

Cineole Oxidation Products in Biogenic Secondary Organic Aerosol

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Detailed organic speciation of summer time PM10 collected in Melbourne, Australia, indicated the presence of numerous monoterpene oxidation products that have previously been reported in the literature. In addition, two highly oxygenated compounds with molecular formulae $C_9H_{14}O_6$ (MW 218) and $C_{10}H_{16}O_6$ (MW 232) previously unreported, were detected during a period associated with high temperatures and bushfire smoke. These two compounds were also present in laboratory-produced secondary organic aerosol (SOA) through the reaction of OH radicals with 1,8-cineole (eucalyptol), which is emitted by Eucalyptus trees. The retention times and mass spectral behavior of the highly oxygenated compounds in high-performance liquid chromatography (LC) coupled to electrospray ionization-time-of-flight mass spectrometry (MS) in parallel to ion trap MS of agree perfectly between the ambient samples and the laboratory-produced SOA samples, suggesting that 1,8-cineole is the precursor of the highly oxygenated compounds. The proposed structure of the compound with molecular formula $C_{10}H_{16}O_6$ was confirmed by synthesis of a reference compound. The two novel compounds were identified as diaterebic acid acetate (2-[1-(acetyloxy)-1-methylethyl]succinic acid, $C_9H_{14}O_6$) and diaterpenylic acid acetate (3-[1-(acetyloxy)-1-methylethyl]glutaric acid, $C_{10}H_{16}O_6$) based on the consideration of reaction mechanisms, the structure of a reference compound and the interpretation of mass spectral data. Depending on the experimental conditions, the SOA yields determined in chamber experiments ranged between 16-20% for approximately 25 ppb of hydrocarbon consumed. The concentrations of these compounds were as high as 50 ng m^{-3} during the summer time in Melbourne. This study demonstrates the importance and influence of local vegetation patterns on SOA chemical composition.

The work presented here is appendant to JRA1-WP2 (Testing and optimisation of the PTR-MS for various simulation chamber conditions. Development of HPLC-MS techniques for the analysis of particulate products.