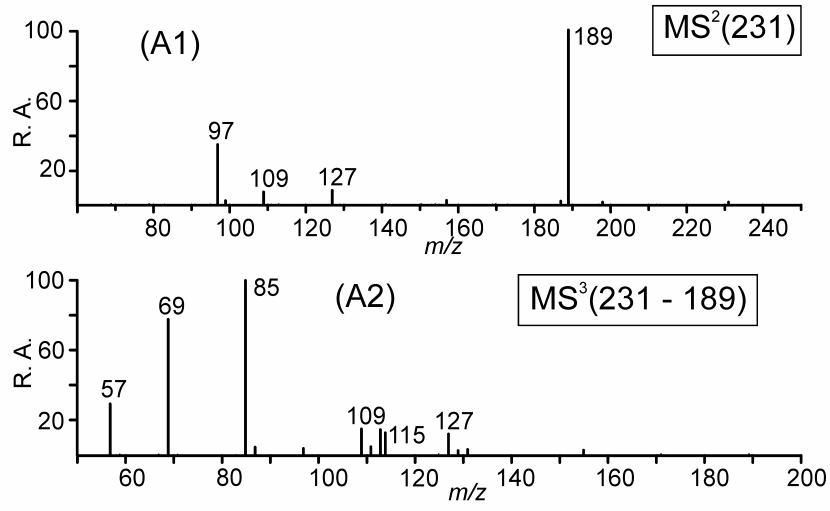


Figure S4: (–)ESI-MS^n (n = 2, 3) data obtained for the deprotonated MW 232 compound with RT 22.1 min present in α-pinene ozonolysis SOA (Fig. 1). The fragmentation behavior is distinctly different from that of deprotonated diaterpenylic acid acetate, and starts with the loss of 44 u (CO_2) instead of 60 u (acetic acid) (Scheme S4).

5. Mass spectral characterization of the major MW 358 product from ambient aerosol

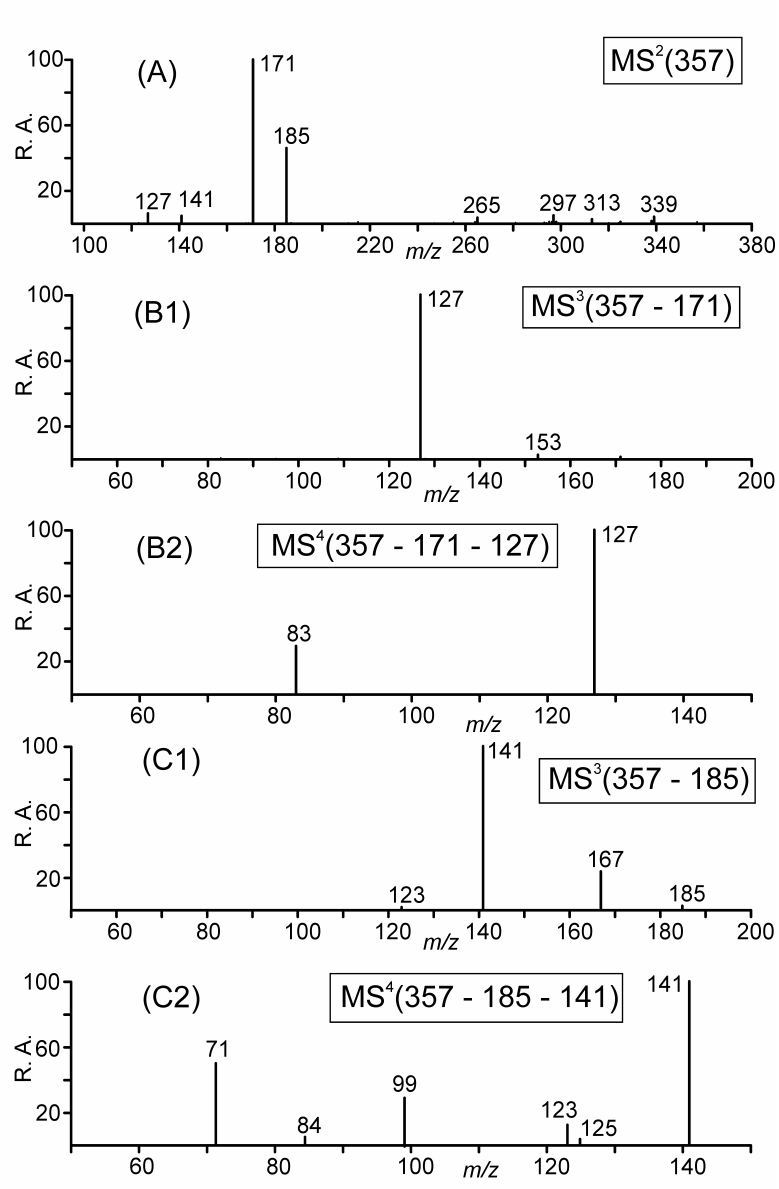


Figure S5: (–)ESI-MS^n data obtained for the MW 358 compound present in ambient fine aerosol (RT 24.6 min, Fig. 2): (A) *m/z* 357 MS^2 spectrum; (B1) and (B2) higher-order *m/z* 357 → *m/z* 171 MS^n (n = 3, 4) spectra; and (C1) and (C2) higher-order *m/z* 357 → *m/z* 185 MS^n (n = 3, 4) spectra.

6. Mass spectral characterization of the minor MW 344 β-pinene SOA product co-eluting with the major MW 358 product

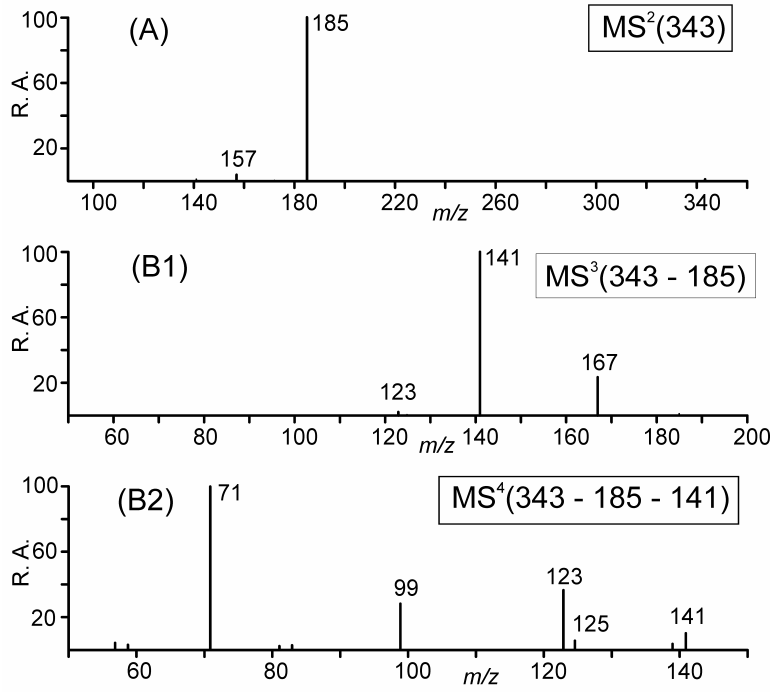
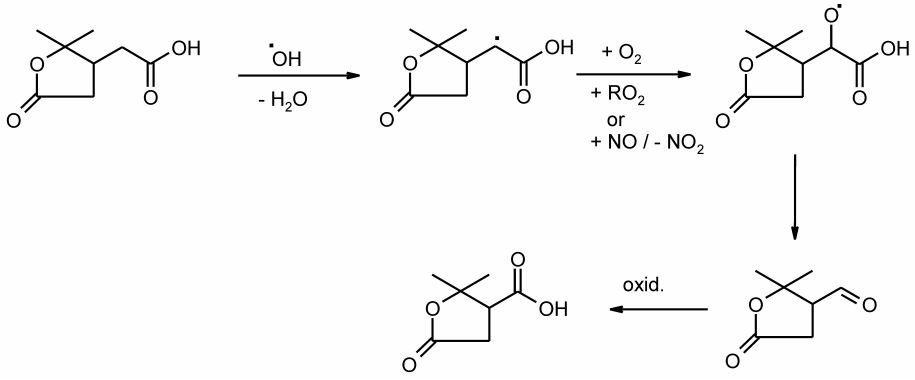


Figure S6: (–)ESI-MS^n data obtained for the MW 344 compound present in β-pinene ozonolysis SOA that co-elutes with the major MW 358 compound (RT 24.7 min, Fig. 1): (A) *m/z* 343 MS^2 spectrum; and (B1) and (B2) higher-order *m/z* 343 → *m/z* 185 MS^n (n = 3, 4) spectra. The higher-order *m/z* 343 → *m/z* 157 MS^n (n = 3, 4) spectra (not shown) were consistent with terebic acid (Fig. S7). The MW 344 dimer is assigned to the diester formed between diaterebic acid and pinic acid.

7. Formation pathway of terebic acid

(–)ESI-MS^n data obtained for terebic acid (reference compound) are presented in Figure S7, while pathways leading to terebic acid through further processing of terpenylic acid are given in Scheme S5.



Scheme S5: Proposed formation of terebic acid from terpenylic acid through an OH radical-initiated reaction.

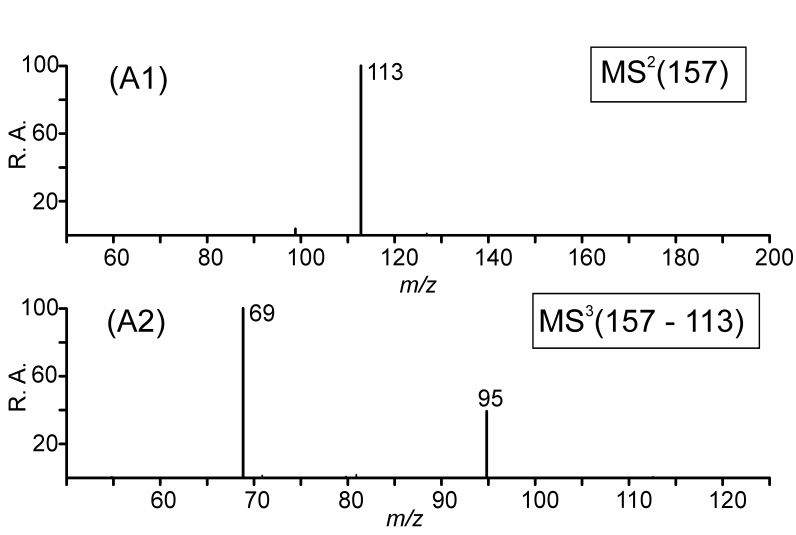


Figure S7: (–)ESI-MS^n (n = 2, 3) data obtained for terebic acid (reference).

8. Mass spectral characterization of a minor MW 344 α-pinene SOA product eluting before the major MW 358 product

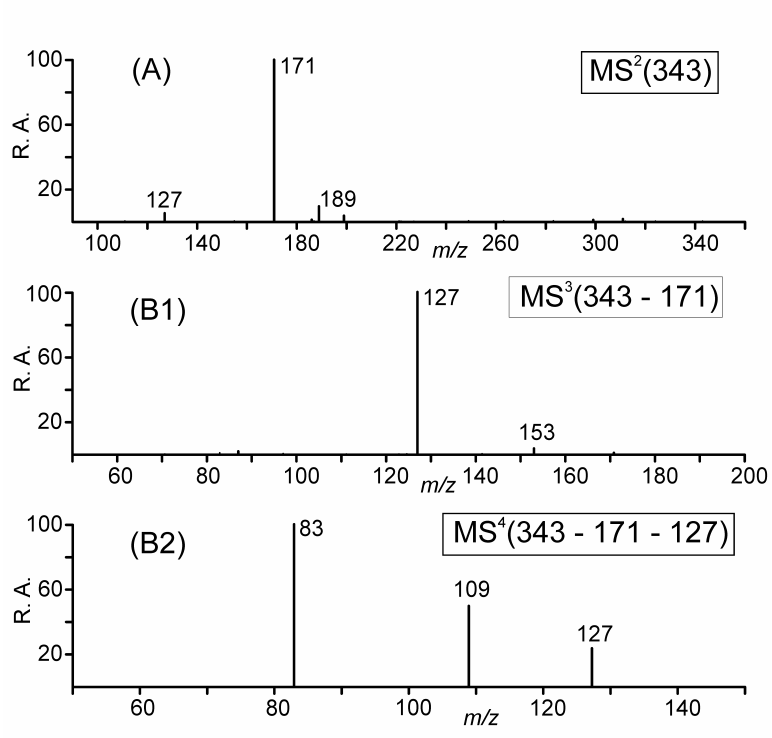


Figure S8: (–)ESI-MS^n data obtained for the MW 344 compound present in α-pinene ozonolysis SOA that elutes before the major MW 358 compound (RT 23.6 min, Fig. 1): (A) *m/z* 343 MS^2 spectrum; and (B1) and (B2) higher-order *m/z* 357 → *m/z* 171 MS^n (n = 3, 4) spectra. The dimer is tentatively assigned to the diester formed between diaterpenylic acid and terpenylic acid.

References

Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D., and Larsen, B. R.: Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone, Environ. Sci. Technol., 34, 1001–1010, 2000.

Maenhaut, W., Raes, N., Chi, X., Cafmeyer, J., and Wang, W.: Chemical composition and mass closure for PM2.5 and PM10 aerosols at K-puszta, Hungary, in summer 2006, X-Ray Spectrom., 37, 193–197, 2008.

Warnke, J., Bandur, R., and Hoffmann, T.: Capillary-HPLC-ESI-MS/MS method for the determination of acidic products from the oxidation of monoterpenes in atmospheric aerosol samples, Anal. Bioanal. Chem., 385, 34–45, 2006.