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Characterization of polar organosulfates in secondary organic aerosol from the unsaturated aldehydes 2-*E*-pentenal, 2-*E*-hexenal, and 3-*Z*-hexenal

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Abstract. We show in the present study that the unsaturated aldehydes 2-*E*-pentenal, 2-*E*-hexenal, and 3-*Z*-hexenal are biogenic volatile organic compound (BVOC) precursors for polar organosulfates with molecular weights (MWs) 230 and 214, which are also present in ambient fine aerosol from a forested site, i.e., K-puszta, Hungary. These results complement those obtained in a previous study showing that the green leaf aldehyde 3-*Z*-hexenal serves as a precursor for MW 226 organosulfates. Thus, in addition to isoprene, the green leaf volatiles (GLVs) 2-*E*-hexenal and 3-*Z*-hexenal, emitted due to plant stress (mechanical wounding or insect attack), and 2-*E*-pentenal, a photolysis product of 3-*Z*-hexenal, should be taken into account for secondary organic aerosol and organosulfate formation. Polar organosulfates are of climatic relevance because of their hydrophilic properties and cloud effects. Extensive use was made of organic mass spectrometry (MS) and detailed interpretation of MS data (i.e., ion trap MS and accurate mass measurements) to elucidate the chemical structures of the MW 230, 214 and 170 organosulfates formed from 2-*E*-pentenal and indirectly from 2-*E*-hexenal and 3-*Z*-hexenal. In addition, quantum chemical calculations were performed to explain the different mass spectral behavior of 2,3-dihydroxypentanoic acid sulfate derivatives, where only the isomer with the sulfate group at C-3 results in the loss of SO_3. The MW 214 organosulfates formed from 2-*E*-pentenal are explained by epoxidation of the double bond in the gas phase and sulfation of the epoxy group with sulfuric acid in the particle phase through the same pathway as that proposed for 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from the isoprene-related α,β-unsaturated aldehyde methacrolein in previous work (Lin et al., 2013). The MW 230 organosulfates formed from 2-*E*-pentenal are tentatively explained by a novel pathway, which bears features of the latter pathway but introduces an additional hydroxyl group at the C-4 position. Evidence is also presented that the MW 214 positional isomer, 2-sulfooxy-3-hydroxypentanoic acid, is unstable and decarboxylates, giving rise to 1-sulfooxy-2-hydroxybutane, a MW 170 organosulfate. Furthermore, evidence is obtained that lactic acid sulfate is generated from 2-*E*-pentenal. This chemistry could be important on a regional and local scale where GLV emissions such as from grasses and cereal crops are substantial.

1 Introduction

Volatile organic compounds (VOCs) are ubiquitous in the troposphere, playing a key role as precursors for ozone and secondary organic aerosol (SOA). The formation and aging of SOA has received considerable attention during the last 2 decades because of its potential impact on climate and human health. Major classes of SOA precursors studied include alkanes, alkenes, aromatic hydrocarbons, and oxygenated compounds, both from anthropogenic and biogenic origin. Among the biogenic VOCs that are precursors for SOA, isoprene and monoterpenes have received ample attention (for a review, see Hallquist et al., 2009), while other reactive VOCs such as green leaf volatiles (GLVs) have been far less examined. However, recent studies demonstrate that GLVs are also potential precursors for biogenic SOA (Hamilton et al., 2009; Harvey et al., 2014; Jain et al., 2014; Richards-Henderson et al., 2014; Shalamzari et al., 2014).

GLVs comprise unsaturated C_6 compounds that are released by plants when they are wounded (e.g., grass cutting, animal grazing, storms) or attacked by insects (Piesik et al., 2011; Brilli et al., 2012). They are named after their specific "green" odor, the fresh scent emitted by green plants, and play a crucial role in plant–plant and plant–insect communication (Hatanaka, 1993; Holopainen, 2004; Scala et al., 2013). GLVs are formed in plant leaves from the unsaturated fatty acids linoleic and α-linolenic acid, which are essential constituents of cell membrane lipids, by biochemical conversion with the enzymes lipoxygenase and hydroperoxide lyase (Hatanaka, 1993). One of the most abundant GLVs, 3-Z-hexenal, is formed by the cleavage of α-linolenic acid, and it partly isomerizes to 2-E-hexenal. Both alkenals can be further metabolized by an alcohol dehydrogenase and alcohol acyltransferase (D'Auria et al., 2007) to the corresponding alcohols and their esters (Matsui, 2006).

GLVs also have a potential role in tropospheric chemistry as they may serve as precursors for ozone and SOA (Pinto et al., 2007; Holopainen, 2011; Hartikainen et al., 2012; Harvey et al., 2014). Recently, the GLVs 3-Z-hexen-1-ol and 3-Z-hexenyl acetate as well as methyl salicylate, methyl jasmonate, and 2-methyl-3-butene-2-ol have also been shown to undergo aqueous-phase oxidation with the hydroxyl radical and to result in considerable SOA yields ranging from 10 to 88 % (Richards-Henderson et al., 2014). SOA formation through photooxidation and ozonolysis was first studied at the molecular level for the GLVs 3-Z-hexen-1-ol and 3-Z-hexenyl acetate by Hamilton et al. (2009) with liquid chromatography combined with positive ion electrospray ionization mass spectrometry using lithium as a cationization agent. This study demonstrated that 3-hydroxypropanal, the primary oxidation product of 3-Z-hexen-1-ol, can hydrate and undergo further reactions with other aldehydes, resulting in SOA dominated by higher-molecular-weight (MW) oligomers, while, in contrast, considerably fewer higher-MW species are detected in the SOA produced from 3-Z-hexenyl acetate. SOA formation was recently examined from turf grass volatiles (Jain et al., 2014), which comprise 3-Z-hexen-1-ol and 3-Z-hexenyl acetate, with near-infrared laser desorption–ionization aerosol mass spectrometry, and the ozonolysis SOA profile was found to closely resemble that of 3-Z-hexen-1-ol and to be dominated by low-volatility, higher-MW compounds such as oligoesters. In addition, there is recent evidence that 3-Z-hexenal results in polar m/z 225 (MW 226) organosulfates (OSs) through photooxidation and/or ozonolysis (Shalamzari et al., 2014). It should be noted that the investigated ambient aerosol was from K-puszta, Hungary, a rural area with intensive agriculture, where at the time that the samples were collected (May–June) hay was harvested and crops were cultivated. GLV chemistry might be important on a regional and local scale where emissions such as from grasses and cereal crops are substantial. It is also well possible that in urban residential areas GLV chemistry might be as important as isoprene chemistry. A field study conducted at a site in Belgium (i.e., a polluted residential/forest site in Brasschaat, Antwerp) indicated substantial concentrations of a m/z 225 organosulfate, originating from 3-Z-hexenal, i.e., 6.8 ± 10.1 ng m^{-3} vs. 9.0 ± 11.6 ng m^{-3} for the isoprene SOA-related 2-methyltetrol sulfates (Gómez-González et al., 2012).

OSs are potential marker compounds for SOA formation occurring under acidic conditions by particle-phase reactions with sulfuric acid (Surratt et al., 2007b), formed by oxidation of sulfur dioxide, which is mainly from anthropogenic origin in continental regions of the globe (Smith et al., 2011). In addition to formation through reaction of sulfuric acid with epoxide-containing SOA compounds from the oxidation of β-pinene (Iinuma et al., 2007), isoprene (Surratt et al., 2010; Lin et al., 2013), and 2-methyl-3-buten-2-ol (Zhang et al., 2012), OSs may also result from the reactive uptake of unsaturated compounds in the particle phase and reaction with the sulfate anion radical (Rudzinski et al., 2009; Nozière et al., 2010; Schindelka et al., 2013; Szmigielski, 2013; Schöne et al., 2014). Furthermore, OSs may also be formed by uptake of tertiary organonitrates in the particle phase and nucleophilic substitution of the nitrate by a sulfate group, as shown in the case of 2-methyltetrol sulfates (Darer et al., 2011; Hu et al., 2011).

Organosulfates are ubiquitous compounds in our environment, formed not only from BVOCs but also from anthropogenic VOCs such as aromatics (Kundu et al., 2013; Riva et al., 2015). It has been suggested that they are a significant component of fine ambient aerosol (e.g., Surratt et al., 2008; Lukács et al., 2009; Hawkins et al., 2010; Tolocka and Turpin, 2012). Using Fourier transform infrared measurements, Hawkins et al. (2010) determined that 4 ± 8 % of the organic mass of continental outflow aerosols over the southeast Pacific Ocean during the VOCALS–REx 2008 campaign was due to organosulfates during periods of high organic and sulfate concentrations. The annual average contribution of organosulfates to organic mass for 12 sites in the Unites States was found to be 5–10 % using an S-estimation method and was higher during warm months when photochemical oxidation chemistry is most active (Tolocka and Turpin, 2012). It was shown that organosulfates correspond to a substantial fraction of fine ambient summer aerosol, which was determined with S-estimation methods to be as high as 30 % of the total organic mass (Surratt et al., 2008) and to correspond to 6–12 % of the bulk sulfur mass at K-puszta, Hungary (Lukács et al., 2009).

The present study focuses on the chemical characterization of m/z 169, 213 and 229 OSs formed from the C_5-unsaturated aldehyde 2-E-pentenal, which is a known photolysis product of 3-Z-hexenal (O'Connor et al., 2006), as well as from the C_6-unsaturated aldehydes 2-E-hexenal and 3-Z-hexenal. In a previous study (Gómez-González et al., 2008), it was shown that fine ambient aerosol ($PM_{2.5}$) contains polar m/z 213 OSs (i.e., sulfate esters of 2,3-dihydroxypentanoic acid), which could be related to 2-E-pentenal, have the same magnitude (peak area) as the m/z 215 OSs that originate from isoprene (Surratt et al., 2007a, 2008), and are formed through sulfation of intermediary C_5-epoxydiols (Surratt et al., 2010). Formation pathways for the m/z 213 and 229 OSs that originate from 2-E-pentenal are proposed, thereby considering a known route leading to OSs, namely, the route established for 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein in the presence of NO_x ($NO + NO_2$), which, like 2-E-pentenal, is also an α,β-unsaturated aldehyde (Lin et al., 2013).

A first step in understanding the impact of an unknown organosulfate (or any organic compound) in the environment is its characterization at the molecular level, as this knowledge allows one to obtain information on its VOC precursor and its formation process (for a review, see Nozière et al., 2015). Only after its molecular structure has been established can ambient monitoring studies be considered involving quantitative measurements, which allow one to obtain further insights into its formation.

In order to chemically characterize the unknown OSs from 2-E-pentenal, 3-Z-hexenal, and 2-E-hexenal in detail, laboratory smog chamber experiments were conducted in the present study, and the organosulfate profiles were compared with those of ambient fine ($PM_{2.5}$) aerosol collected from K-puszta, Hungary, a rural site with mixed deciduous–coniferous vegetation and agricultural land. Only the results obtained for 2-E-pentenal SOA are discussed, since it was found that 2-E-hexenal and 3-Z-hexenal SOA contains the same OSs. For the chemical analysis, liquid chromatography combined with negative ion electrospray ionization mass spectrometry (LC/(−)ESI–MS) was performed by using reversed-phase LC using a trifunctionally bonded C_{18} stationary phase (Safi Shalamzari et al., 2013). Use was made of high-resolution MS to infer the elemental composition, while ion trap (IT) MS was employed to obtain information about functional groups and their position in the molecules, a state-of-the-art analytical methodology which has proven its usefulness in previous studies on the molecular characterization of organosulfates (Gómez-González et al., 2008; Surratt et al., 2008; Safi Shalamzari et al., 2013; Shalamzari et al., 2014) and SOA (for a review, see Nozière et al., 2015). Since the structural characterization is only based on MS data, the proposed structures should be regarded as tentative. In addition, quantum chemical calculations were performed to gain some insight into the distinctive mass spectral behavior of positional isomers containing neighboring sulfate, hydroxyl, and carboxyl groups.

2 Experimental

2.1 Chemicals

Methanol (ULC–MS grade) used for sample preparation and as LC mobile phase, and acetonitrile (HPLC supra-gradient grade) were from Biosolve NV (Valkenswaard, the Netherlands). *Cis*-pinonic acid (purity: 98 %; for MS signal optimization) was from Sigma-Aldrich (St. Louis, MI, USA). High-purity water (18.2 MΩ cm; total organic carbon, 2 ppb) used for redissolving aerosol extracts and preparing the aqueous LC mobile phase was generated with a Milli-Q water purification system (Millipore, Bedford, MA, USA). 2-E-pentenal (purity: 95 %), 2-E-hexenal (purity: 98 %) and 3-Z-hexenal (50 % solution in triacetin) used for smog chamber experiments and 2-E-pentenoic acid (purity: 98 %) used for the dark aqueous-phase experiments with the sulfate anion radical were from Sigma-Aldrich.

2.2 Aerosol samples

2.2.1 Laboratory SOA samples

Table 1 summarizes the conditions for the biogenic VOC chamber experiments used in the present study. The experiments were conducted in a 14.5 m^3 stainless-steel chamber with 40 µm Teflon-coated walls (Kleindienst et al., 2007). The temperatures, aerosol size distributions, and relative humidities, as well as the O_3, nitric oxide (NO), and NO_x concentrations were continuously measured. OH radicals and ozone were generated through NO_x photochemistry in the presence of volatile organics and in the absence of an OH scavenger. A mixture of sulfuric acid (SA) and ammonium sulfate (AS) (1 : 1; w/w) was used as seed aerosol to create acidity in the chamber. The experiments were conducted in the dynamic mode (i.e., continuously stirred tank reactor). Reactants such as NO and the VOC precursor were continuously added from high-pressure cylinders to the reaction chamber through a mixing manifold. NO was obtained at a concentration of 1500 ppm (Air Gas, Raleigh, NC, USA). An assay from the tank showed the NO purity to be 99.7 %, with the major impurity being nitrogen oxide (NO_2). The steady-state nature of chamber operation allows for filter

Table 1. Chamber conditions for experiments used for the structural characterization of unknown organosulfates related to 2-*E*-pentenal, 2-*E*-hexenal, and 3-*E*-hexenal SOA. Abbreviations: AS, ammonium sulfate; SA, sulfuric acid; RH, relative humidity.

Sample code	Hydrocarbon	Hydrocarbon conc.		NO_x^* conc.	O_3 conc.	OC conc.	Seed type conc.	Other conditions
ER625-GF5	2-*E*-pentenal	Initial:	4.8 ppmC	280 ppb	–	–	AS : SA (1 : 1; w/w)	4 light banks 516 nmol m^{-3}
		Steady state:	1.1 ppmC	178 ppb	207 ppb	4.9 µg m^{-3}	28 µg m^{-3}	$[H^+]$air RH: 27 %
ER627-GF10	3-*Z*-hexenal	Initial:	2.5 ppmC	290 ppb	–	–	AS : SA (1 : 1; w/w)	4 light banks 439 nmol m^{-3}
		Steady state:	0.3 ppmC	200 ppb	280 ppb	5 µg m^{-3}	30 µg m^{-3}	$[H^+]$air RH: 29 %
ER684-GF5	2-*E*-hexenal	Initial:	11.3 ppmC	400 ppb	–	–	AS : SA (1 : 1; w/w)	4 light banks 587 nmol m^{-3}
		Steady state:	4.3 ppmC	195 ppb	207 ppb	20.1 µg m^{-3}	26 µg m^{-3}	$[H^+]$air RH: 30 %

* All the initial NO_x was NO. The NO_2 contaminant was 0.3 %.

sampling for extended periods for determining the composition of the resultant SOA. Once steady-state conditions were attained (24 h), samples for determining the composition of the SOA were collected on Teflon-impregnated glass fiber filters (Pallflex Fiberfilm, Pall Corporation, Port Washington, NY, USA). The filters were extracted three times with 10 mL of methanol in an ultrasonic bath for 10 min. It was verified for 2-*E*-pentenal SOA that extraction with methanol of the targeted m/z 213 and 229 organosulfates did not result in formation of more hydrophobic (later-eluting) methyl ester derivatives at m/z 227 and 241, considering that such artifacts have been reported for glycolic acid sulfate ester (Olson et al., 2011). The extracts were combined and concentrated in a rotary evaporator at 35 °C and 200 mbar to approximately 1 mL, filtered through a Teflon filter (0.45 µm), and evaporated to dryness under a nitrogen stream. The residue was redissolved in 1 mL of methanol and divided into two portions, which were dried under nitrogen, and one of the portions was stored at −20 °C until use, because not all analyses could be performed at the same time. A fresh or unfrozen portion was redissolved in 250 µL of methanol : water (1 : 1; v/v) by first dissolving the fraction in 125 µL of methanol and then adding 125 µL of water. Afterwards, the sample was analyzed with LC/(−)ESI–MS using an aliquot of 5 µL.

2.2.2 Aqueous-phase reaction products of 2-*E*-pentenoic acid

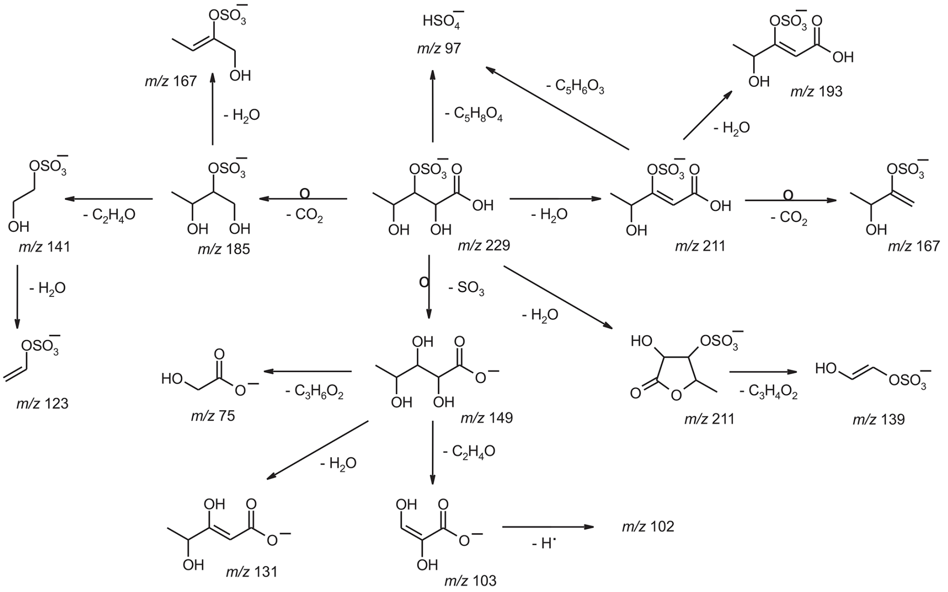
Aqueous-phase reaction products of 2-*E*-pentenoic acid, containing 3-sulfooxy-2-hydroxypentanoic acid, were obtained following the method reported by Ziajka and Rudzinski (2007) with some adaptations. The formation of organosulfates is based on attack of the double bond with the sulfate radical anion (e.g., Rudzinski et al., 2009); the reaction is shown in Scheme S1 in the Supplement. A round-bottom flask of 50 mL volume was filled with 30 mL of an aqueous solution that contained dissolved atmospheric oxygen, sodium sulfite (SIV) (4.7×10^{-3} M), and 2-*E*-pentenoic acid (9.6×10^{-3} M). The pH of the solution was adjusted to 3.1 with 0.1 M H_2SO_4, and the autoxidation of sulfite by the dissolved atmospheric oxygen was catalyzed by injecting a small aliquot of $Fe_2(SO_4)_3$ catalyst solution (2.5×10^{-5} M). The experiment was carried out at 25 ± 0.1 °C, and the 2-*E*-pentenoic acid reaction products were sampled after 5 min.

2.2.3 Ambient fine aerosol

Archived $PM_{2.5}$ (particulate matter with an aerodynamic diameter ≤ 2.5 µm) aerosol samples collected from K-puszta, Hungary, during the BIOSOL (Formation mechanisms, marker compounds, and source apportionment for BIOgenic atmospheric aeroSOLs) campaign between 22 May and 29 June 2006 were used. Information about the site, the sampling campaign, and storage of samples can be found in a previous article (Maenhaut et al., 2008). Information about the preparation of a pooled day- and nighttime sample and the workup of the sample, involving extraction with methanol, can be found in Safi Shalamzari et al. (2013). Samples containing 570 µg of organic carbon were analyzed with LC/(−)ESI–MS using an aliquot of 5 µL.

2.3 Liquid chromatography–mass spectrometry

The LC/ESI-ITMS analysis was carried out using a Surveyor Plus system (pump and autosampler) (Thermo Scientific, San Jose, CA, USA) connected to an Atlantis T3 column (2.1 × 150 mm, 3 µm particle size, Waters, Milford, MA, USA), which provides some retention for the polar



Scheme 1. Proposed fragmentation routes for the m/z 229 organosulfate, related to 2-E-pentenal SOA and tentatively assigned to 3-sulfooxy-2,4-dihydroxypentanoic acid, on the basis of detailed interpretation of MS^2, MS^3, and accurate mass data.

organosulfate compounds under investigation. The mobile phases for reversed-phase (RP)-LC consisted of 50 mM ammonium formate buffer pH 3 and methanol. Information about the applied LC–MS gradient program and the operation conditions of the linear ion trap mass spectrometer (LXQ, Thermo Scientific) can be found in Safi Shalamzari et al. (2013).

Accurate mass measurements were carried out using a Synapt G2-S high-definition MS (HDMS) instrument (Waters) equipped with an electrospray ion source and quadrupole–time-of-flight type mass analyzer. The instrument was controlled and recorded data were processed using MassLynx V4.1 software (Waters). The chromatographic separation was performed with ultra-performance LC (UPLC) using an HSS T3 column (2.1 × 100 mm; 1.8 µm particle size; Waters), which, like the Atlantis T3 column (Waters), contains a stationary phase based on trifunctionally bonded C_{18} chains and results in the same elution order for the targeted organosulfates. The retention times on the HSS T2 column were as follows: sulfuric acid, 0.60 min; 2-methyltetrol organosulfates, 0.80 and 0.91 min; 3-sulfooxy-2,4-dihydroxypentanoic acid, 0.62 min; 2-sulfooxy-3-hydroxypentanoic acid, 0.65 min; 3-sulfooxy-2-hydroxypentanoic acid, 0.91 min; and 1-sulfooxy-2-hydroxybutane, 1.45 min. The measurements were only carried out for the ambient K-puszta $PM_{2.5}$ aerosol extract and were mainly performed to obtain accurate mass data on the deprotonated molecules and their MS^2 product ions.

2.4 Quantum chemical calculations

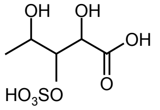
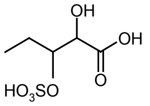
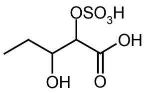
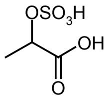
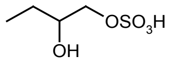
Calculations on the sulfate anionic forms of isomeric 2,3-dihydroxypentanoic acid sulfates, 3-sulfooxy-2-hydroxypentanoic acid, and 2-sulfooxy-3-hydroxypentanoic acid were performed using the Gaussian09 suite of programs (Frisch et al., 2009), applying density functional theory (DFT) with the B3LYP functional (Stephens et al., 1994) and the 6-311-G* basis set, as it is implemented in Gaussian09. Geometry optimizations were performed for the isolated molecules in the gas phase.

3 Results and discussion

3.1 Organosulfate profiles in ambient fine aerosol due to SOA from 2-E-pentenal, 3-Z-hexenal, and 2-E-hexenal

Figure 1 shows selected LC–MS chromatographic data obtained for K-puszta fine aerosol, including a base peak chromatogram (BPC) and extracted ion chromatograms (EICs) at m/z 215, 229, 213, and 169, corresponding to the deprotonated forms of OSs related to isoprene (m/z 215) and 2-E-pentenal, 3-Z-hexenal, and 2-E-hexenal (m/z 229, 213, and 169, respectively). The m/z 229, 213, and 169 compounds will be tentatively identified using detailed interpretation of MS data and discussed in the following sections. The LC–MS chromatographic data reveal that the targeted OSs at m/z 229, 213, and 169 have a substantial peak area compared to that of the m/z 215 compounds in ambient fine aerosol, which correspond to isoprene SOA compounds, i.e., sulfate

Table 2. Tentatively identified organosulfates with chromatographic and mass spectral data (retention time, m/z, elemental formula, and m/z of main product ions). The retention times are given for the compounds identified in SOA.

Identified organosulfates	Retention time (min)	m/z (measured) (formula)	m/z product ions
 3-sulfooxy-2,4-dihydroxy-pentanoic acid	2.5	229.0021 ($C_5H_9O_8S^-$)	MS^2(229): 211, 195, 149, 97 MS^3(229–149): 131, 103, 75 MS^3(229–185): 167, 153, 141, 123 MS^3(229–211): 193, 181, 167, 139, 97
 3-sulfooxy-2-hydroxypentanoic acid	3.7	213.0071 ($C_5H_9O_7S^-$)	MS^2(213): 195, 133, 97 MS^3(213–133): 75
 2-sulfooxy-3-hydroxypentanoic acid	2.4	213.0065 ($C_5H_9O_7S^-$)	MS^2(213): 195, 181, 169, 97 MS^3(213–169): 151, 137, 97 MS^4(213–169–137): 81, 73
 lactic acid sulfate	2.8	168.9807 ($C_3H_5O_6S^-$)	MS^2(169): 151, 125, 97
 1-sulfooxy-2-hydroxybutane	4.1	169.0177 ($C_4H_9O_5S^-$)	MS^2(169): 151, 137, 97 MS^3(169–137): 81, 73

esters of the 2-methyltetrols, formed by sulfation of intermediary C_5-epoxydiols (Surratt et al., 2007a, 2008, 2010). The structures of the identified organosulfates with their retention time, elemental formula, measured m/z value, and m/z values of main product ions are summarized in Table 2.

3.2 Structural characterization of m/z 229 organosulfates related to 2-E-pentenal

Figure 2 shows selected LC–MS chromatographic data (m/z 229 EICs) for ambient fine aerosol and SOA generated from 2-E-pentenal in the presence of acidic seed aerosol, as well as selected MS data (MS^2 and MS^3 product ion spectra). Selected LC–MS data (m/z 229 EICs and MS^2 spectra) for SOA generated from 2-E-hexenal and 3-Z-hexenal, showing that m/z 229 compounds are also formed, are provided in Fig. S1 in the Supplement. Accurate mass measurement of the m/z 229 OSs present in K-puszta fine aerosol led to the elemental formula of $C_5H_9O_8S^-$ (RT 2.5 min; measured mass: 229.0021; error: +0.3 mDa. RT 2.2 min: measured mass: 229.0009; error: −0.9 mDa). Additional MS^3 data obtained for the m/z 229 OSs present in K-puszta fine aerosol are given in Fig. S2. Detailed interpretation of the MS data led to the assignment of the m/z 229 OSs as stereoisomeric forms of a sulfate ester of 2,3,4-trihydroxypentanoic acid, i.e., 3-sulfooxy-2,4-dihydroxypentanoic acid (Table 2; Scheme 1). The presence in the m/z 229 MS^2 spectra (Fig. 2) of the bisulfate [HSO_4^-] ion (m/z 97) as well as the loss of SO_3 (80 u) leading to m/z 149 is consistent with an organosulfate, whereas the losses of H_2O (18 u) and CO_2 (44 u), affording m/z 211 and 185, indicate a hydroxyl and a carboxyl group, respectively (e.g., Romero and Oehme, 2005; Yi et al., 2006; Gómez-González et al., 2008; Safi Shalamzari et al., 2013; Shalamzari et al., 2014). Other diagnostic ions formed upon further fragmentation of m/z 149 include m/z 131 (loss of H_2O), m/z 103 (loss of C_2H_6O), and m/z 75 (loss of $C_3H_6O_2$). The sulfate group is located at the C-3 position based on diagnostic product ions formed by

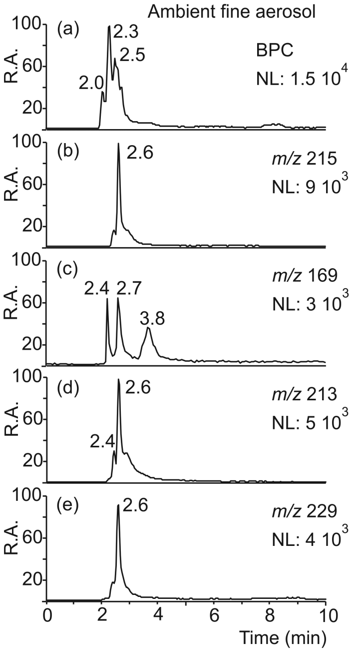


Figure 1. Selected LC–MS chromatographic data using RP-LC obtained for ambient fine aerosol, including a base peak chromatogram (BPC) and extracted ion chromatograms (EICs) at m/z 215, 169, 213 and 229, corresponding to organosulfates related to isoprene (m/z 215; 2-sulfooxy-1,3,4-trihydroxy-2-methylbutane) and OSs related to 2-*E*-pentenal and indirectly to 2-*E*-hexenal and 3-*Z*-hexenal (m/z 229, 213, and 169). The retention times of the solvent front (containing unretained material) and sulfuric acid, which can be seen in the BPC **(a)**, were 2.0 and 2.3 min. For the molecular structures of the m/z 229, 213, and 169 organosulfates, see Table 2. Abbreviation: NL, normalization level.

further fragmentation of m/z 185 (Fig. S2) at m/z 167, 153, 141, and 123 (Scheme 1). Ions formed by further fragmentation of m/z 211 (Fig. S2) to m/z 193, 181, 167, and 97 are also explained in Scheme 1.

Furthermore, it is noted that the m/z 229 profiles obtained for K-puszta fine aerosol and 2-*E*-pentenal (Fig. 2) are quite comparable, revealing a major compound eluting at 2.5 min, while additional later-eluting isomers could be observed for 3-*Z*-hexenal and 2-*E*-hexenal SOA (Fig. S1). Since only the m/z 229 peak eluting at 2.5 min is found in ambient fine aerosol, no attention is given to the latter later-eluting 3-*Z*-hexenal and 2-*E*-hexenal SOA isomers. As 2,3,4-trihydroxypentanoic acid has three chiral carbon atoms, several stereoisomeric forms (theoretically eight) are indeed possible. An early-eluting m/z 229 isomer (RT 2.2 min) is detected in fine ambient aerosol that is not formed from 2-*E*-pentenal, 3-*Z*-hexenal, and 2-*E*-hexenal. Selected MS data for the latter isomer are provided in Fig. S3 in the Supplement. It can be seen that the MS data only differ from those of the major peak at RT 2.5 min by the relative abundances of the product ions, consistent with stereoisomers.

3.3 Proposed formation pathway for m/z 229 organosulfates formed from 2-*E*-pentenal

As discussed above, m/z 229 compounds detected in 2-*E*-pentenal SOA could be assigned to 3-sulfooxy-2,4-dihydroxypentanoic acid. The detection of these compounds in 3-*Z*-hexenal SOA is in line with the fact that 2-*E*-pentenal is a photolysis product of 3-*Z*-hexenal (O'Connor et al., 2006). The formation of 2-*E*-pentenal through photolysis of 2-*E*-hexenal has not been reported so far, but it is very likely that it may also be formed in this way.

A possible formation pathway leading to the structurally characterized isomeric m/z 229 organosulfates is proposed in Scheme 2, which bears features of the pathway proposed for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein, which, like 2-*E*-pentanal, is also an α,β-unsaturated aldehyde (Lin et al., 2013). Reactions (1) in Scheme 2 are inspired by the latter pathway, involving abstraction of the hydrogen atom of the aldehyde group with the OH radical, followed by reaction with molecular oxygen and NO_2, resulting in 2-*E*-pentenoylperoxynitrate. Reactions (2) in Scheme 2 introduce a nitrate group at the C-4 position, which hydrolyzes in the particle phase in the presence of sulfuric acid. Peroxy radicals (RO_2) react with NO to from organic nitrates (or alkoxy radicals) in the presence of NO (Chen et al., 1998), whereas organic nitrates ($RONO_2$) hydrolyze to form alcohols and nitric acid in aqueous media (Boschan et al., 1955; Sato, 2008). Reactions (3) and (4) in Scheme 2 are similar to those established for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein (Lin et al., 2013), involving formation of an epoxy group in the gas phase and reaction of the latter with sulfuric acid in the particle phase. A possible reason for the failure to detect 2-sulfooxy-3,4-dihydroxypentanoic acid is its instability, as has been observed for m/z 213 organosulfates (Sect. 3.4).

3.4 Structural characterization of m/z 169 and 213 organosulfates related to 2-*E*-pentenal

Figure 3 shows selected LC–MS chromatographic data (m/z 213 EICs) for ambient fine aerosol and 2-*E*-pentenal SOA, as well as selected MS data (MS^2 and MS^3 product ion spectra). Analysis of the m/z 213 peaks in ambient fine aerosol (Fig. 3a) eluting between 2.4 and 2.7 min shows that different isomers are present. Accurate mass measurement of the m/z 213 OSs present in K-puszta fine aerosol led to the elemental formula of $C_5H_9O_7S^-$ (RT 2.4 min: measured mass: 213.0065; error: −0.4 mDa. RT 2.6 min: measured mass: 213.0071; error: +0.2 mDa). The major peak in fine ambient aerosol at RT 2.6 min could, on the basis of the MS data (Fig. 3e–g), be assigned to isomeric 4,5-dihydroxypentanoic acid sulfate esters, which have been structurally characterized in previous work and will not be further discussed here as these isomers are not related to 2-*E*-

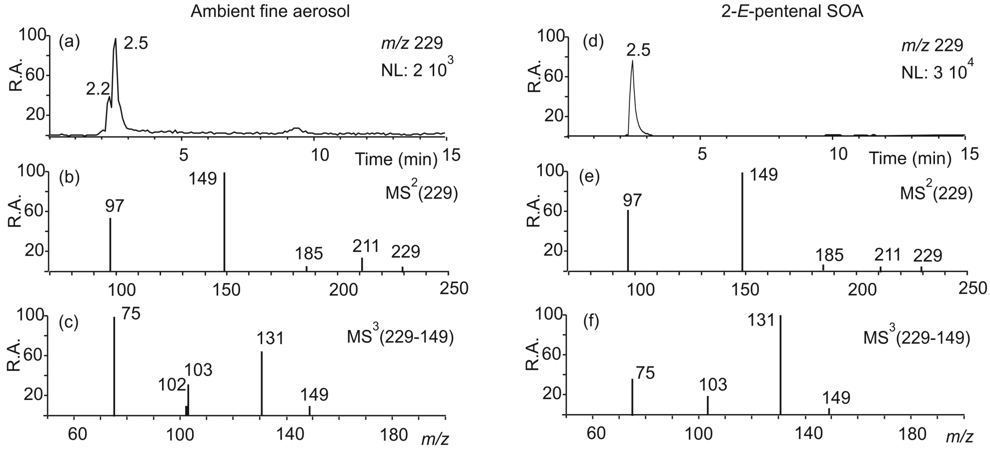
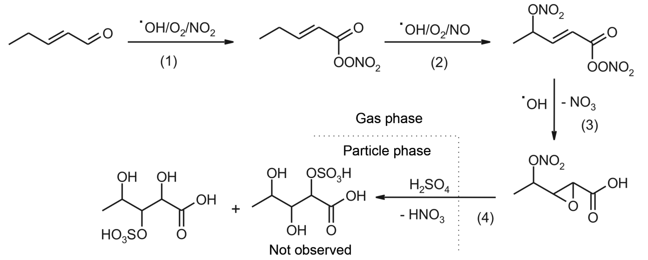


Figure 2. Selected LC–MS chromatographic data (m/z 229 EICs) for **(a)** ambient fine aerosol and **(d)** SOA generated from 2-E-pentenal in the presence of acidic seed aerosol, as well as selected MS data (MS^2 or MS^3 product ion spectra) for the peak eluting at 2.5 min in **(b, c)** ambient aerosol and **(e, f)** 2-E-pentenal SOA.



Scheme 2. Proposed formation pathway for m/z 229 (MW 230) organosulfates related to 2-E-pentenal (and indirectly to 3-Z-hexenal and 2-E-hexenal SOA), which occur in ambient fine aerosol and are tentatively assigned to 3-sulfooxy-2,4-dihydroxypentanoic acid. The suggested route shares features of the mechanism reported for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein (Lin et al., 2013).

pentenal SOA (Gómez-González et al., 2008). Two m/z 213 peaks can be distinguished in 2-E-pentenal SOA (Fig. 3k) exhibiting distinctly different mass spectra, of which the first peak at 2.4 min (Fig. 3l–n) is also present in fine ambient aerosol (Fig. 3b–d). Analysis of the MS data obtained for fine ambient aerosol shows that the second m/z 213 isomer present in 2-E-pentenal SOA (Fig. 3o and p) also occurs in fine ambient aerosol (Fig. 3h and i) but that there is co-elution with the 4,5-dihydroxypentanoic acid sulfate esters (Fig. 3e and g). Furthermore, it can be seen that the second-eluting m/z 213 isomer present in 2-E-pentenal SOA is also formed in aqueous-phase sulfation of 2-E-pentenoic acid (Fig. 3q–s). It is noted that the second-eluting m/z 213 isomer in 2-E-pentenal SOA (RT 3.7 min), which elutes as a broad peak, differs in retention time from the same m/z 213 isomer (with the same MS characteristics) occurring in fine ambient aerosol (RT 2.7 min) and aqueous-phase 2-E-pentenoic acid reaction products (RT 2.5 min). A possible reason for this unusual chromatographic behavior is injection of the (hydrophobic) SOA sample leading to a change in the LC column characteristics. In addition, it can be seen that the same m/z 213 isomers are detected in 3-Z-hexenal and 2-E-hexenal SOA (Fig. S4).

Based on the detailed interpretation of the MS data (Scheme 3), the two m/z 213 isomers related to 2-E-pentenal SOA are tentatively attributed to 2-sulfooxy-3-hydroxypentanoic acid and 3-sulfooxy-2-hydroxypentanoic acid for the first- and second-eluting isomers, respectively (Table 2). The first isomer mainly fragments through loss of CO_2 (44 u) and further upon MS^3 and MS^4 fragments to m/z 137 and 73. The second isomer (RT 3.7 min) fragments through loss of SO_3 (80 u), affording m/z 133, which in turn upon MS^3 fragments further to m/z 75 through the loss of propenal (58 u). The distinctly different fragmentation behavior of the two isomers was addressed through quantum chemical calculations. Figure 4a and b display the lowest-energy conformers of the acid with the sulfate group at C-3 and C-2, respectively. Transfer of the carboxyl proton to the oxygen atom linked to C-3 and C-2, respectively, followed by geometry optimization leads to loss of SO_3 by breaking the relevant sulfur–oxygen bond, for both isomers: the resulting structures are presented in Fig. 4c and d, respectively. However, the energetics of both processes are different: while for the C-3 isomer (Fig. 4a and c) this is accompanied by an energy increase of 85.30 kJ mol^{-1}, the corresponding value for the C-2 isomer (Fig. 4b and d) is 128.41 kJ mol^{-1}, or just over 50 % higher. This suggests that the loss of SO_3 is considerably less unfavorable for the C-3 isomer than for the C-2 isomer, in agreement with the observations from the mass spectra.

Attention was also given to m/z 169 organosulfates because it was found that they result from the degradation of a m/z 213 OS, as will be discussed in detail below. Fig-

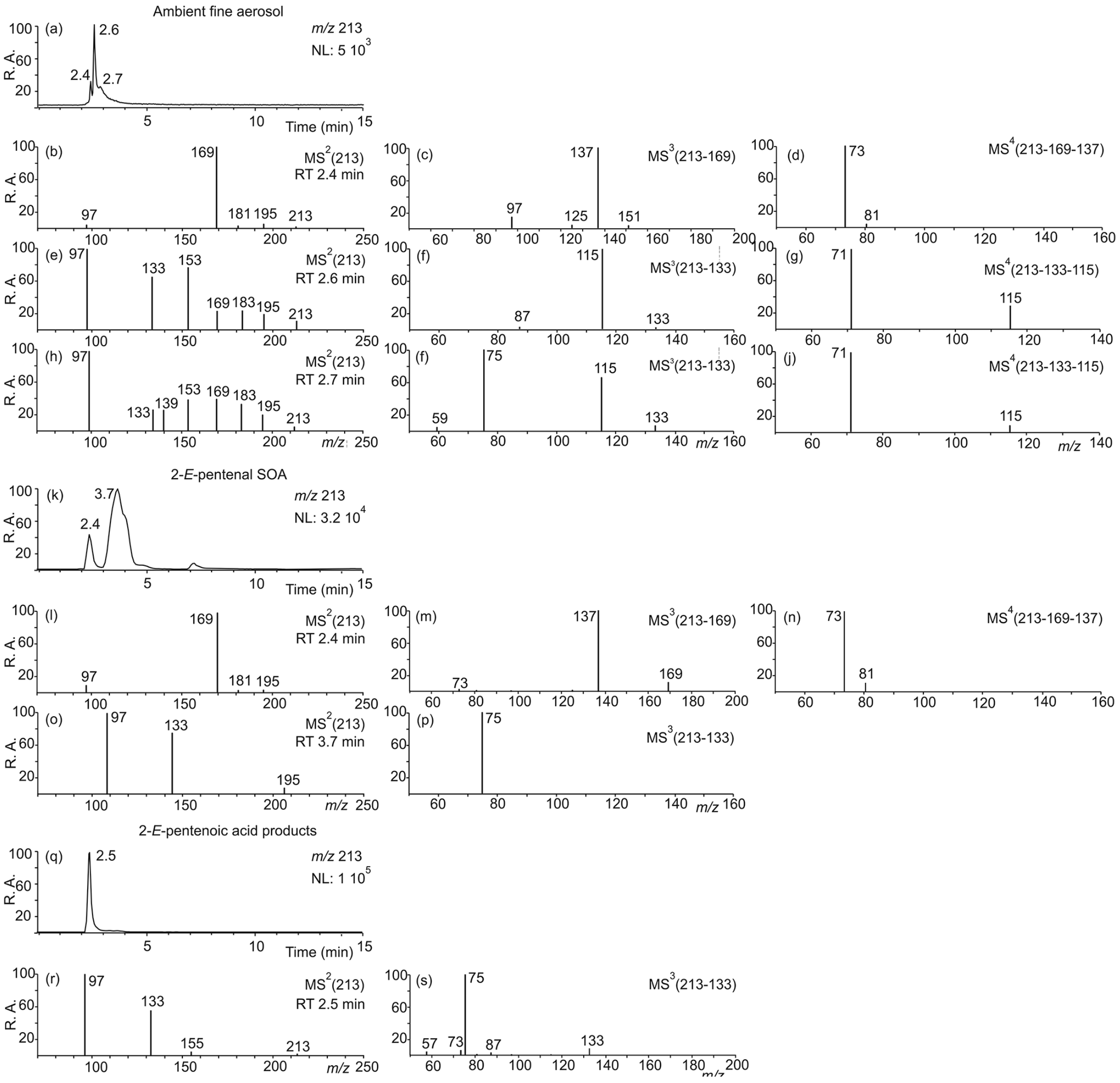
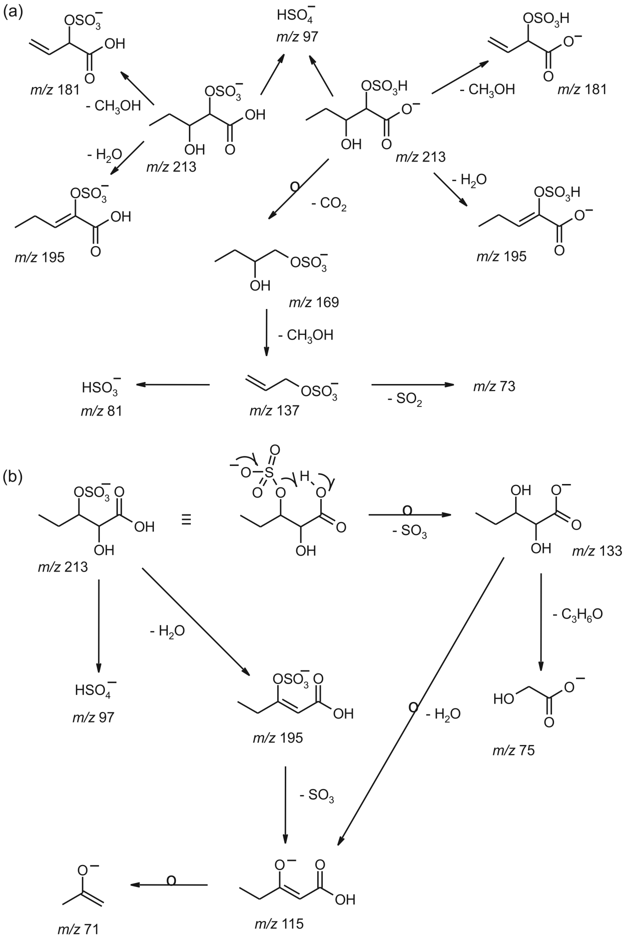


Figure 3. Selected LC–MS chromatographic data (m/z 213 EICs) and selected MS data (MS^2, MS^3, and MS^4 product ion spectra) for ambient fine aerosol **(a–j)**, 2-E-pentenal smog chamber SOA **(k–p)**, and 2-E-pentenoic acid aqueous-phase reaction products **(q–s)**. Abbreviation: NL, normalization level.

ure 5 shows selected LC–MS chromatographic data (m/z 169 EICs) obtained for ambient fine aerosol and 2-E-pentenal SOA, as well as selected MS data (MS^2 and MS^3 product ion spectra). Three peaks can be distinguished in the m/z 169 EICs, of which the first peak co-elutes with the first-eluting m/z 213 OS (2.4 min), tentatively attributed to 2-sulfooxy-3-hydroxypentanoic acid. This co-elution behavior was also noted under improved chromatographic separation conditions where two Atlantis T3 columns were used in series (results not shown). It thus appears that 2-sulfooxy-3-hydroxypentanoic acid is unstable upon electrospray ionization. A possible fragmentation mechanism involving decarboxylation and resulting in m/z 169 is provided in Scheme 3a. The second peak (RT 2.7 min: measured mass, 168.9807; error: −2.9 mDa; elemental formula, $C_3H_5O_6S^-$) is tentatively attributed to lactic acid sulfate, a known organosulfate, which has been reported in ambient fine aerosol (Olson et al., 2011; Safi Shalamzari et al., 2013; Hettiyadura et al., 2015). The third peak (RT 3.8 min: measured mass, 169.0177; error: +0.6 mDa; elemental formula, $C_4H_9O_5S^-$) reveals a fragmentation pattern that perfectly matches that of the first m/z 169 peak, which is due to decarboxylation. It is thus very likely that this compound results from decarboxylation of the corresponding m/z 213 OS; however, on the basis of this study it could not be determined where the degradation takes place (i.e., on the filter during sampling, during sample workup, or during analysis). Furthermore, it was confirmed that the m/z 169 compounds that are present in 2-E-pentenal SOA are also formed from 3-Z-hexenal and 2-E-hexenal (Fig. S5). Based on MS data



Scheme 3. Proposed fragmentation routes for m/z 213 organosulfates, related to 2-*E*-pentenal SOA and tentatively assigned to **(a)** 2-sulfooxy-3-hydroxypentanoic acid and **(b)** 3-sulfooxy-2-hydroxypentanoic acid, on the basis of detailed interpretation of MS^2, MS^3, MS^4, and accurate mass data. For the fragmentation of the m/z 169 compound, formed by decomposition, see **(a)**.

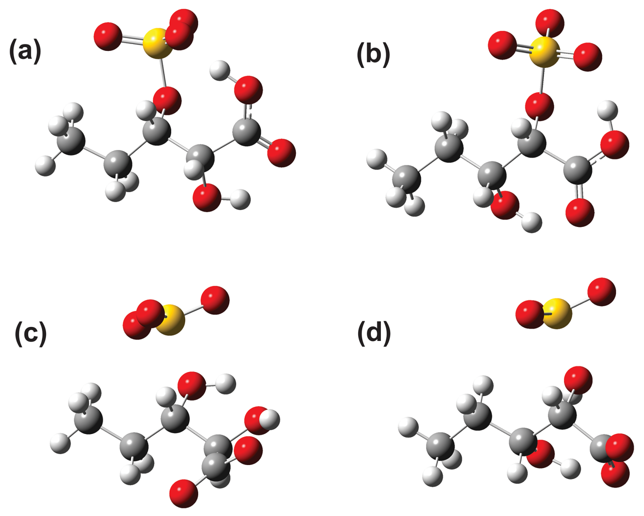


Figure 4. Optimized gas-phase geometries of the lowest-energy conformers of the MW 214 sulfate derivatives of 2,3-dihydroxypentanoic acid with the sulfate group located at **(a)** C-3 and **(b)** C-2, and the associated optimized structures (**c, d**, respectively) after transfer of the carboxyl proton.

the product with RT 3.8 min in ambient fine aerosol (4.1 min in 2-*E*-pentenal SOA) is tentatively assigned to 1-sulfooxy-2-hydroxybutane (Scheme 3).

The instability of 2-sulfooxycarboxylic acids due to decarboxylation also provides an explanation of why in the case of methacrolein only the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid has been reported (Gómez-González et al., 2008; Surratt et al., 2008; Safi Shalamzari et al., 2013) and not that of its positional isomer, 2-sulfooxy-3-hydroxy-2-methylpropanoic acid.

3.5 Proposed formation pathway for m/z 213 organosulfates formed from 2-*E*-pentenal

As discussed above, m/z 213 compounds detected in 2-*E*-pentenal SOA could be tentatively assigned to positional isomeric OSs of 2,3-dihydroxypentanoic acid, i.e., 2-sulfooxy-3-hydroxypentanoic acid and 3-sulfooxy-2-hydroxypentanoic acid. Their detection in 2-*E*-hexenal and 3-*Z*-hexenal SOA is logical as other organosulfates, i.e., the m/z 229 compounds (Sects. 3.2 and 3.3), could also be found in the latter SOA and the fact that 2-*E*-pentenal is a photolysis product of 3-*Z*-hexenal (O'Connor et al., 2006). A possible formation pathway leading to the structurally characterized isomeric m/z 213 organosulfates is proposed in Scheme 4. The suggested pathway is based on the mechanism reported for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein (Lin et al., 2013). It involves a sequence of reactions, comprising epoxidation of the double bond of 2-*E*-pentenal with the OH radical and reaction of the epoxy group with sulfuric acid in the particle phase. The results obtained in this study further suggest that the formation of the m/z 213 sulfate derivatives of 2,3-dihydroxypentanoic acid likely does not result from reactive uptake of 2-*E*-pentenal as only one positional isomer (3-sulfooxy-2-hydroxypentanoic acid) could be generated in the aqueous-phase sulfation of 2-*E*-pentenoic acid, whereas two positional isomers (the latter and 2-sulfooxy-3-hydroxypentanoic acid) are detected in both 2-*E*-pentenal SOA and fine ambient aerosol. The formation of 3-sulfooxy-2-hydroxypentanoic acid in the aqueous-phase reaction of 2-*E*-pentenoic acid with the sulfate radical anion (Scheme S1) is caused by stabilization of the resulting intermediate C-2 radical upon attack of the double bond with the sulfate radical anion.

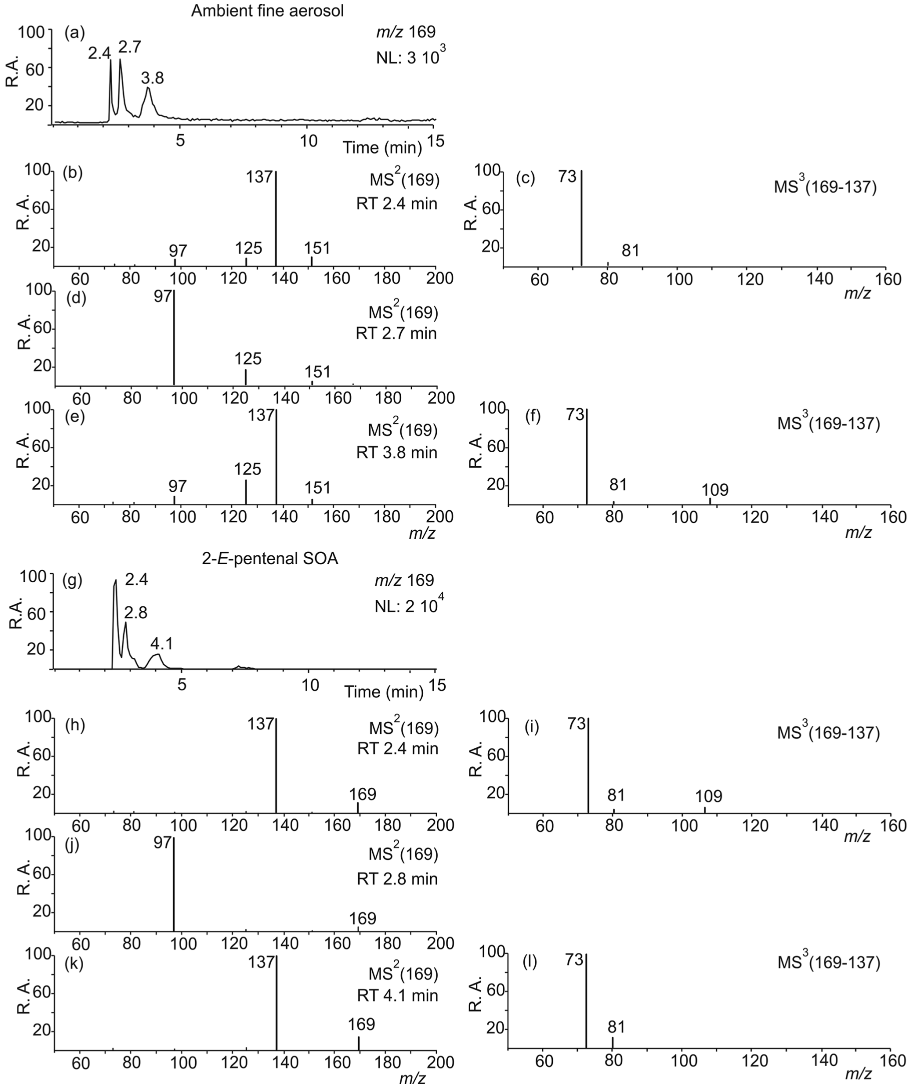
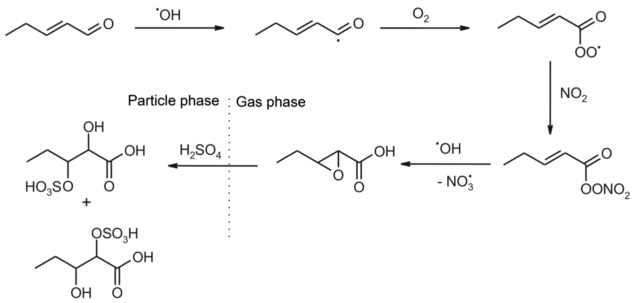


Figure 5. Selected LC–MS chromatographic data (m/z 169 EICs) and selected MS data (MS^2 or MS^3 product ion spectra) for ambient fine aerosol **(a–f)** and 2-E-pentenal SOA **(g–l)**. Abbreviation: NL, normalization level.

4 Conclusions and perspectives

We show in the present study that the unsaturated aldehydes 2-E-pentenal, 2-E-hexenal, and 3-Z-hexenal can be converted into polar organosulfates with m/z 229 and 213. These results are in line with a previous study that found that the green leaf aldehyde 3-Z-hexenal serves as a precursor for m/z 225 organosulfates (Shalamzari et al., 2014). Thus, in addition to isoprene, the green leaf volatiles 2-E-hexenal and 3-Z-hexenal, as well as 2-E-pentenal, a photolysis product of 3-Z-hexenal, should be taken into account for organosulfate formation. These results imply that biogenic volatile organic compounds such as the green leaf volatiles, which are emitted due to plant stress (mechanical wounding or insect attack), are a potential source of polar organosulfates and SOA.

Extensive use was made of organic mass spectrometry and detailed interpretation of mass spectral data to elucidate the chemical structures of the m/z 229, 213, and 169 organosulfates formed from 2-E-pentenal. In addition, quantum chemical calculations were performed to explain the different mass spectral behavior of 3-sulfooxy-2-hydroxypentanoic acid and 2-sulfooxy-3-hydroxypentanoic acid, where the isomer with the sulfate group at C-3 results in the loss of SO_3. The m/z 213 organosulfates formed from 2-E-pentenal are explained by the same route as that reported for 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein, which, like 2-E-pentenal, is also an α,β-unsaturated aldehyde. The pathway involves formation of an epoxide in the gas phase and sulfation of the epoxy group with sulfuric acid in the particle phase. The m/z 229 organosulfates formed from 2-E-pentenal are



Scheme 4. Proposed formation pathway for m/z 213 organosulfates related to 2-E-pentenal (and indirectly to 3-Z-hexenal and 2-E-hexenal SOA), which occur in ambient fine aerosol and are tentatively assigned to 2-sulfooxy-3-hydroxypentanoic acid and 3-sulfooxy-2-hydroxypentanoic acid. The suggested mechanism is based on that reported for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanoic acid from methacrolein (Lin et al., 2013).

tentatively explained by a novel pathway that bears features of the latter pathway but introduces an additional hydroxyl group. Evidence is also presented that the m/z 213 OS, 2-sulfooxy-3-hydroxypentanoic acid, is unstable and decarboxylates, giving rise to 1-sulfooxy-2-hydroxybutane, a m/z 169 organosulfate. The instability of 2-sulfooxy carboxylic acids due to decarboxylation also provides an explanation of why in the case of the isoprene-related methacrolein only 3-sulfooxy-2-hydroxy-2-methylpropanoic acid has been detected in previous studies and not its isomer, 2-sulfooxy-3-hydroxy-2-methylpropanoic acid. Furthermore, it could be shown that lactic acid sulfate is generated from 2-E-pentenal. With regard to the proposed pathways for organosulfate formation from unsaturated aldehydes, further research is warranted to gain additional mechanistic insights.

The Supplement related to this article is available online at doi:10.5194/acp-16-7135-2016-supplement.

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