

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.

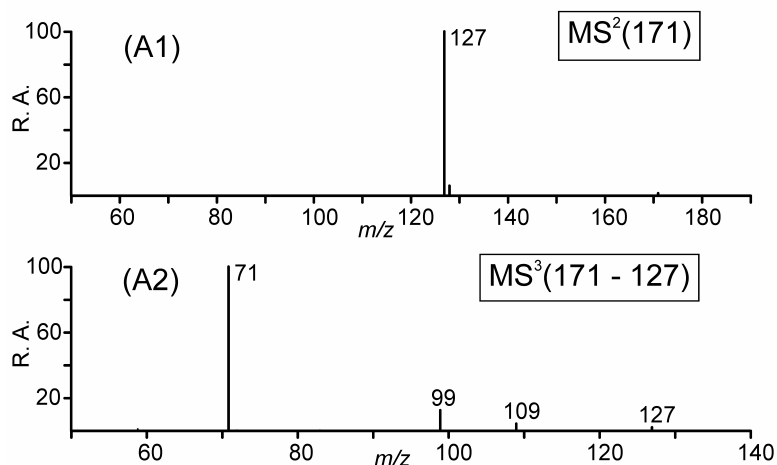
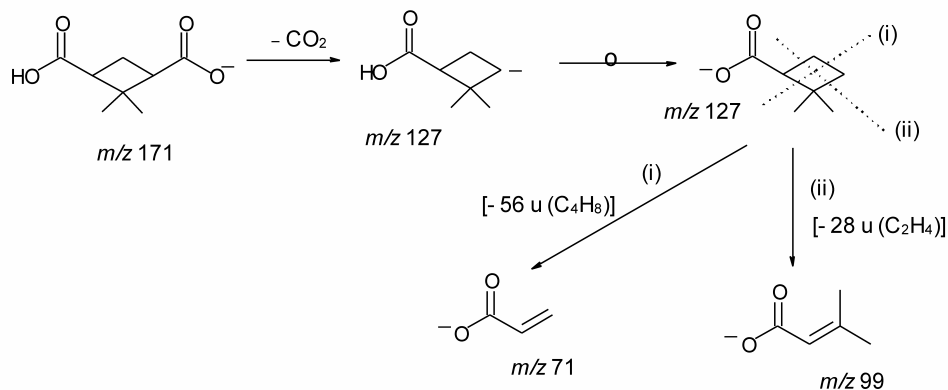


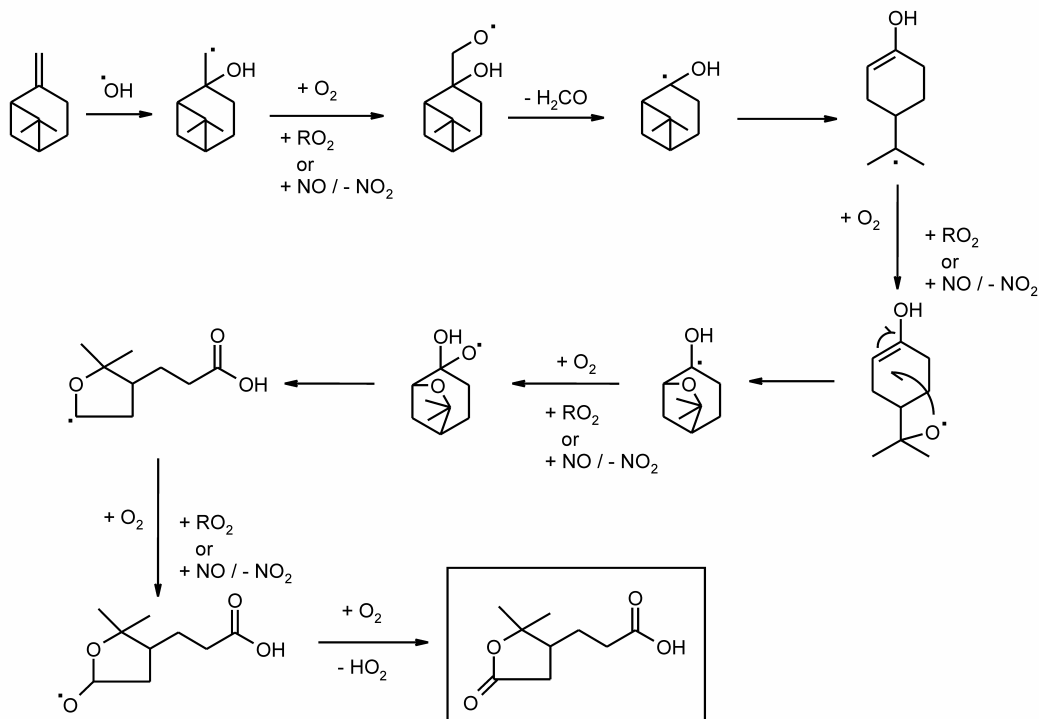
Figure S1: (-)ESI- MS^n ($n = 2, 3$) data for the minor MW 172 compound attributed to *cis*-norpinic acid.



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

3. Possible formation pathway of homoterpenylic acid from β -pinene

The formation of terpenylic acid and diaterpenylic acid acetate 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 S2). 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.



Scheme S2: Pathways leading to the formation of homoterpenylic acid from β -pinene through OH radical-initiated reactions.

4. Mass spectral data for a MW 232 product isobaric to diaterpenylic acid acetate

(-)-ESI-MS data obtained for the MW 232 product with RT 22.1 min isobaric to diaterpenylic acid acetate present in α -pinene SOA (Fig. 1) are presented in Figure S2. The fragmentation behavior is distinctly different from that of deprotonated diaterpenylic acid acetate (Scheme 1b), and starts with the loss of 42 u (ketene or propene) instead of 60 u (acetic acid).

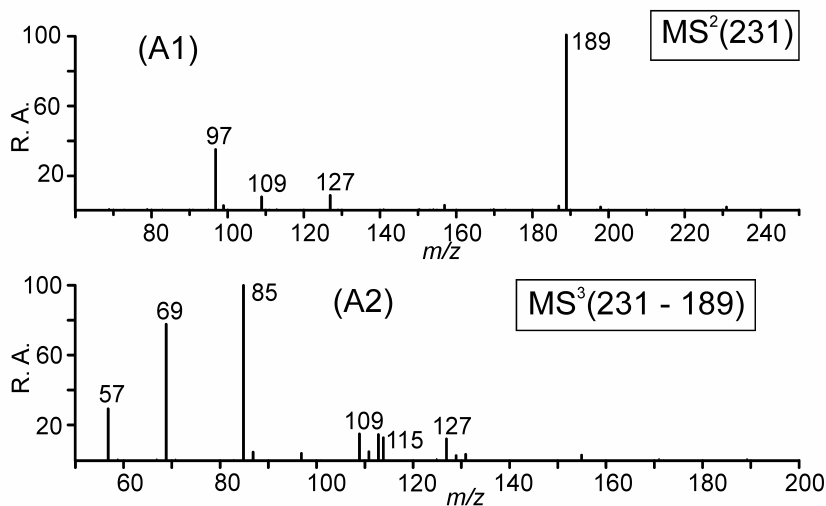


Figure S2: (-)-ESI-MSⁿ ($n = 2, 3$) data obtained for the deprotonated MW 232 compound with RT 22.1 min present in α -pinene ozonolysis SOA (Fig. 1).

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

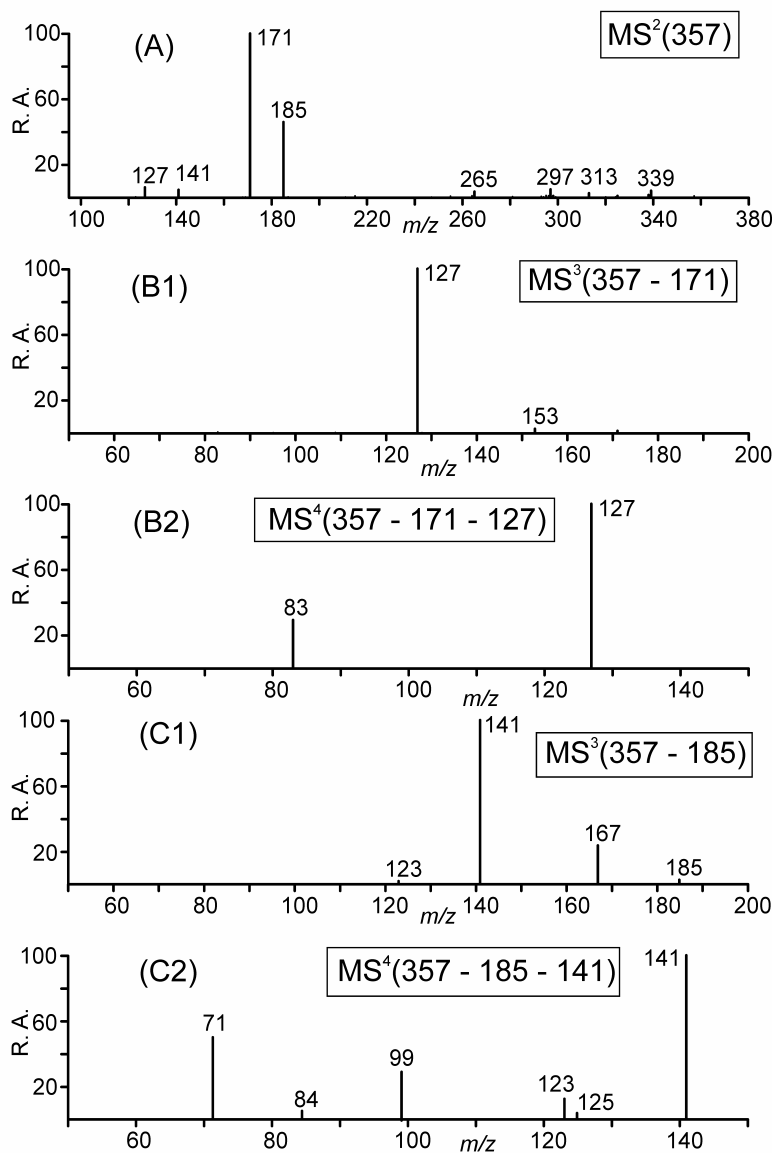


Figure S3: (–)ESI- MS^n data obtained for the MW 358 compound present in ambient fine aerosol (RT 24.6 min, Fig. 2): (A) m/z 357 MS^2 spectrum; (B1) and (B2) higher-order m/z 357 \rightarrow m/z 171 MS^n ($n = 3, 4$) spectra; and (C1) and (C2) higher-order m/z 357 \rightarrow m/z 185 MS^n ($n = 3, 4$) spectra.

6. Mass spectral characterization of the weak MW 344 β -pinene SOA product co-eluting with the relatively abundant MW 358 product

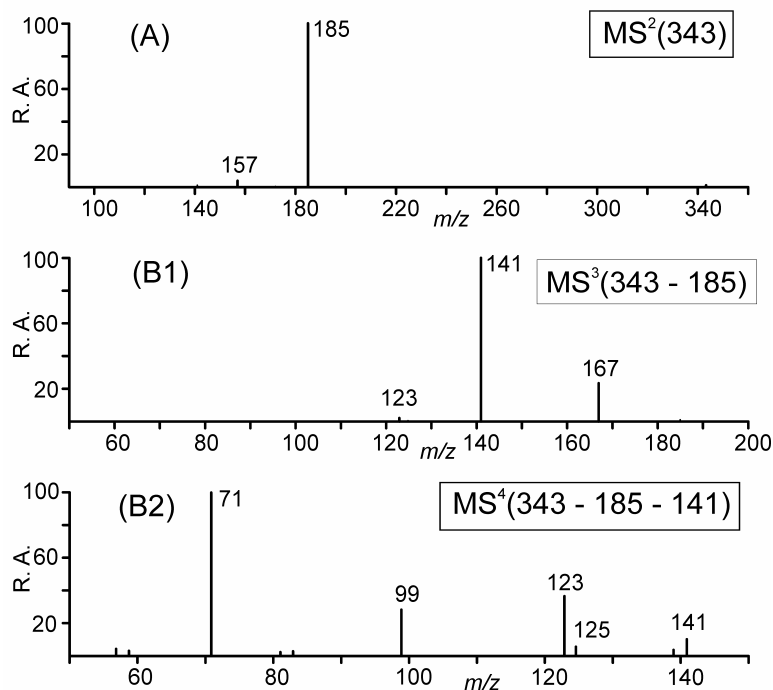
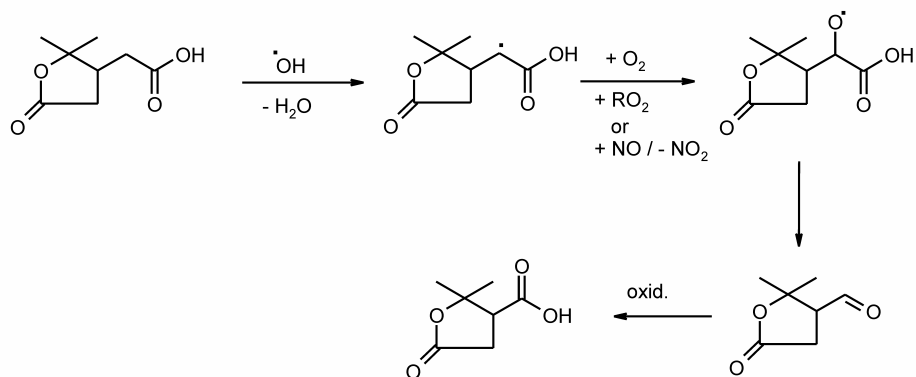


Figure S4: (-)ESI-MSⁿ data obtained for the MW 344 compound present in β -pinene ozonolysis SOA that co-elutes with the relatively abundant MW 358 compound (RT 24.7 min, Fig. 1): (A) m/z 343 MS² spectrum; and (B1) and (B2) higher-order m/z 343 \rightarrow m/z 185 MSⁿ ($n = 3, 4$) spectra. The higher-order m/z 343 \rightarrow m/z 157 MSⁿ ($n = 3, 4$) spectra (not shown) were consistent with terebic acid (Fig. 3D; Scheme 1d). The MW 344 dimer is assigned to the diester formed between diaterbic acid and pinic acid.

7. Formation pathway of terebic acid

Pathways leading to terebic acid through further processing of terpenylic acid are given in Scheme S3. The fourth step, i.e., the oxidation of terebic aldehyde, is assumed to occur in the particle phase.



Scheme S3: Proposed formation of terebic acid from terpenylic acid through an OH radical-initiated reaction.

8. Mass spectral characterization of the weak MW 344 α -pinene SOA product eluting before the relatively abundant MW 358 product

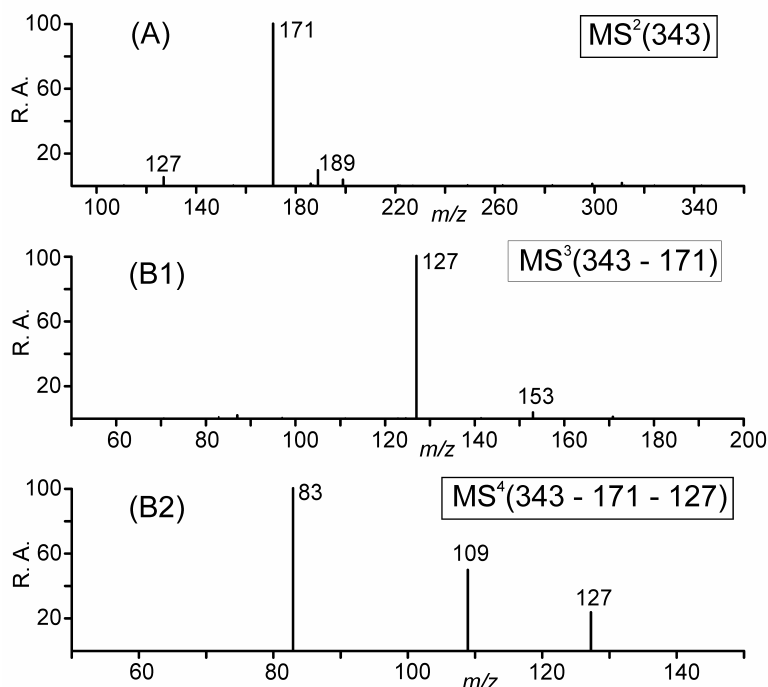


Figure S5: (–)ESI-MSⁿ data obtained for the MW 344 compound present in α -pinene ozonolysis SOA that elutes before the relatively abundant MW 358 compound (RT 23.6 min, Fig. 1): (A) m/z 343 MS² spectrum; and (B1) and (B2) higher-order m/z 357 \rightarrow m/z 171 MSⁿ ($n = 3, 4$) spectra. The dimer is tentatively assigned to the diester formed between diaterpenylic acid and terpenylic acid.

References

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