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Supplement of

High-molecular-weight esters in α -pinene ozonolysis secondary organic aerosol: structural characterization and mechanistic proposal for their formation from highly oxygenated molecules

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S1. Previous MS data obtained on the MW 358 ester in the negative ion mode

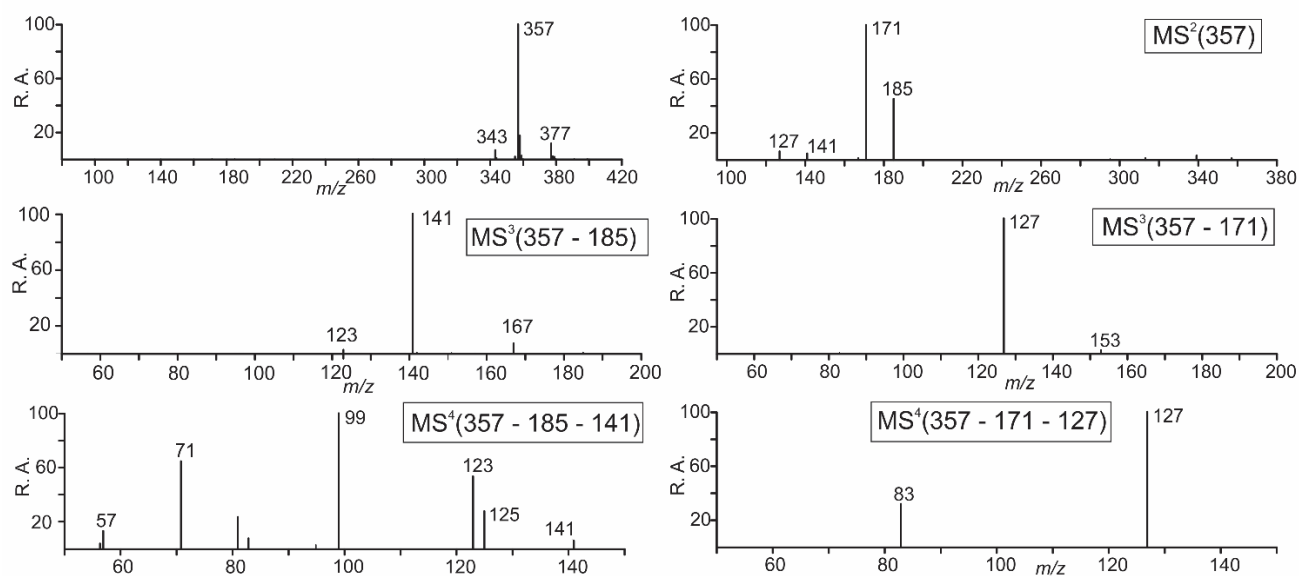


Fig. S1. MS data obtained in the negative ion ESI mode for the MW 358 ester from α -pinene/O₃ SOA. The MS² and MS³ data obtained on m/z 185 in MS² support a *cis*-pinic acid residue, while those on m/z 171 in MS² point to a diaterpenylic acid residue. The data are taken from Yasmeen et al. (2010) (Fig. 5).

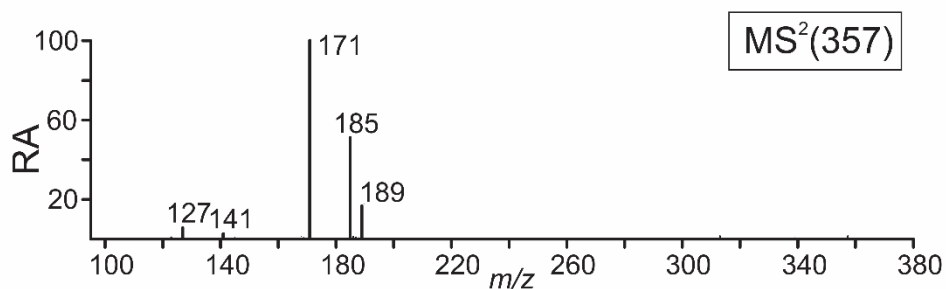
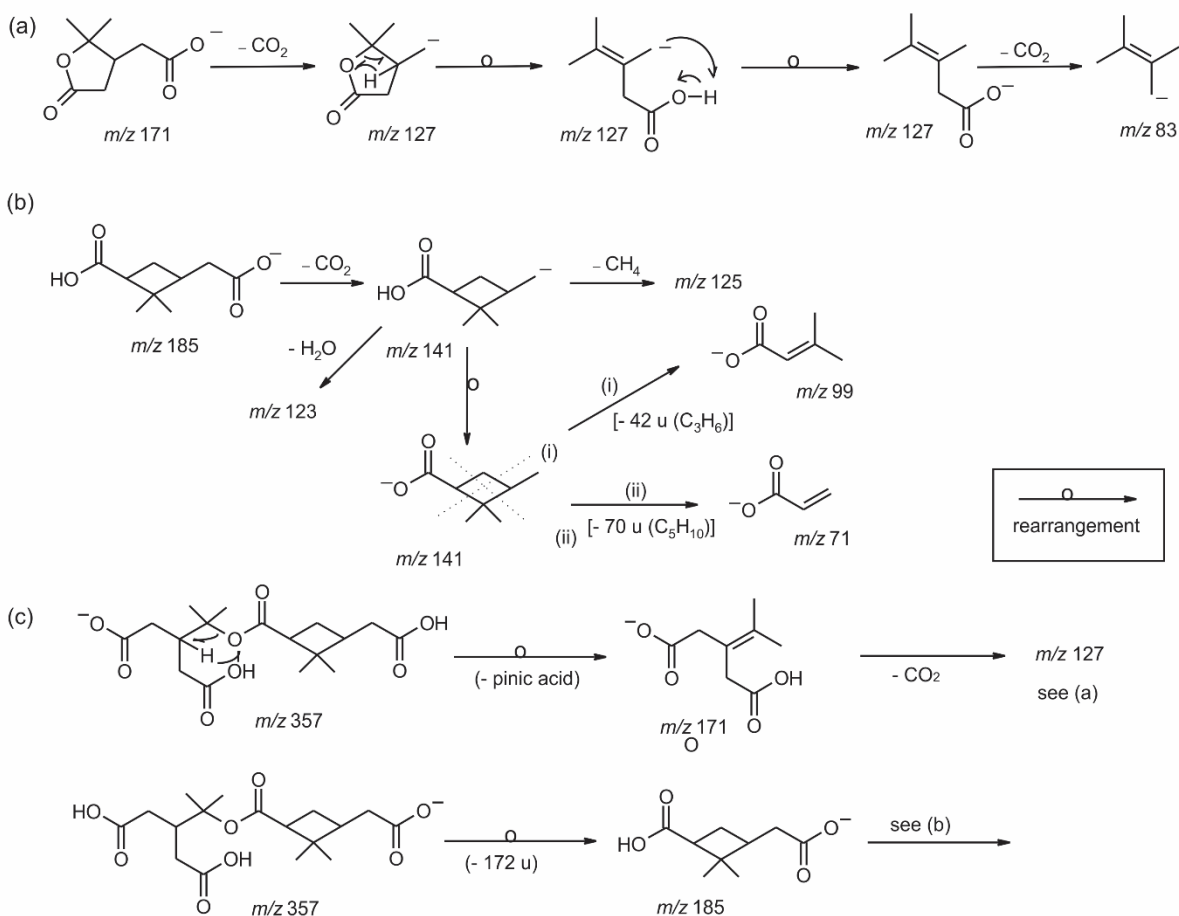
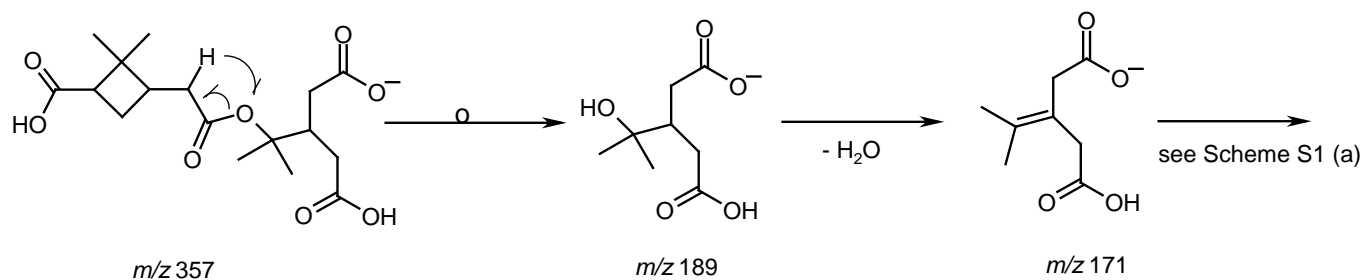


Fig. S2. MS data obtained in the negative ion ESI mode for the minor MW 358 ester from β -pinene/O₃ SOA. The MS² and MS³ data (not shown) obtained on m/z 185 support a *cis*-pinic acid residue, those on m/z 171 a diaterpenylic acid residue, and those on m/z 189 are consistent with diaterpenylic acid (Scheme S2). The data are taken from Yasmeen et al. (2010) (Fig. 6).



Scheme S1. Proposed fragmentation mechanism for m/z 171 (terpenylic acid) (a) and m/z 185 (*cis*-pinic acid) (b) and m/z 357 (MW 358 compound from α -pinene/ O_3 SOA) (c). The data are taken from Yasmeen et al. (2010) (Scheme 1).



Scheme S2. Proposed fragmentation mechanism for m/z 357 (minor MW 358 compound from β -pinene/ O_3 SOA) resulting in a m/z 189 product ion (Fig. S2).

S2. LC data obtained on α -pinene/ O_3 SOA

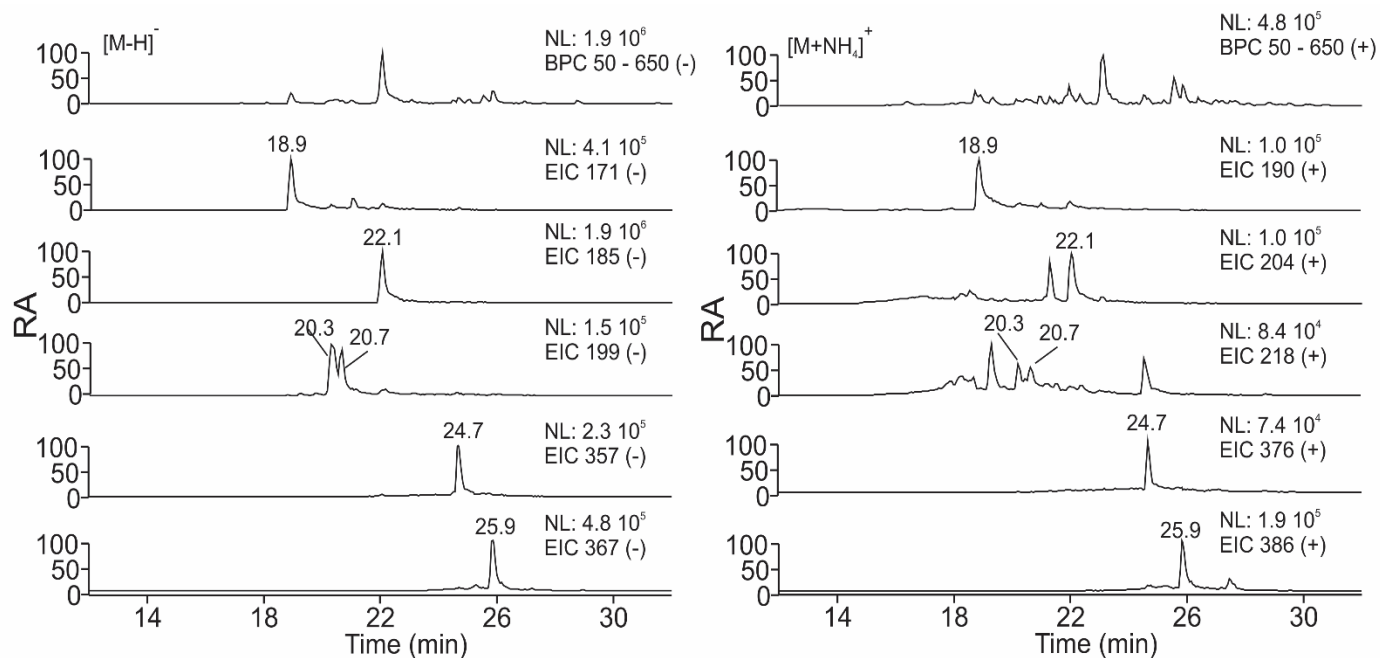


Fig. S3. Base peak chromatograms (BPCs) and extracted ion chromatograms (EICs) of the non-derivatized α -pinene/ O_3 SOA sample. EICs are presented for the monomeric and hetero-dimeric species with their isomeric compounds: m/z 171 (terpenylic acid), m/z 185 (*cis*-pinic acid), m/z 199 (7-hydroxypinonic acid + isomer), m/z 357 (MW 358 ester) and m/z 367 (MW 368 ester) in the negative ion mode (left panel) and in the positive ion mode (right) as corresponding ammonium adduct ions. Abbreviation: NL, normalization level.

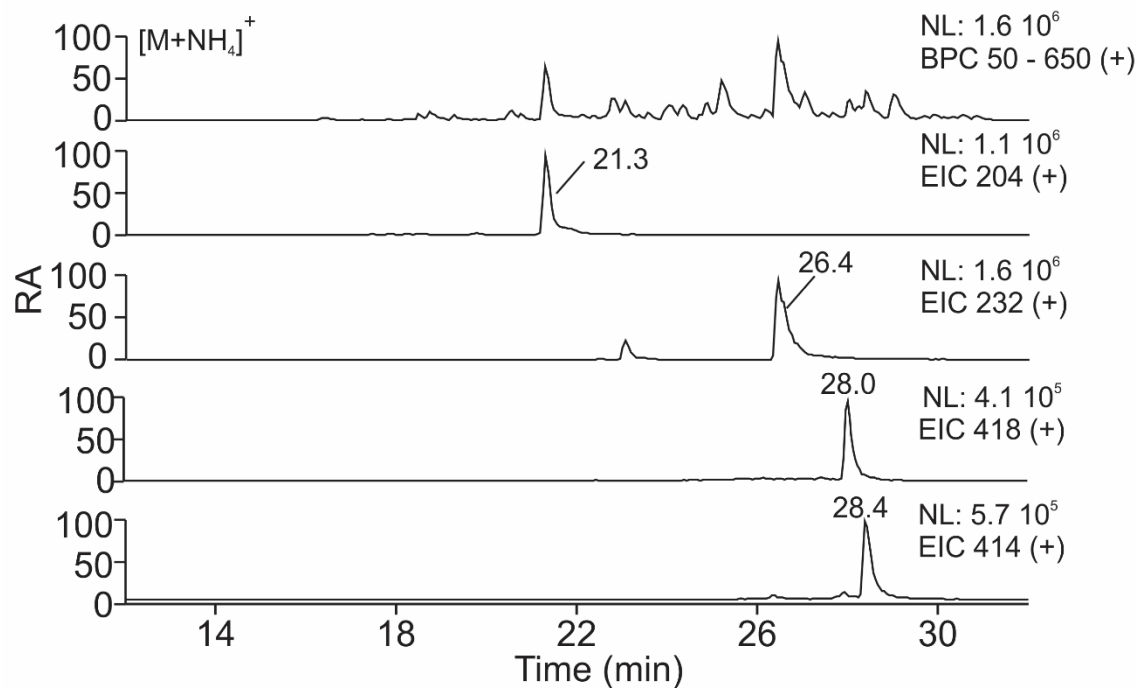
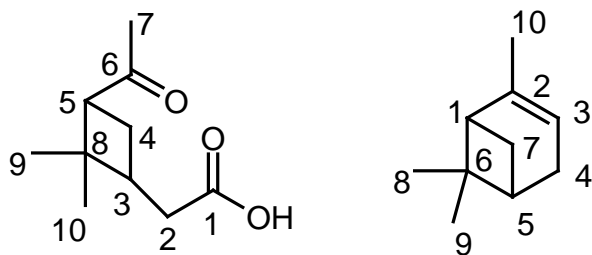


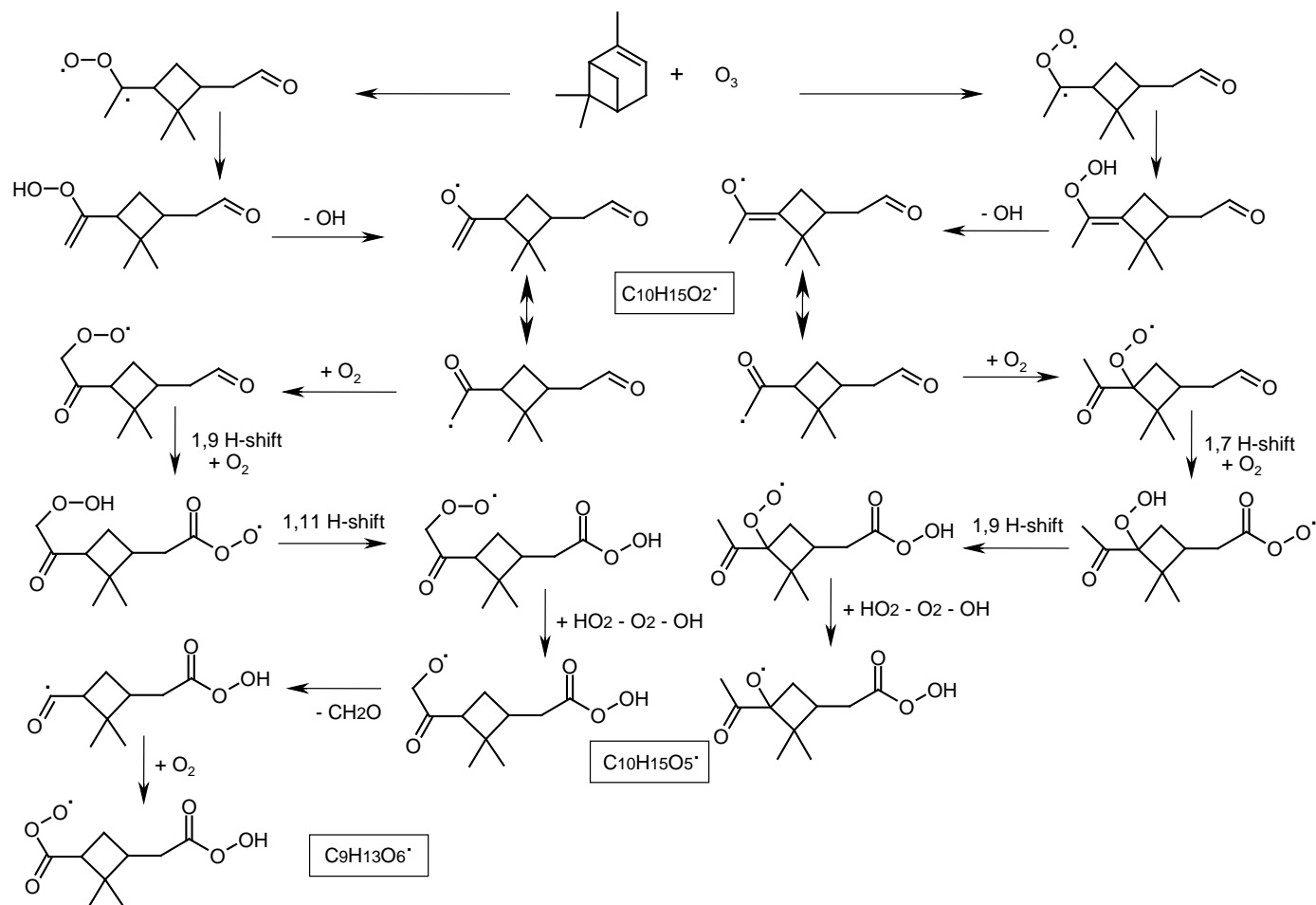
Fig. S4. Base peak chromatograms (BPCs) and extracted ion chromatograms (EICs) of the methylated α -pinene/ O_3 SOA sample. EICs are presented for corresponding methylated terpenylic acid (m/z 190), *cis*-pinic acid and isomeric compounds (i.e., hydroxypinonic acids) (m/z 232), the trimethylated MW 358 compound (m/z 418) and the dimethylated MW 368 compound (m/z 414) detected as ammonium adduct ions in the positive ionization mode. Abbreviation: NL, normalization level.

S3. Labeling of *cis*-pinonic acid



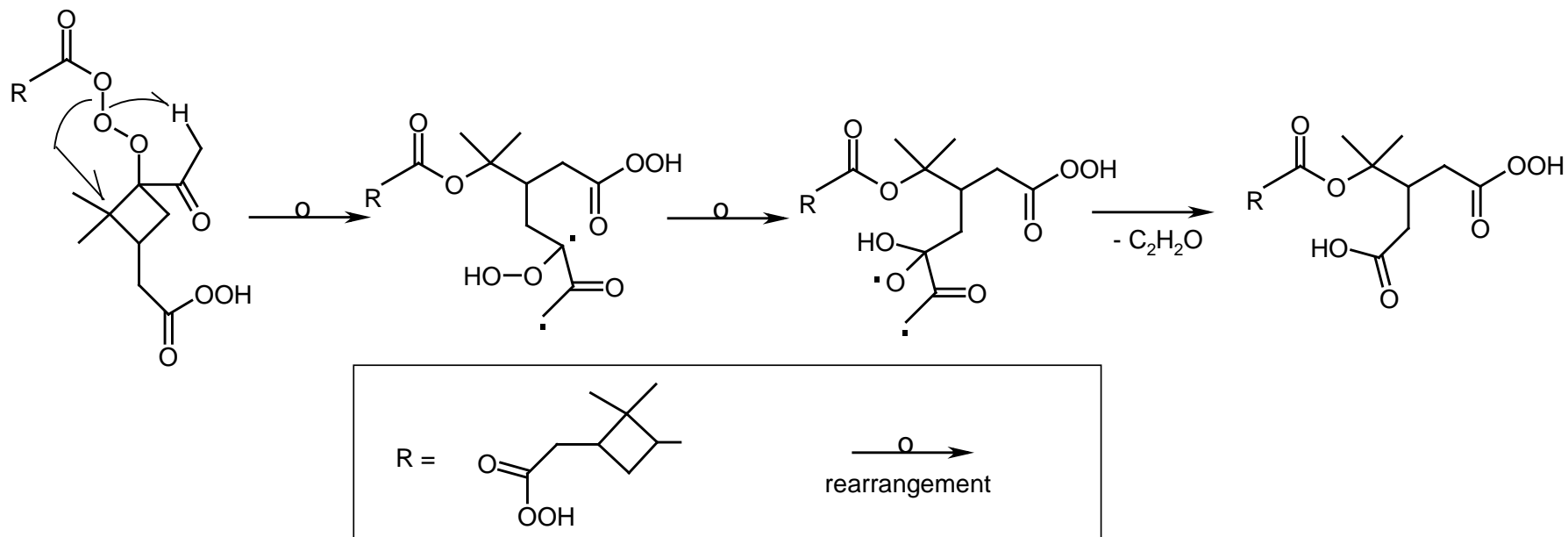
Scheme S3. Labeling of *cis*-pinonic acid (left). It is noted that another labeling (right) has also been applied in previous studies (Yu et al., 1999; Glasius et al., 2000; Larsen et al., 2001; Winterhalter et al., 2003), based on the α -pinene skeleton. In the latter system, 10-hydroxypinonic acid corresponds to 7-hydroxypinonic acid.

S4. Mechanistic details related to the radicals involved in formation of the MW 368 and 358 esters



Scheme S4. Proposed mechanism leading to the formation of the alkoxy radicals related to 7- and 5-hydroxy-pinonic acid (adapted from Zhang et al., 2017) and the acyl peroxy radical related to *cis*-pinonic acid. A $C_{10}H_{15}O_2^\bullet$ radical produced through the vinyl-hydroperoxide channel serves as the precursor for subsequent autooxidation reactions. H-transfers can take place because of the favorable *syn* orientation of the substituents on the dimethylcyclobutane ring.

S5. Mechanistic details related to the formation of the MW 358 ester



Scheme S5. Proposed rearrangement involved in the loss of ketene from species (**d**) that is related to the MW 358 ester (Scheme 6). For clarity, the reactions are formulated stepwise, but the loss of ketene is assumed to occur in a concerted manner.

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