



Molecular characterization of polar organosulfates in secondary organic aerosol from the green leaf volatile 3-Z-hexenal

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Much information is available about secondary organic aerosol (SOA) formation from terpenes, including mono- and sesquiterpenes, and isoprene. However, information about SOA formation from green leaf volatiles (GLVs), an important class of biogenic volatile organic compounds, which are emitted when plants are wounded or attacked by insects, is very scarce. In the present study, we provide evidence that 3-Z-hexenal is a potential precursor for SOA through formation of organosulfates. Organosulfate formation from 3-Z-hexenal was studied by conducting smog chamber photooxidation experiments in the presence of NO and acidic ammonium seed aerosol, where OH radicals were generated from the NO_x mediated photochemical chain reactions. The focus of the study was on the structural characterization of products, i.e. organosulfates (OSs) with a molecular weight (MW) of 226, which are also present in ambient fine aerosol from a forested site (K puszta, Hungary) at a substantial relative abundance that is comparable to that of the MW 216 isoprene-related OSs. Polar OSs are of climatic relevance because of their capacity to increase the hydrophilic properties of aerosols and as such their cloud-condensation nuclei effects. Two different liquid chromatography (LC) techniques were employed to separate the polar OSs: the first technique uses a reversed-phase trifunctionally bonded C18 stationary phase, whereas the second one is based on ion-pairing C18 LC using dibutylammonium acetate as ion-pairing reagent. With regard to mass spectrometry (MS) techniques, use was made of high-resolution MS to determine the accurate mass (measured mass, 225.00809; elemental composition, C₆H₉O₇S) as well as linear ion trap MS to obtain detailed structural information. The MW 226 OSs were structurally characterized as sulfated derivatives of 3,4-dihydroxyhex-2-enoic acid with the sulfate group positioned at C-3 or C-4. The formation of these OSs is explained through photooxidation in the gas phase resulting in a hydroperoxide, followed by acid-catalyzed rearrangement into an epoxyhydroxide and subsequent sulfation of the epoxy group in the particle phase.

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