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

Ariane Kahnt (1), Yoshiteru Iinuma (2), Frank Blockhuys (3), Christian van Alsenoy (3), Anke Mutzel (2), Reinhilde Vermeylen (1), John Offenberg (4), Michael Lewandowski (4), Mohammed Jaoui (5), Tadeusz Kleindienst (4), Olaf Böge (2), Hartmut Herrmann (2), Willy Maenhaut (1,6), and Magda Claeys (1)

(1) Department of Pharmaceutical Sciences, University of Antwerp, Belgium, (2) Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany, (3) Department of Chemistry, University of Antwerp, Belgium, (4) National Exposure Research Laboratory, United States Environmental Protection Agency, Research Triangle Park, North Carolina, USA, (5) Alion Science and Technology, P.O. Box 12313, Research Triangle Park, North Carolina, USA, (6) Department of Analytical Chemistry, Ghent University, Belgium

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 \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-pinene in future studies.

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References:
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