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Structural characterization of 2-hydroxyterpenylic acid, an abundant oxygenated marker compound for α-pinene secondary organic aerosol in ambient fine aerosol

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A highly hydrophilic and oxygenated MW 188 compound is commonly observed in substantial abundance in atmospheric aerosol samples and was proposed in previous studies as an α-pinene-related marker compound that is associated with ageing processes (1).
Paradoxically, the MW 188 compound is usually observed at low abundance in chamber-generated α-pinene-secondary organic aerosol (SOA) (2), pointing to a non-achievement in crucial reaction conditions. Furthermore, the occurrence of several isobaric isomers did not lead to a complete assignment for individual MW 188 compounds from laboratory generated SOA samples in former studies. For the most abundant MW 188 compound two structures have been proposed, i.e. a C8-monohydroxycarboxylic acid structure (2-hydroxyterpenylic acid) (3), and a C8-hydroxydicarboxylic acid structure (hydroxynorpinic acid) (4).
Results will be presented here from a comprehensive mass spectrometric analysis of the most abundant MW 188 compound as 2-hydroxyterpenylic acid. The application of liquid chromatographic/electrospray ionization – ion trap mass spectrometry in both negative and positive ion modes in combination with collision-induced dissociation, as well as the utilisation of a soft derivatisation technique followed by analysis of the formed methyl ester derivatives using the latter technique and gas chromatography/electron ionization mass spectrometry enabled a comprehensive characterization of MW 188 isomers. Theoretical calculations were performed to support the assignment of 2-hydroxyterpenylic acid diastereoisomers. In addition, a positional isomer of 2-hydroxyterpenylic acid, the 4-hydroxyterpenylic acid, was tentatively identified, which is also of atmospheric relevance as it could be detected in ambient fine aerosol. Results from a time-resolved α-pinene photooxidation experiment do not support that the 2 hydroxyterpenylic acid is a marker compound for aged SOA. Compared to terpenylic acid it should rather be regarded as a higher-generation product of the α-pinene oxidation cascade.
This study presents a comprehensive chemical data set for a more complete structural characterization of hydroxyterpenylic acids in ambient fine aerosol, which sets the foundation to better understand the atmospheric fate of α-pinene in future studies.

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