

## Supporting Information

### Campholenic aldehyde ozonolysis: A mechanism leading to specific biogenic secondary organic aerosol constituents

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### Additional Supplementary Figures

Filter samples from the campholenic aldehyde chamber experiments were compared to laboratory-generated SOA samples ( $\alpha$ -pinene oxide/O<sub>3</sub>/acidic seed and  $\alpha$ -pinene/O<sub>3</sub>) and an ambient filter (K-pusztá) to establish possible formation pathways for specific oxidation products, more specifically, to support that campholenic aldehyde can serve as their precursor and that these oxidation products are atmospherically relevant. Therefore, individual compounds were compared for matching retention times, and their MS<sup>2</sup> and MS<sup>3</sup> fragmentation behaviours. Furthermore, compounds possibly containing carbonyl groups were converted into corresponding DNPH-derivatives and were further examined in terms of mass spectrometry as summarised in Table 5 (main text).

## 1. Chromatographic and mass spectral data for individual compounds

### 1.1 MW 156 (detected as mono-DNPH derivative at $m/z$ 335)

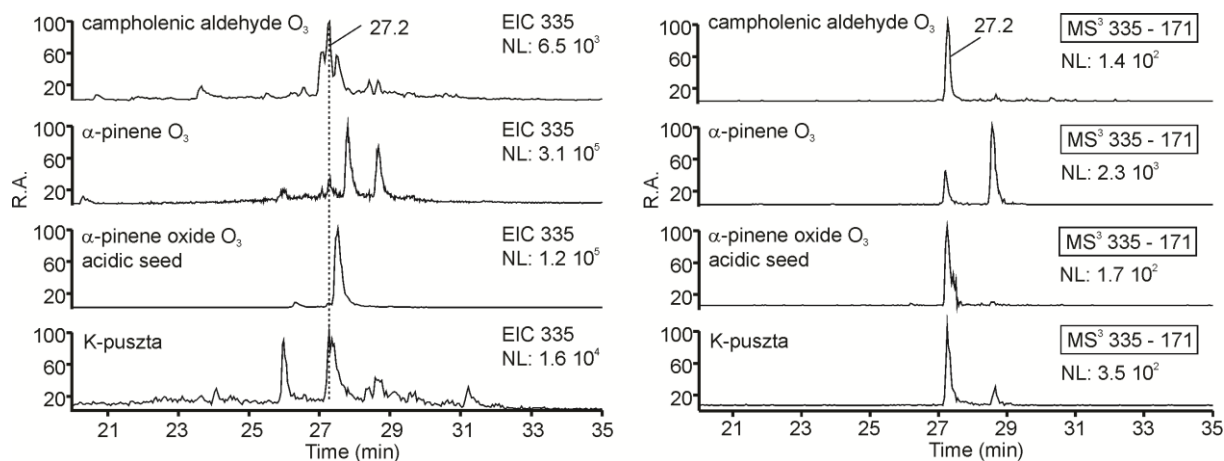


Figure SI-1. Extracted Ion Chromatograms (EICs) at  $m/z$  335 for DNPH-derivatised extracts from campholenic aldehyde/O<sub>3</sub>, α-pinene oxide/O<sub>3</sub>/acidic seed and α-pinene/O<sub>3</sub> SOA and an ambient filter sample (left) and corresponding chromatograms from the MS<sup>3</sup> study (right).

### 1.2 MW 172 (terpenylic acid)

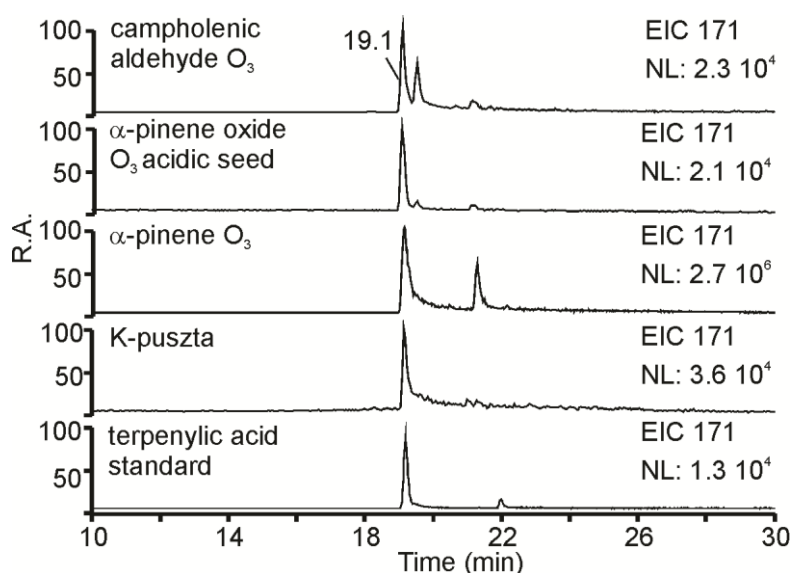


Figure SI-2. Extracted Ion Chromatograms (EICs) at  $m/z$  171 from campholenic aldehyde/O<sub>3</sub>, α-pinene oxide/O<sub>3</sub>/acidic seed, α-pinene/O<sub>3</sub> SOA, an ambient filter sample, and terpenylic acid.

### 1.3 MW 188 compounds

Three abundant  $m/z$  187 compounds were detected from the campholenic aldehyde ozonolysis SOA, which could also be observed from a  $\alpha$ -pinene oxide/ $O_3$ /acidic seed and a  $\alpha$ -pinene/ $O_3$  experiment, and an ambient filter sample (Fig. SI-3). The compound eluting at 16.9 min is present at high abundance in the ambient filter sample, showing its atmospheric importance.

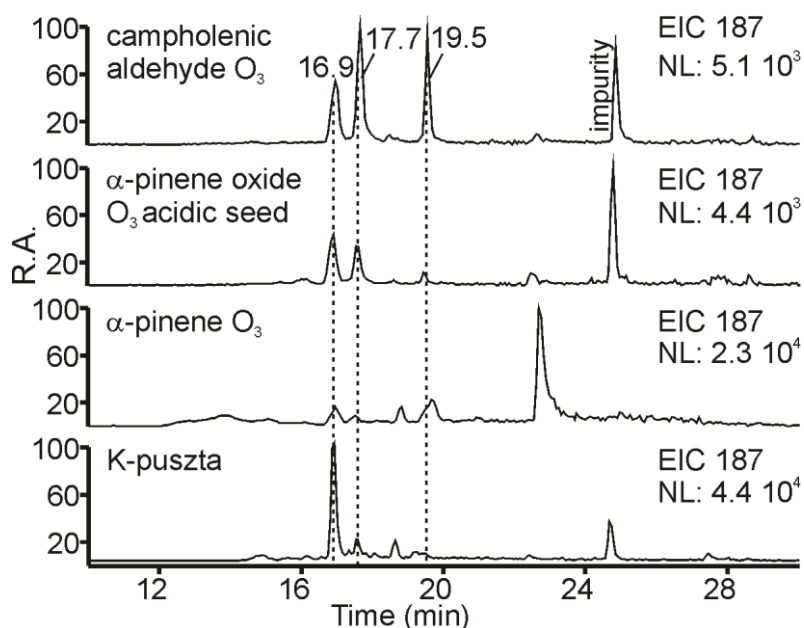


Figure SI-3. Extracted Ion Chromatograms (EICs) at  $m/z$  187 from campholenic aldehyde/ $O_3$ ,  $\alpha$ -pinene oxide/ $O_3$ /acidic seed and  $\alpha$ -pinene/ $O_3$  SOA, and an ambient filter sample.

Based on the product ion spectra (Fig. SI-4 – SI-6), the  $m/z$  187 compound eluting at 16.9 min showed the best agreement between the chamber SOA and ambient samples. Taking into account this observation, the MW 188 compound eluting at 16.9 min is likely formed from the further reaction of campholenic aldehyde.  $MS^2$  and  $MS^3$  data for this MW 188 compound have been already reported by Yasmeeen et al. (2011) from an ambient SOA sample. The MS data obtained in the current study are in agreement with those reported in the cited study.

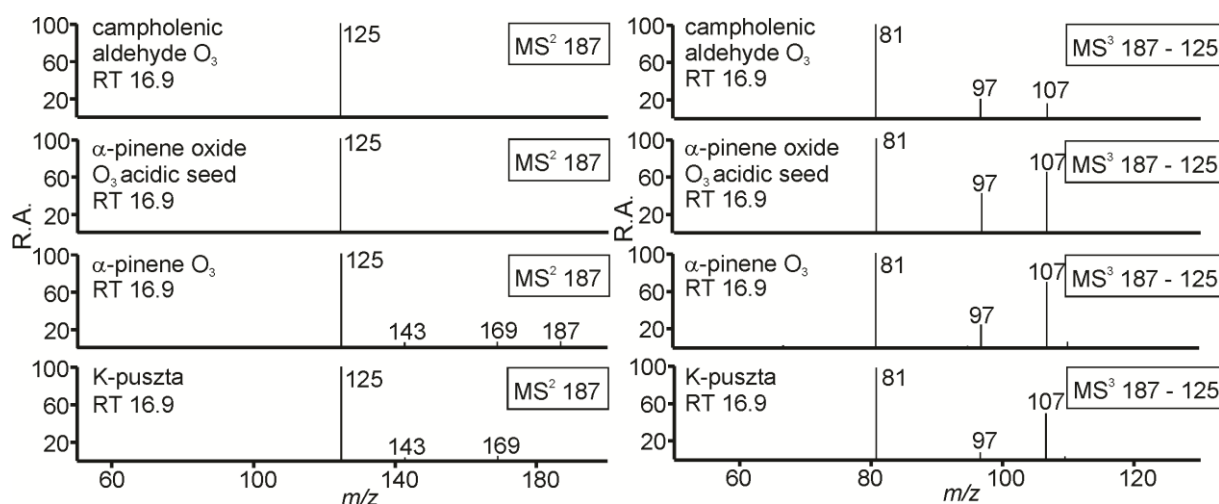


Figure SI-4. (-)ESI-MS data for the  $m/z$  187 compound eluting at 16.9 min.

Also the later-eluting MW 188 compound at 17.7 min and its fragmentation behaviour has been already described in the literature from ambient samples (Yasmeen et al., 2011). Although a matching chromatographic behaviour was observed between the laboratory-generated SOA samples and the ambient sample in the present study, the product ion spectra revealed a difference in their structures (Fig. SI-5).

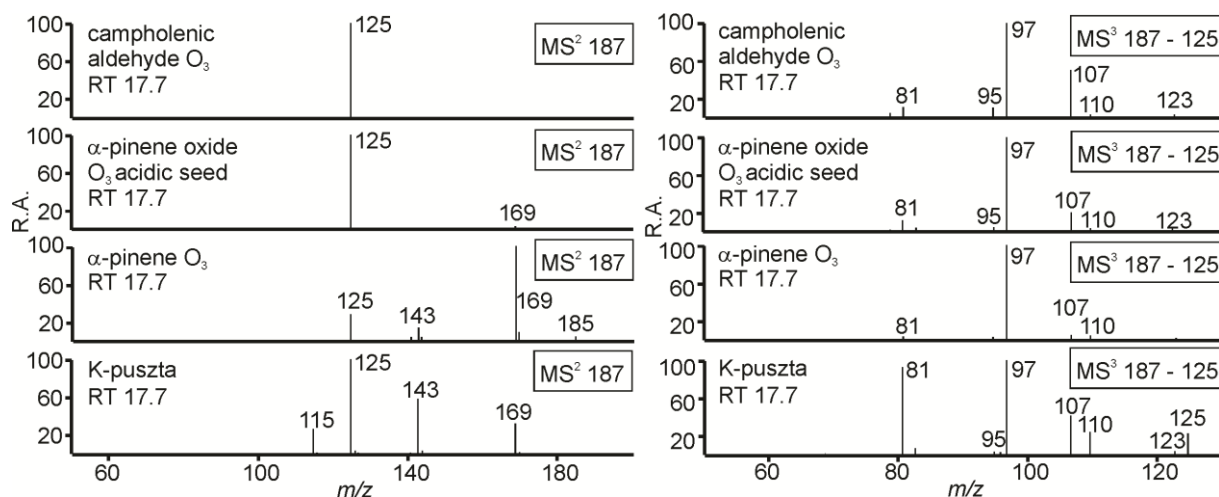


Figure SI-5. (-)ESI-MS data for the  $m/z$  187 compound eluting at 17.7 min.

The MW 188 compound eluting at 19.5 min revealed a strong product ion at  $m/z$  143 from the  $MS^2$  data that results from the loss of  $CO_2$ . A comparison to the literature with the reported  $MS^2$  product ion spectrum suggests that this compound corresponds to a mono-aldehydic precursor of 3-methyl-1,2,3-butanetricarboxylic acid (Claeys et al., 2009). Although the obtained  $MS^2$  product ion spectra agreed reasonably well for all the investigated SOA

samples in this study (Fig. SI-6, left), the MS<sup>3</sup> ( $m/z$  187  $\rightarrow$   $m/z$  143) data revealed differences (Fig. SI-6, right). Further studies are warranted to elucidate the chemical structure of this MW 188 compound.

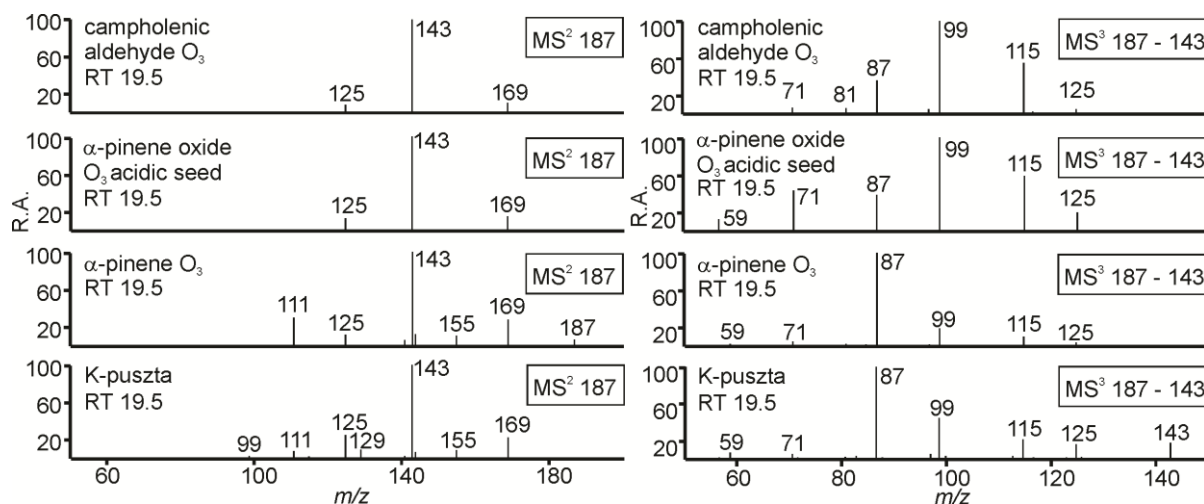


Figure SI-6. (-)ESI-MS data for the  $m/z$  187 compound eluting at 19.5 min.

#### 1.4 MW 200 compounds

Two  $m/z$  199 compounds were detected from the campholenic aldehyde/O<sub>3</sub> SOA sample, which were also observed in the α-pinene/O<sub>3</sub> SOA and the ambient sample at a retention time of 20.8 and 22.0 min (Fig. SI-7).

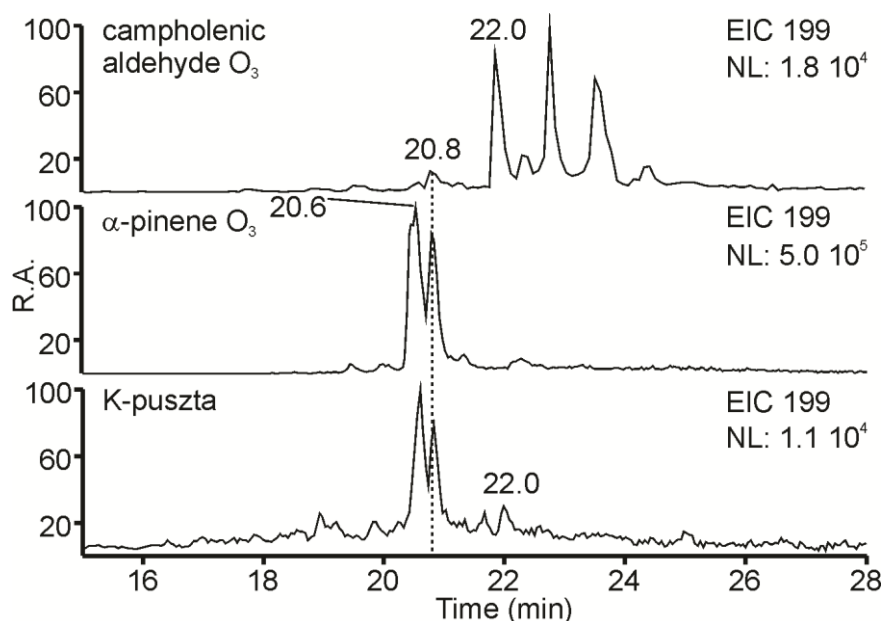


Figure SI-7. Extracted Ion Chromatograms (EICs) at  $m/z$  199 from campholenic aldehyde/O<sub>3</sub> and α-pinene/O<sub>3</sub> SOA, and an ambient filter sample.

The abundant peak at 20.6 min, which was solely observed from  $\alpha$ -pinene ozonolysis and for the K-pusztta sample, was assigned to 10-hydroxy-pinonic acid, based on its chromatographic behaviour and comparison to literature data (Claeys et al., 2013). Recorded spectra for the compound eluting at 20.6 min in the  $\alpha$ -pinene/ $O_3$  SOA and the ambient sample are only provided for completeness here, as 10-hydroxy-pinonic formation can be hardly explained from campholenic aldehyde ozonolysis. However, it must be noted that slightly different product ions were observed for the proposed 10-hydroxy-pinonic acid (RT 20.6 min), when the  $\alpha$ -pinene SOA and the ambient sample were compared (Fig. SI-8). Although the obtained  $MS^2$  and  $MS^3$  data ( $m/z$  199  $\rightarrow$   $m/z$  181) from the  $\alpha$ -pinene/ $O_3$  SOA appeared similar to the published data (Yasmeen et al., 2012), small differences were noted in the ambient aerosol sample. As shown in Figure SI-8, the  $MS^2$  fragmentation revealed an additional  $m/z$  127 product ion that was not present in  $\alpha$ -pinene/ $O_3$  SOA in this study, and was also not observed by Yasmeen et al. (2012), who investigated  $\alpha$ -pinene/OH SOA. It might be possible that a positional isomer of 10-hydroxy-pinonic acid co-elutes, leading to the additional product ion observed in the  $MS^2$  product ion spectrum for the ambient sample.

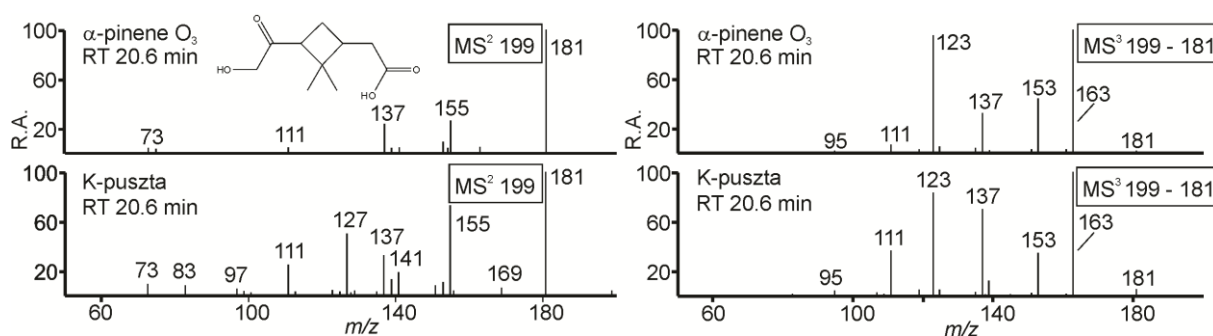


Figure SI-8.  $MS^2$  product ion spectra (left) of the  $m/z$  199 compound eluting at 20.6 min, assigned as 10-hydroxy pinonic acid, and the corresponding  $MS^3$  data (right) from  $\alpha$ -pinene ozonolysis SOA and the ambient filter sample.

Two specific campholenic aldehyde  $m/z$  199 compounds were also detected in the ambient SOA sample, eluting at 20.8 and 22.0 min. Their  $MS^2$  product ion spectra are provided in Figures SI-9 and SI-10. The compound eluting at 20.8 min showed the loss of  $H_2O$  and  $CO_2$  in the  $MS^2$  product ion spectra (Fig. SI-9, left). Although the resulting main product ions ( $m/z$  181 and 155) were also observed in the  $MS^2$  data from  $\alpha$ -pinene SOA and the ambient filter samples, additional product ions were observed in the latter ones. Based on the  $MS^3$  data ( $m/z$  199  $\rightarrow$   $m/z$  181) clear differences between the  $m/z$  199 compounds from campholenic aldehyde and  $\alpha$ -pinene SOA were observed (Fig. SI-9, right).

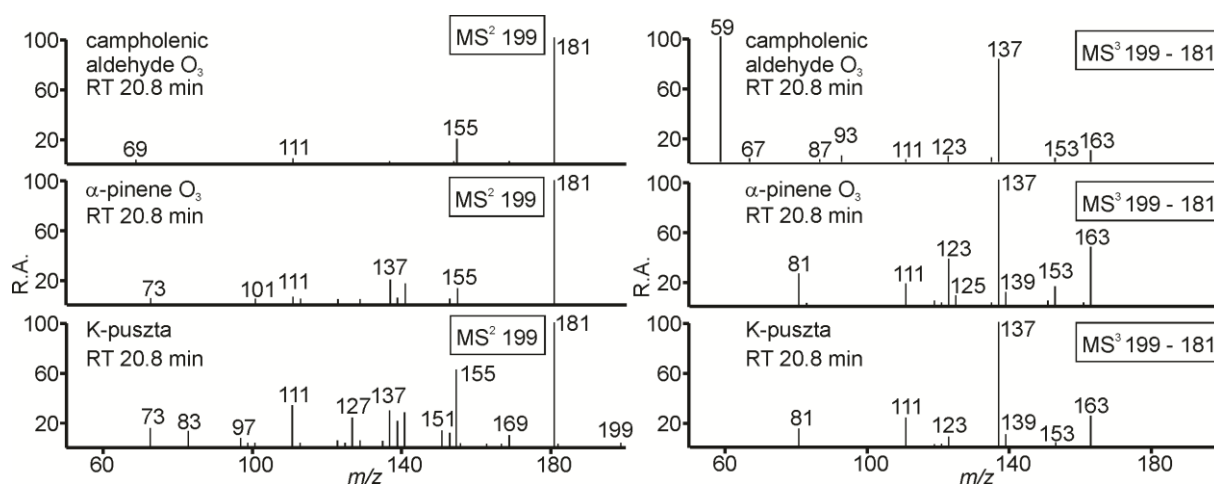


Figure SI-9. MS<sup>2</sup> product ion spectra (left) of the  $m/z$  199 compound eluting at 20.8 min, and the corresponding MS<sup>3</sup> data (right) from campholenic aldehyde/O<sub>3</sub> and  $\alpha$ -pinene/O<sub>3</sub> SOA, and an ambient filter sample.

The  $m/z$  199 compound eluting at 22 min in the campholenic aldehyde/O<sub>3</sub> SOA sample could also be observed from the ambient aerosol sample (Fig. SI-7) so that further studies on this compound were performed. Similar product ion spectra were obtained upon MS<sup>2</sup> and MS<sup>3</sup> ( $m/z$  199  $\rightarrow$   $m/z$  181) fragmentation of campholenic aldehyde/O<sub>3</sub> SOA and the K-pusztta sample, as shown in Figure SI-10. The relative abundance of individual product ions was slightly different; a possible reason for this phenomenon is that the internal energy of the precursor ion is somewhat different. A structure for a possible MW 200 compound has been proposed based on the reaction of ozone with campholenic aldehyde (Table 4, main text) in the present study. Considering the observed product ions, which correspond to the loss of H<sub>2</sub>O, CO<sub>2</sub> and CO, the proposed dicarbonyl-carboxylic acid structure seems reasonable.

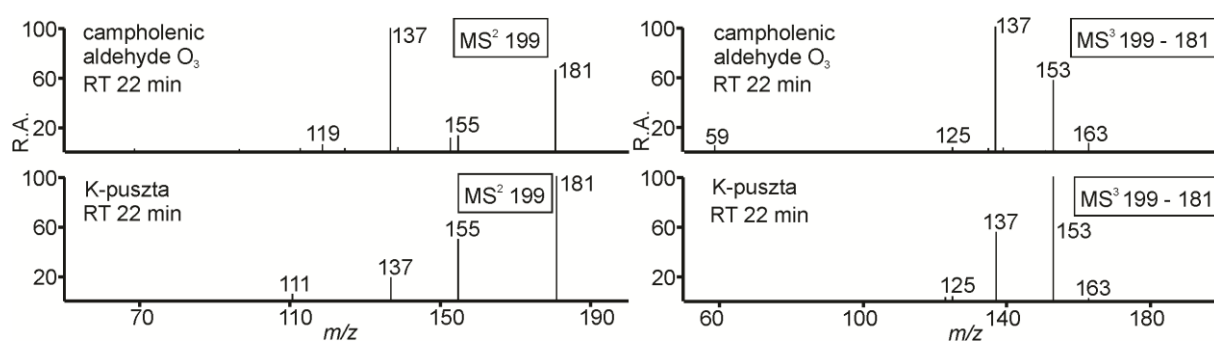


Figure SI-10. MS<sup>2</sup> product ion spectra (left) of the  $m/z$  199 compound eluting at 22 min, and corresponding MS<sup>3</sup> data (right) from campholenic aldehyde/O<sub>3</sub> SOA and an ambient filter sample.

A possible fragmentation mechanism is given in Figure SI-11. However, as no authentic standard was available and several  $m/z$  199 compounds were detected from the campholenic aldehyde SOA sample, the proposed structure should be regarded as tentative.

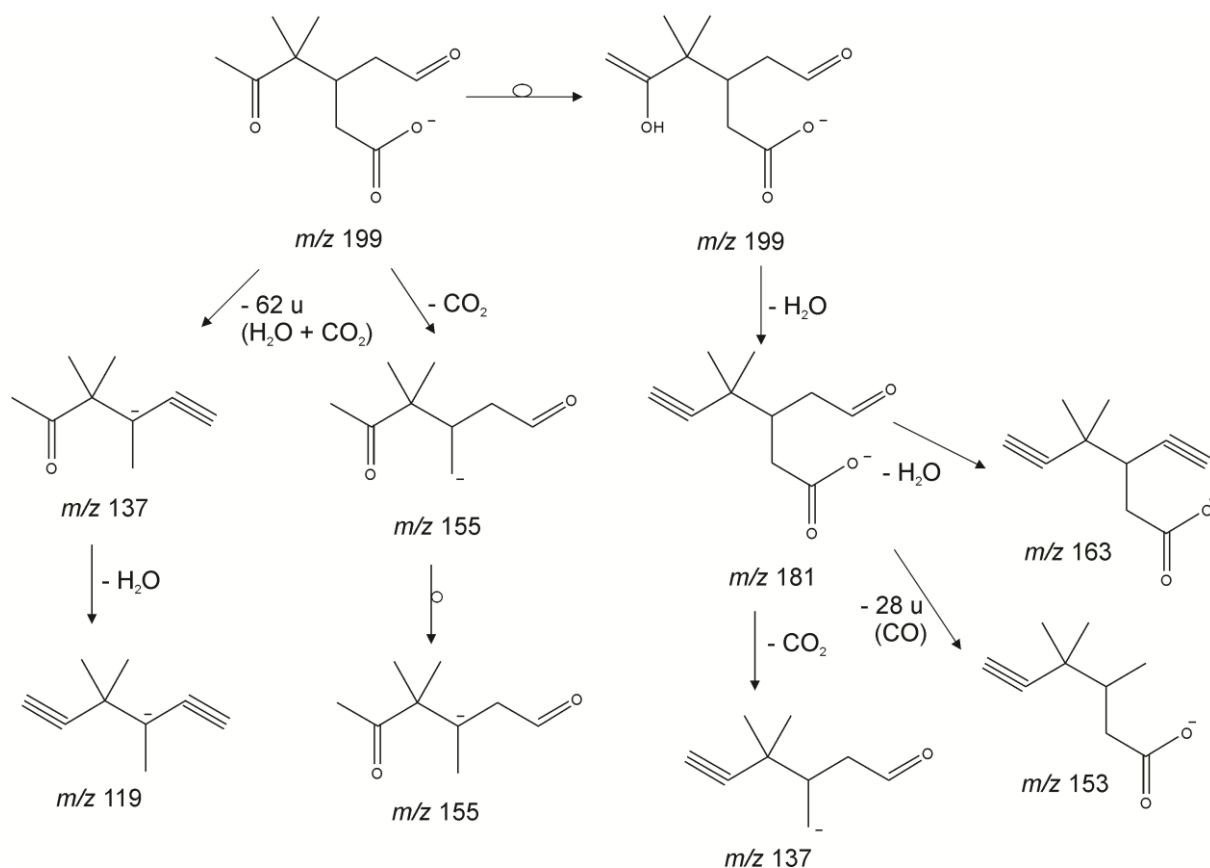


Figure SI-11. Tentative structure and proposed fragmentation mechanism of the  $m/z$  199 compound.

### Corresponding DNPH-derivatives for MW 200 compounds

To support the presence of carbonyl groups in the MW 200 compound, the filter samples were also derivatised with DNPH. Both, the corresponding mono-DNPH derivative ( $m/z$  379) and another di-DNPH derivative ( $m/z$  559) were detected, pointing to the presence of several and structurally different MW 200 compounds. A highly complex mixture was obtained from the DNPH-derivatised filter samples, revealing several isomers. From the  $\text{MS}^2$  data it can be concluded that the  $m/z$  379 compound eluting at 27.1 min is a DNPH-derivatised compound as the typical DNPH fragments ( $m/z$  182, 178, 152, and 122) were detected (Fig. SI-12). Additionally, the loss of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  was observed, consistent with a hydroxy-carboxylic acid structure. As highly diverse individual mass spectra were recorded from all the investigated aerosol samples in this study, no further structural information could be derived. Interferences from the complex sample matrix might also be a reason for the observed inconsistency in the mass spectral data.



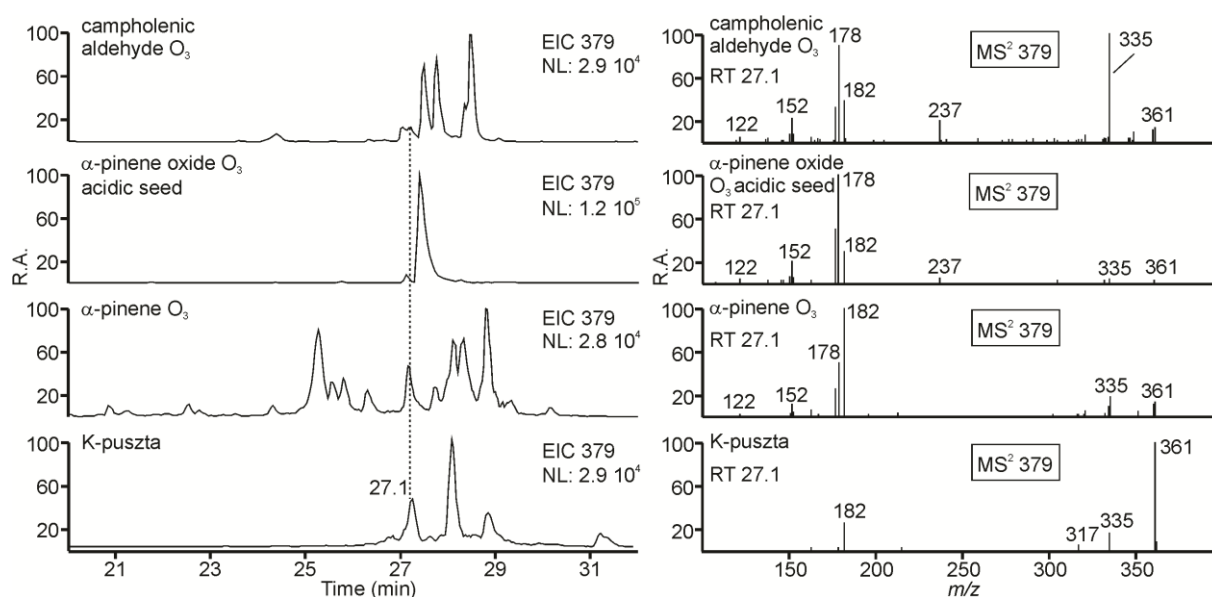


Figure SI-12. Extracted Ion Chromatograms (EICs) of a mono-DNPH-derivatised compound ( $m/z$  379), corresponding to a MW 200 compound (left), from all the investigated filter samples and its respective MS<sup>2</sup> product ion spectra (right).

A similarly diverse chromatogram and individual mass spectral data were obtained from a possible di-DNPH-derivative ( $m/z$  559) of a MW 200 compound (Fig. SI-13). The fragmentation revealed the loss of H<sub>2</sub>O and CO<sub>2</sub>, which was dominant from the K-pusztta sample together with some other characteristic product ions, as shown in Figure SI-13 (right). Based on the proposed structure, given in Figure SI-11 for the non-derivatised compound, the observed product ions from the fragmentation of the di-DNPH-derivative  $m/z$  559 can be explained (Fig. SI-14). Nevertheless, the proposed structure remains tentative, as no authentic standard was available.

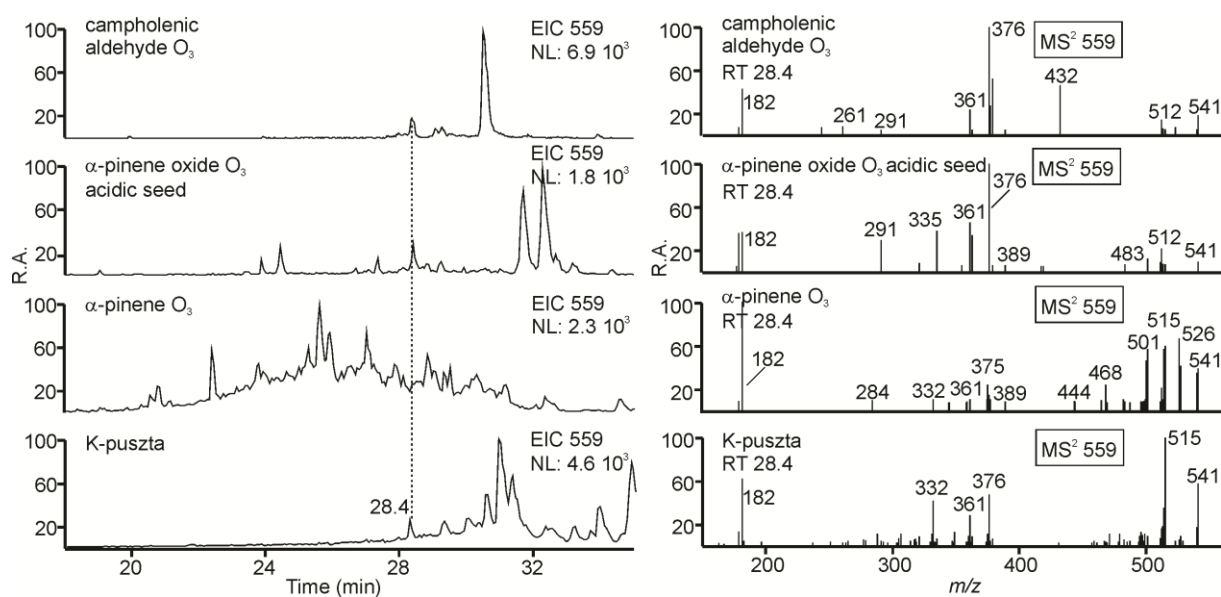


Figure SI-13. Extracted Ion Chromatograms (EICs) of the di-DNPH-derivatised compound ( $m/z$  559), corresponding to a MW 200 compound (left), and its respective  $MS^2$  product ion spectra (right).

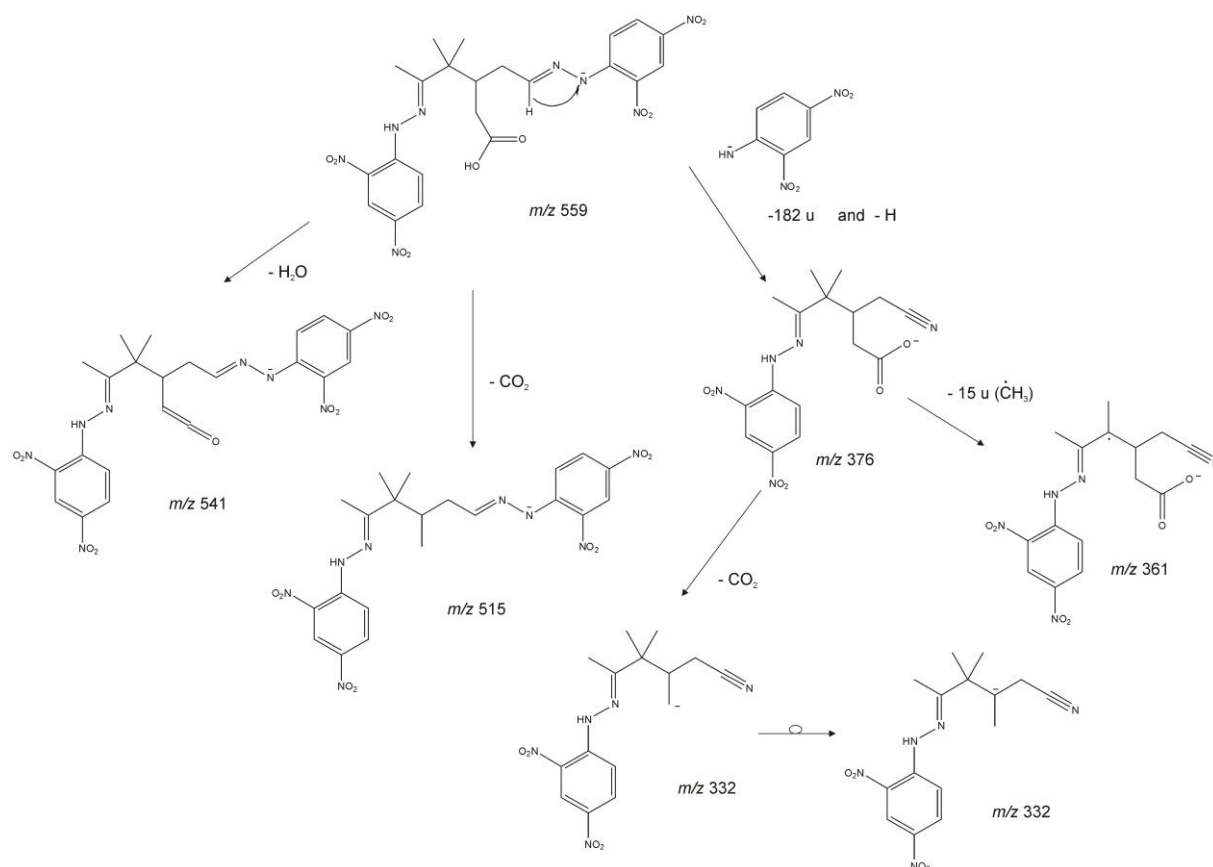


Figure SI-14. Proposed fragmentation mechanism for the di-DNPH-derivatised compound ( $m/z$  559), corresponding to a MW 200 compound.

### 1.5 MW 202 compound

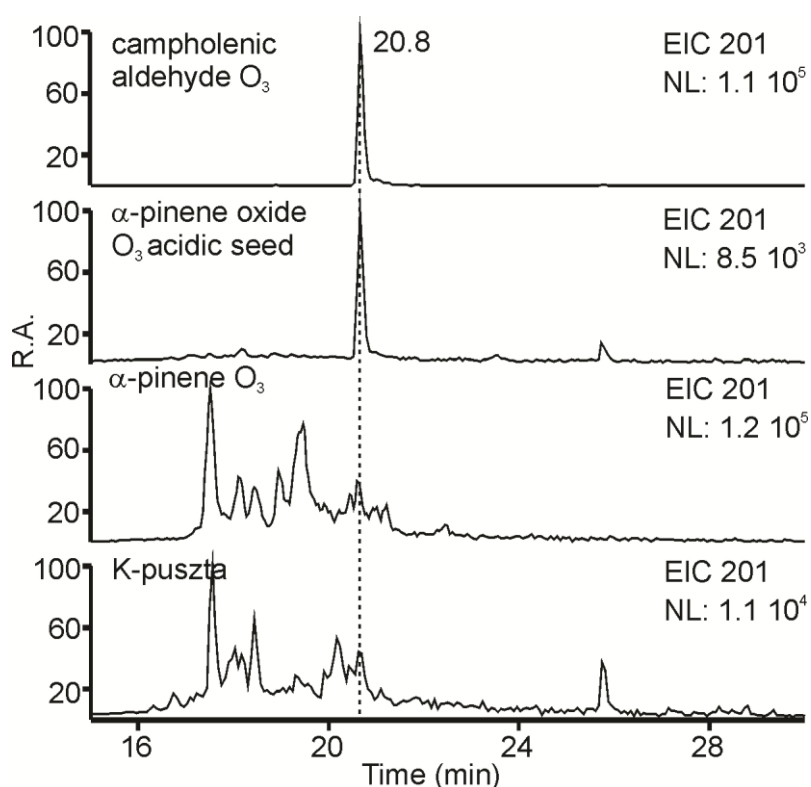


Figure SI-15. Extracted Ion Chromatograms (EICs) at  $m/z$  201 from campholenic aldehyde/ $O_3$ ,  $\alpha$ -pinene oxide/ $O_3$ /acidic seed, and  $\alpha$ -pinene/ $O_3$  SOA, and an ambient filter sample.

### Corresponding DNPH-derivatives for MW 202 compounds

Although a corresponding mono-DNPH-derivative ( $m/z$  381) for a MW 202 compound could be detected from the campholenic aldehyde ozonolysis and the  $\alpha$ -pinene oxide/ $O_3$ /acidic seed experiment, its presence could not be confirmed from the  $\alpha$ -pinene/ $O_3$  SOA and an ambient sample (Fig. SI-16, left). Nevertheless, from the  $MS^2$  data ( $m/z$  381) the loss of  $H_2O$  and  $CO_2$  was observed (Fig. SI-16, right), corroborating its proposed structure as a  $C_9$ -carbonyl-dicarboxylic acid.

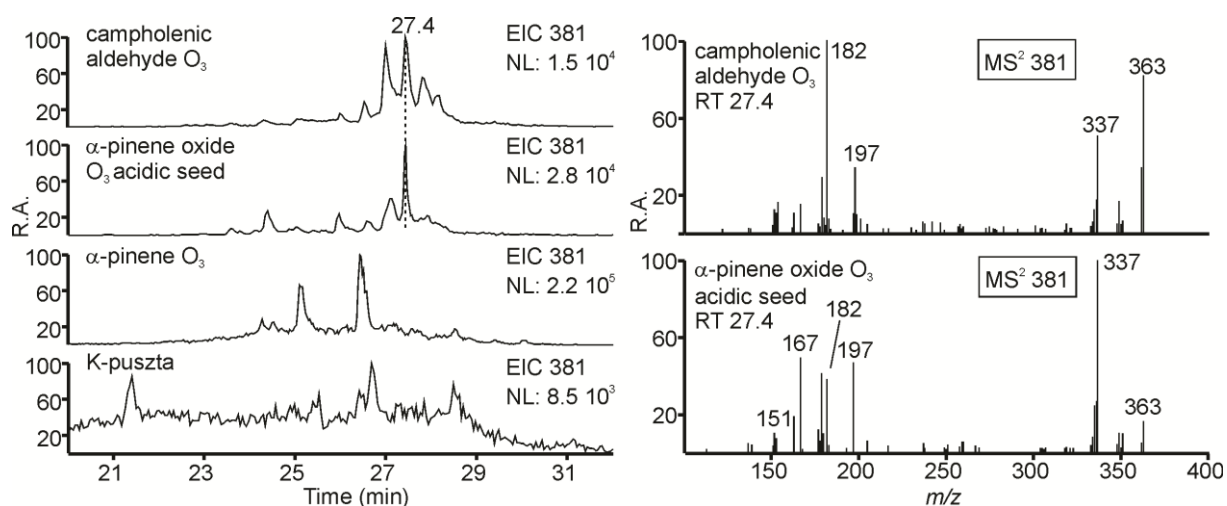


Figure SI-16. Extracted Ion Chromatograms (EICs) of the mono-DNPH-derivatised compound ( $m/z$  381), corresponding to a MW 202 compound (left), and the respective product ion spectra (right) from the compound eluting at 27.4 min.

### 1.6 MW 216 compound

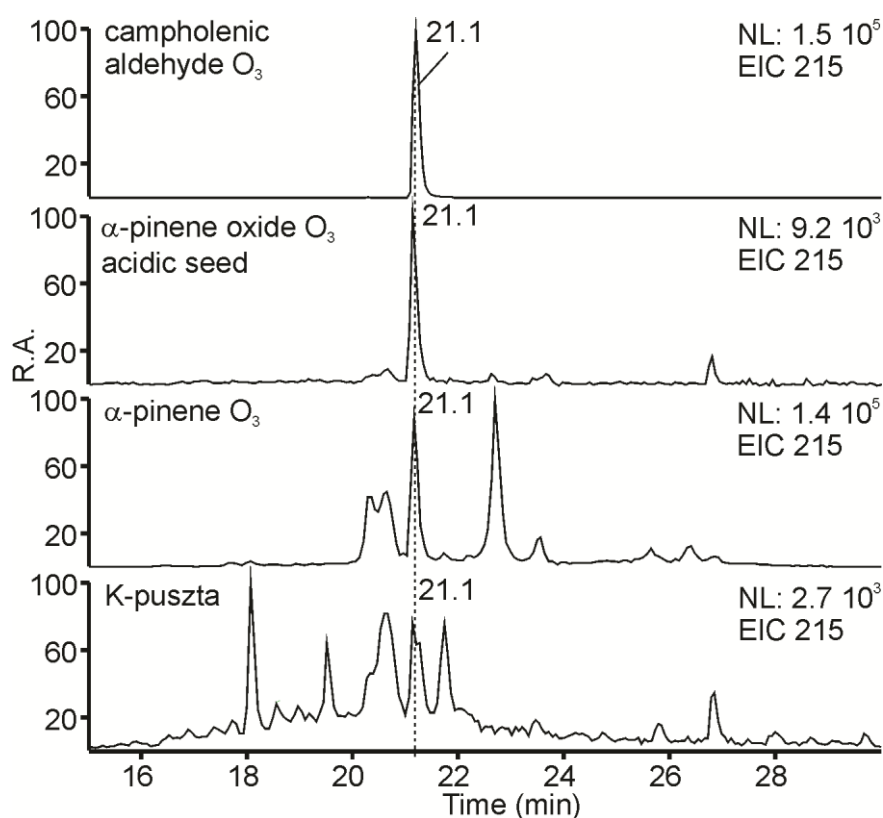


Figure SI-17. Extracted Ion Chromatograms (EICs) at  $m/z$  215 from campholenic aldehyde/ $O_3$ ,  $\alpha$ -pinene oxide/ $O_3$ /acidic seed,  $\alpha$ -pinene/ $O_3$  SOA, and an ambient filter sample.

## Corresponding DNPH-derivatives for MW 216 compounds

The derivatisation with DNPH enabled the detection of several corresponding mono-derivatives ( $m/z$  395) for MW 216 compounds. The compound with a RT of 28.2 min was present in all the investigated filter samples (Fig. SI-18, left) but no clear agreement in terms of its mass spectral fragmentation behaviour was observed (Fig. SI-18, right).

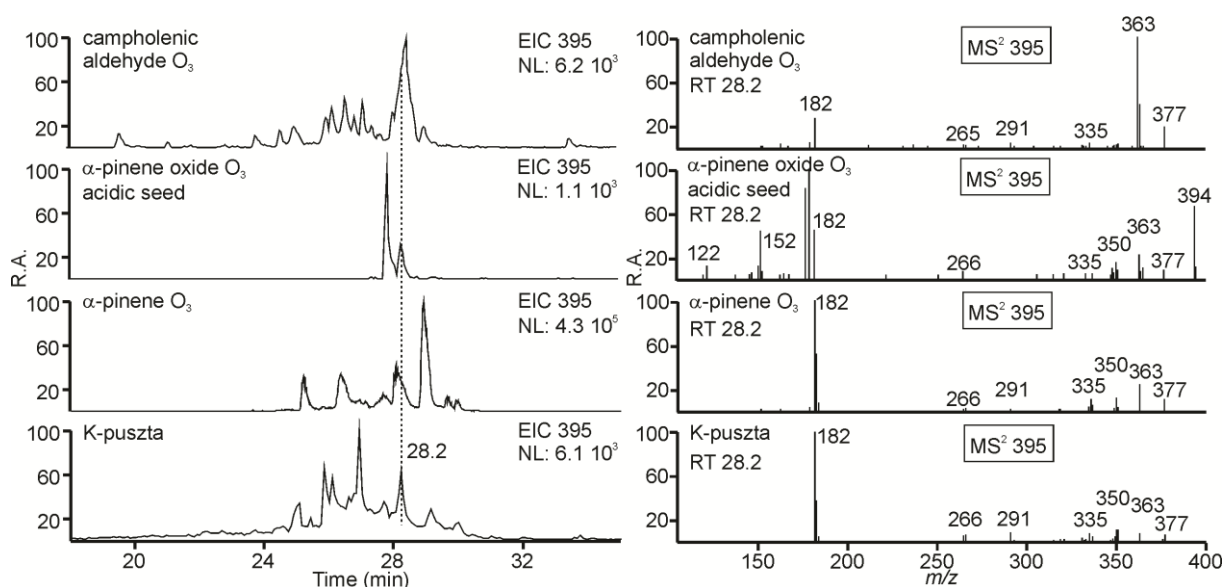


Figure SI-18. Extracted Ion Chromatograms (EICs) of the mono-DNPH-derivatised compound ( $m/z$  395), corresponding to a MW 216 compound (left), and their respective product ion spectra (right).

## 1.7 MW 230 compound

A  $m/z$  229 compound (C<sub>10</sub>H<sub>14</sub>O<sub>6</sub>) was described recently as a specific campholenic aldehyde tracer with an atmospheric abundance comparable to *cis*-pinic acid (Iinuma et al., 2013). It is noted that slightly different results were obtained in the present study. Although an abundant  $m/z$  229 compound with a RT of 20.0 min was detected in both the campholenic aldehyde/O<sub>3</sub> and the α-pinene oxide/O<sub>3</sub>/acidic seed SOA samples, a slightly later-eluting isomer (RT 20.5 min) was present in the α-pinene/O<sub>3</sub> SOA and the ambient filter samples (Fig. SI-19), where the later-eluting compound might correspond to a  $m/z$  229 compound described by Ng et al. (2007). Both the compounds eluting at 20.0 min and that at 20.5 min, showed differences in their fragmentation behaviours (Fig. SI-20, top and bottom, respectively) and hence differ in their chemical structure.

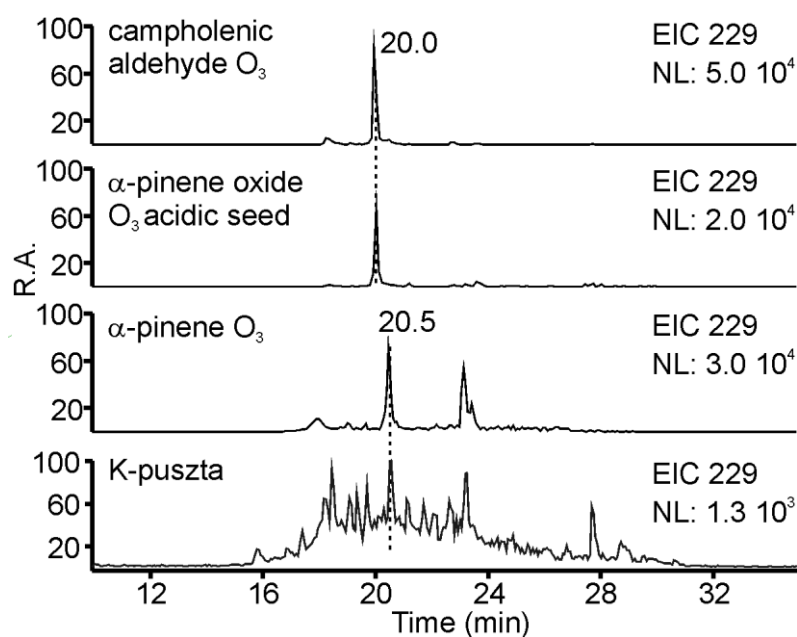


Figure SI-19. Extracted Ion Chromatograms (EICs) at  $m/z$  229 obtained for campholenic aldehyde/ $O_3$ ,  $\alpha$ -pinene oxide/ $O_3$ /acidic seed, and  $\alpha$ -pinene/ $O_3$  SOA, and an ambient filter sample, showing the presence of two isomeric  $m/z$  229 compounds.

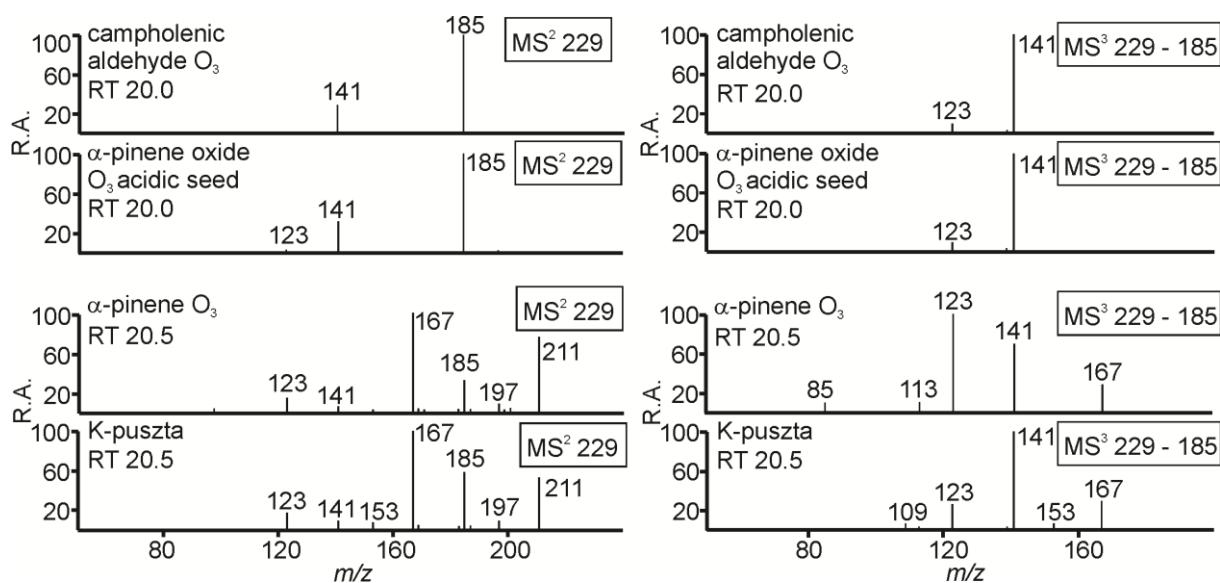


Figure SI-20.  $MS^2$  product ion spectra (left) of the  $m/z$  229 compound eluting at 20.0 min (top) and 20.5 min (down), and the corresponding  $MS^3$  data (right) from campholenic aldehyde/ $O_3$ ,  $\alpha$ -pinene oxide/ $O_3$ /acidic seed and  $\alpha$ -pinene/ $O_3$  SOA, and an ambient filter sample.

## Corresponding DNPH-derivatives for MW 230 compounds

The derivatisation procedure enabled the detection of corresponding DNPH-derivatives that were solely seen from the campholenic aldehyde oxidation and  $\alpha$ -pinene oxide/ $O_3$ /acidic seed SOA samples. Both, mono-DNPH-derivatives at  $m/z$  409 (Fig. SI-21), as well as di-DNPH-derivatives at  $m/z$  589 (Fig. SI-23, left) were detected.

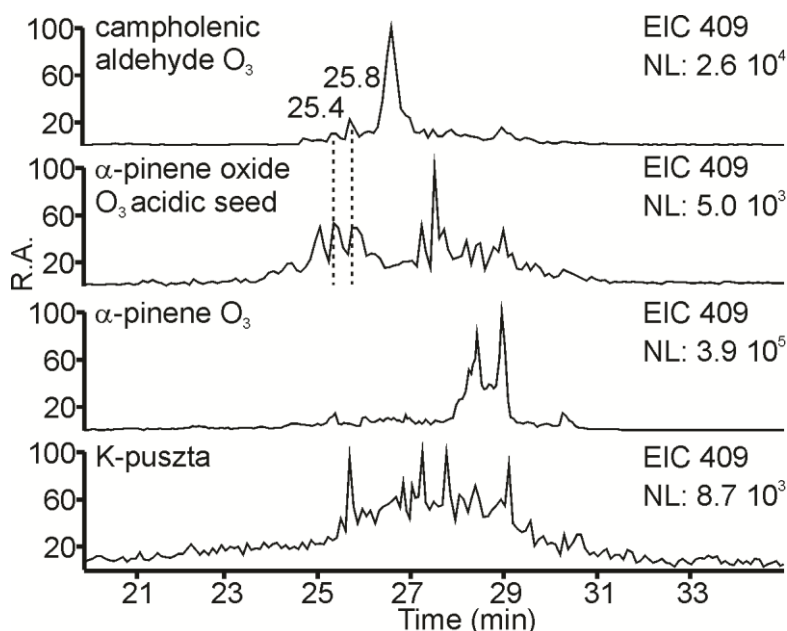


Figure SI-21. Extracted Ion Chromatograms (EICs) of the mono-DNPH-derivatised compound ( $m/z$  409), corresponding to a MW 230 compound.

The detected two mono-DNPH-derivatised compounds at  $m/z$  409 eluting at 25.4 min and 25.8 min, together with their respective  $MS^2$  data, are shown in Figure SI-22 (left and right, respectively).

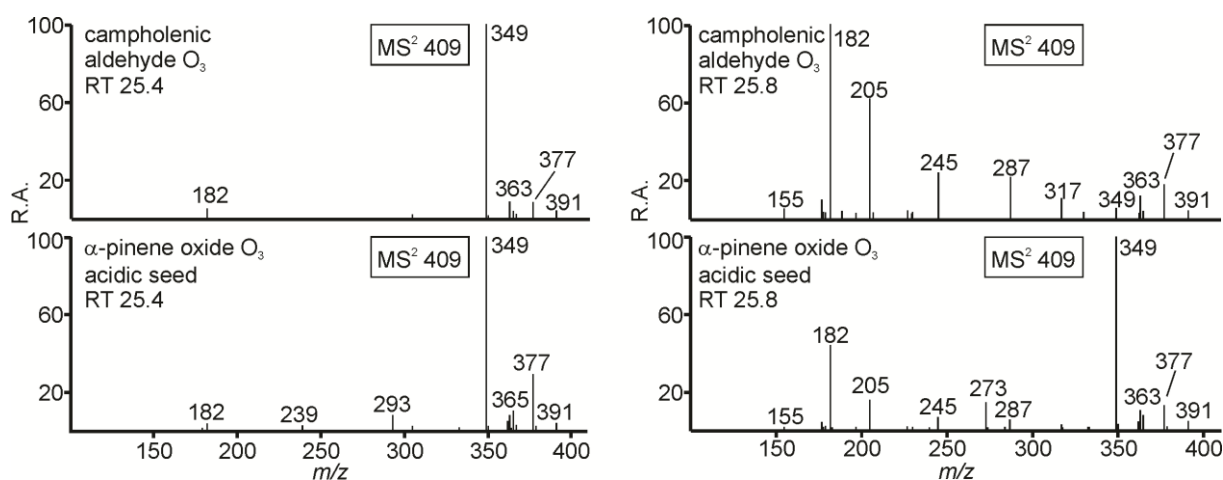


Figure SI-22.  $MS^2$  product ion spectrum of two mono-DNPH-derivatised MW 230 compounds ( $m/z$  409 as DNPH-derivative) eluting at 25.4 (left) and 25.8 min (right).

The chromatogram and the mass spectral data obtained for the di-DNPH compound ( $m/z$  589), corresponding to a MW 230 compound, are shown in Figure SI-23 (left and right, respectively). It can be seen that the product ion spectra do not match well with each other.

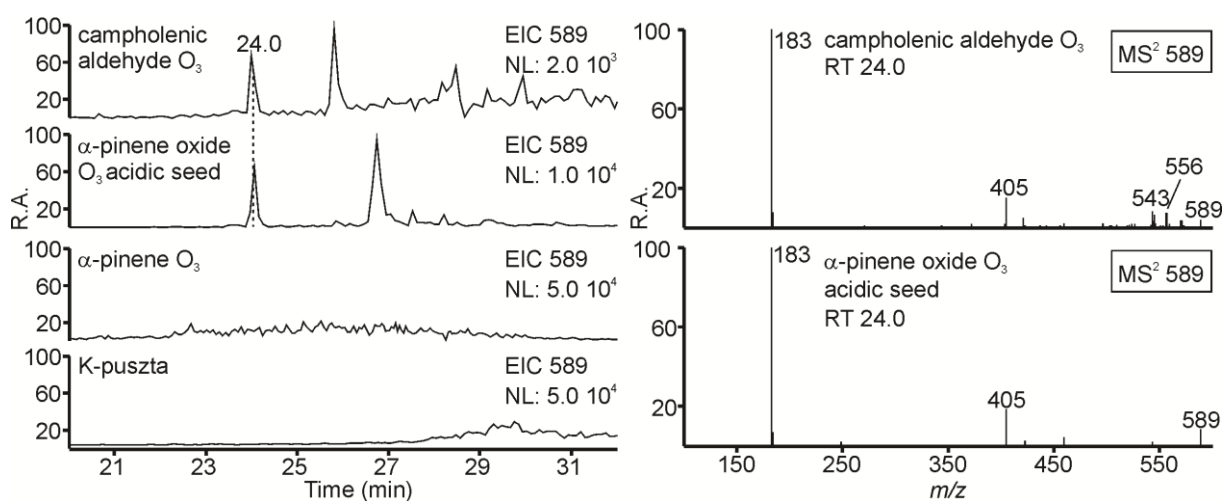


Figure SI-23. Extracted Ion Chromatograms (EICs) of the di-DNPH derivatised compound ( $m/z$  589), corresponding to a MW 230 compound (left), and its respective product ion spectra from campholenic aldehyde/ $O_3$  and  $\alpha$ -pinene oxide/ $O_3$ /acidic seed SOA (right).



### 1.8 MW 232 compounds (DTAA and an unknown)

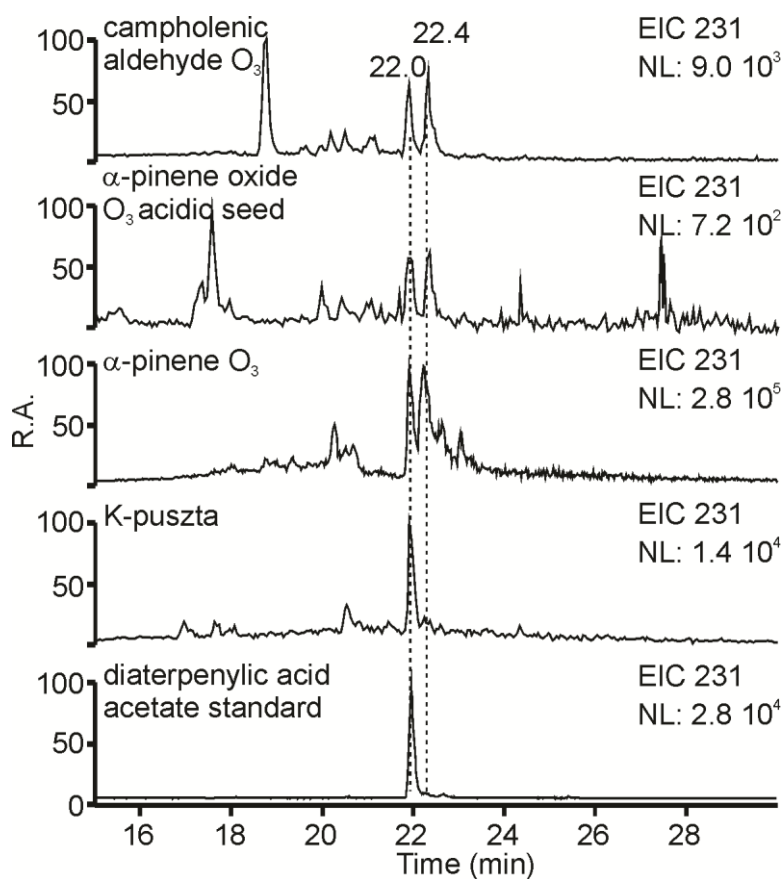


Figure SI-24. Extracted Ion Chromatograms (EICs) at  $m/z$  231 from campholenic aldehyde/ $O_3$ ,  $\alpha$ -pinene oxide/ $O_3$ /acidic seed and  $\alpha$ -pinene/ $O_3$  SOA, an ambient filter sample, and the DTAA standard compound.

The additional  $m/z$  231 isomer eluting at 22.4 min was detected in all the investigated filter samples. Slightly different fragmentation behaviours were observed from the respective  $MS^2$  data. The  $m/z$  231 compound detected from  $\alpha$ -pinene/ $O_3$  SOA and the ambient sample revealed an additional  $m/z$  185 product ion ( $-46$  u) and an abundant product ion at  $m/z$  171 ( $-60$  u), as shown in Figure SI-25 (left).

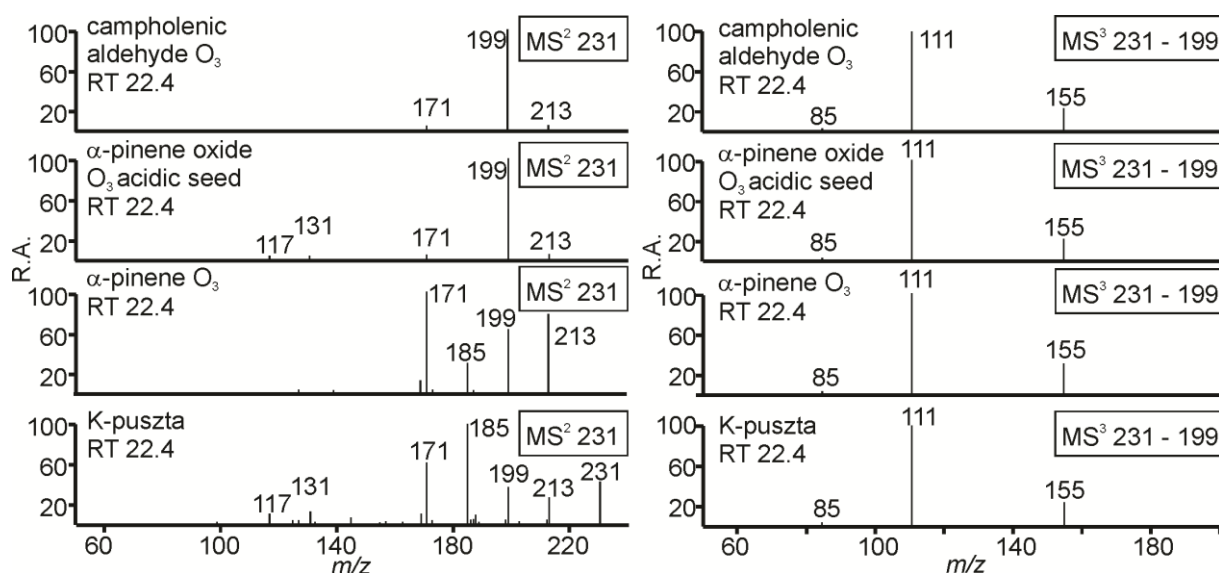


Figure SI-25. MS<sup>2</sup> product ion spectra (left) of the unknown  $m/z$  231 compound eluting at 22.4 min, and the corresponding MS<sup>3</sup> data (right) from campholenic aldehyde/O<sub>3</sub>,  $\alpha$ -pinene/O<sub>3</sub> and  $\alpha$ -pinene oxide/O<sub>3</sub>/acidic seed SOA, and an ambient filter sample.

Based on the slightly distinctive fragmentation behaviour, the unknown MW 232 compound seems to be related to the compound observed in the ambient sample and the one detected from  $\alpha$ -pinene ozonolysis. It likely originates from another precursor compound than campholenic aldehyde and further studies are warranted to elucidate the structure of and gain insight into the formation mechanism of this yet unidentified oxidation product.

## References

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