Antwerp, 1 March 2016

Dear Professor McLaren,

Attached, we are submitting the revised manuscript entitled “Characterization of polar organosulfates in secondary organic aerosol from the unsaturated aldehydes 2-E-pentenal, 2-E-hexenal, and 3-Z-hexenal”, the supplement, and our responses to the reviewers’ comments.

We hope you will find our revised manuscript suitable for publication in Atmospheric Chemistry and Physics.

We also take the opportunity to thank you for handling our manuscript.

Sincerely,

Magda Claeys

Replies to the comments of reviewer #1

We would like to thank the reviewer for thoughtful and constructive comments. Our responses to the detailed comments are as follows:

General comments: My main criticism of the paper is that it is difficult to really understand the impact of this chemistry on a wider scale. The paper is very technical and describes the analysis well. But at the end I'm left wondering whether these are actually important or if they are just well suited to the analysis method. Do the authors think this is a large source of SOA? Is it a global source, regional or local? There is no mention of the potential for anthropogenic emissions of GLV from grass cutting in domestic and within cities (i.e. could they be more important than isoprene OS in these environments?). Do the authors think these species are likely to be found in cities where biogenic and anthropogenic emissions mix. What are the potential impacts of this source?

Response: It is still too early to understand the impact of this GLV chemistry on a wider scale. Unfortunately, there is very little information about emissions of GLVs compared to those of isoprene and terpenes in different environments and even less about SOA formation. However, we believe that GLV chemistry can be of a regional and local importance. GLV emissions in agricultural areas where crops are harvested could be important as well as those in urban residential areas where grass is mown. It has also been reported that lawn mowing contributes to atmospheric aerosol levels in American suburbs (Harvey 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. It is known that herbivory, mechanical injury or pathogen infestation to vegetative tissue of cereal grasses can induce VOC production (Piesik et al., 2011; Brilli et al., 2012). As to urban residential areas, we have some data about a site in Belgium (i.e., a polluted residential/forest site in Brasschaat, Antwerp), where a MW 226 organosulfate, originating from 3-*Z*-hexenal (Shalamzari et al., EST 2013), could be detected with a substantial relative abundance: the concentration of this compound was on average 6.8 ± 10.1 ng m^{-3} versus 9.0 ± 11.6 ng m^{-3} measured for the isoprene SOA-related 2-methyltetrol sulfates (Gómez-González et al., ACP 2012). It is thus well possible that in urban residential areas GLV chemistry might be as important as isoprene chemistry. However, more research is necessary to support this hypothesis.

The introduction has been expanded with the following sentences: "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} versus 9.0 ± 11.6 ng m^{-3} for the isoprene SOA-related 2-methyltetrol sulfates (Gómez-González et al., 2012)."

Specific comments:

Abstract: This needs some text on the relevance of the findings. (see comments above).

Response: The abstract has been expanded as follows taking into account the above general comments: "This chemistry could be important on a regional and local scale where GLV emissions such as from grasses and cereal crops are substantial."

Page 29559, line 27: Change to "reaction of sulphuric acid with epoxide containing"

Response: Suggested correction has been made.

Page 29560, line 17: Here and throughout there are a lot of sentence that start with "AS to". This makes the sentences rather long and hard to follow. Often the sentence just needs to be reversed to be clearer i.e. "It was shown that. . .. .bulk sulphur mass at K-puszta in Hungary"

Response: Suggested changes have been made.

Page 29560, line 27: What do mean by "magnitude"? Is this ion abundance?

Response: With "magnitude" we mean here the peak area observed in the extracted ion chromatogram. This has been clarified in the revised text.

Page 29561, line 11: I think it needs to be clearer here that you are actually characterizing OS from E-pentenal in particular and that the other VOC precursors fall apart to give E-pentenal. I was confused reading this why you were only talking about one set of OS but 3 precursor.

Response: This section has been clarified as follows: "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 (PM2.5) aerosol collected from K-puszta, Hungary, a rural site with mixed deciduous-coniferous vegetation. Only the results obtained for 2-*E*-pentenal SOA are discussed, because it was found that 2-*E*-hexenal and 3-*Z*-hexenal SOA contains the same OSs."

Line 18: Change "resorting" to "using".

Page 29562, line 8, sentence doesn't make sense – preparing used twice.

Line 15: I am not sure you need to explain which VOCs you are using again. Take out "selected".

Page 29563, line 24: Change to "some adaptations".

Page 29564, line 4: Change to "and the 2-E-pentenoic acid reaction products were

Response: Suggested changes have been made.

Page 29565, line 25: I think it needs to be clearer what you mean by "substantial relative abundance" Do you mean peak area, ion intensity?

Response: By "substantial relative abundance" we mean "peak area" here.

Page 29567, line 28: watch tense, only 1 reaction 1.

Response: Correction has been made.

Page 29568, line 3 plus figure: This reaction scheme seems unlikely. Surely the second attack of this molecule will take place at the double bond? Do the authors have an explanation of the reaction adjacent to the unsaturated bond.

Response: We have done an attempt here to explain the formation of MW 230 OSs from 2-*E*-pentenal but have to admit that it is somewhat speculative. Unfortunately, we could not come up with an alternative explanation to accommodate the second hydroxyl group at the C-4 position in the identified MW 230 OS.

Page 29569, line 10: I am not entirely convinced by this explanation. Why is this seen for this peak only? The retention time is not much different but the shape is much worse.

Response: We have tried to find a possible explanation for the unusual chromatographic behavior of the *m/z* 213 isomers present in 2-*E*-pentenal SOA. We have thoroughly reflected on this phenomenon and have to admit that we cannot come up with a more convincing explanation. In our experience the 2-*E*-pentenal SOA was much more hydrophobic than the ambient extract in the sense that it was more difficult to dissolve it in the solvent mixture used for LC/MS analysis (i.e., methanol:water; 1:1, v/v). We also have injected the 2-*E*-pentenal SOA sample in a more diluted form but the peak shapes did not improve.

Line 17: give retention time for second isomer.

Response: The retention time of the second isomer has been provided: 3.7 min.

Line 23-27: I don't think this section is explained particularly well. And the reasoning is hard to follow. Needs more.

Response: The reasoning becomes easier to follow if in addition to Figure 4 (revised) also Scheme 3bis consulted. This section has been revised as follows, also taking into account the concerns of reviewer #2, who requested a thorough discussion using chemical terminology and free energies: "The distinctly different fragmentation behavior of the two isomers was addressed through quantum chemical calculations. Figures 4a and 4b 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 Figs. 4c and 4d, respectively. However, the energetics of both processes are different: while for the C-3 isomer (Figs. 4a and 4c) this is accompanied by an energy increase of 85.30 $kJ.mol^{-1}$, the corresponding value for the C-2 isomer (Figs. 4b and 4d) 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."

Page 29571, line 12: Don’t think you need to explain the structure of methacrolein.

Response: Correction has been made.

Page 29581, table 2: The top section is confusing, making you think it is somehow related to the rest of the table. I would remove this. I don’t think you need to give the structures of the precursors. I would like to see Rt in this table.

Response: The top section has been deleted and RTs have been added.

Replies to the comments of reviewer #2

We thank this reviewer for thoughtful and detailed comments, and constructive criticism. Our responses to the detailed comments are as follows:

1. The importance of this research, potentially the SOA forming potential of green leaf volatiles (GLV) should be more thoroughly developed in the Introduction as suggested by Reviewer 1. For example, what is the potential impact of GLV relative to the more widely studied isoprene and monoterpenes, particularly in terms of emissions and SOA yields? How does its potential impact vary with respect to anthropogenic activity, temperature, and season? What is the potential for GLV to contribute to OS?

Response: The request to comment on the importance of this research in the introduction was also made by reviewer #1. See our response to the general comments raised by this reviewer.

2. Please add the following methodological details: a. The supplier and purity of methanol (page 29563, line 8) b. The duration of sonication for extraction (page 29563, line 8) c. Clarify which of the sample aliquots was analyzed (frozen or not) and the purpose of splitting the two aliquots (page 29563, line 16). d. The conditions under which the ambient samples were stored, since their collection in 2006 (section 2.2.3). e. Clarification is needed regarding the similarity/difference between the two columns used (page 29565, line 2). What was chemically different that impacts retention, or are these interchangeable?

Responses:

(a) The supplier and purity of methanol were mentioned in the original text: Page 29562, lines 3-5.

(b) The duration of sonication for extraction has been mentioned in the revised version: “The filters were extracted 3 times with 10 mL of methanol in an ultrasonic bath for 10 min.”

(c) This section has been clarified as follows: “The residue was redissolved in 1 mL of methanol and divided in two portions, because not all analyses could be performed at the same time. A fresh or unfrozen portion was redissolved in …..”.

(d) For this information, we refer to a previously published article, where the temperature at which the samples were stored is mentioned (i.e., –25 ^{0}C): “Information about the site, sampling campaign and storage of samples can be found in a previous article (Maenhaut et al., 2008).”

(e) The elution order of the targeted compounds was found to be the same but the retention times on the HSS T3 column used for UPLC were shorter. Information on the retention times of the targeted organosulfates has been included. This section has been expanded as follows:

Page 29565, line 5: “……which, as the Atlantis T3 column (Waters), contains a stationary phase based on trifunctionally-bonded C18 chains and results in the same elution order for the targeted organosulfates. The retention times on the HSS T2 column were: 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; 1-sulfooxy-2-hydroxybutane, 1.45 min.”

3. The chromatograms shown in Figure 1 (especially A, B, D, and E) reveal early elution of the major organosulfates (OS) products. It is not clear the extent that these compounds retain relative to unretained components (e.g. sulfate). To clarify this point, the authors should provide the retention time of the solvent front / unretained component and briefly discuss the retention of these compounds relative to the solvent front. Notably, the results do not appear to support the rather strong statement that the Atlantis T3 column "provides retention for the organosulfates compounds under investigation" (page 29564, line 20).

Response: We admit that the identified organosulfates only show a limited retention on the Atlantis T3 column. If we would have to start this work all over again we would consider using a HILIC column, as used in a recent study by Hettiyadura et al. (2015). To address this comment, the retention times of the solvent front (containing unretained material) and sulfuric acid have been mentioned in the legend of Figure 1: "The retention times of the solvent front (containing unretained material) and sulfuric acid, which can be seen in the BPC, were 2.0 and 2.3 min." In addition, we have weakened our statement on the retention of the targeted polar organosulfates on the Atlantis T3 column (page 29564, line 20): "provides some retention for the polar organosulfate compounds under investigation."

4. The authors suggest that *m/z* 213 is an organosulfates unique to GLV (page 29565, line 22; 29560, line 25), overlooking its initial detection in SOA generated from isoprene (Surratt et al. 2008). Because isoprene is a major contributor to biogenic SOA, it is likely also a dominant source of *m/z* 213 (even if the relative abundance of *m/z* 215 is lower).

Response: We are well aware of the detection of *m/z* 213 organosulfates in isoprene SOA, since we were closely involved in the research. However, we failed to detect these compounds in SOA collected from an isoprene/NO_x/SO_2 photooxidation experiment conducted at the US EPA, which, in our experience better simulated the formation of organosulfates formed under ambient conditions, such as, for example, the *m/z* 305 organosulfates, which are also discussed in the Surratt et al. (2008) paper. Furthermore, interpretation of the MS data does not suggest a branched isoprene skeleton related to the *m/z* 215 2-methyltetrol sulfates with a terminal aldehyde but a linear structure. For these reasons, no further attention was paid in the present work to isoprene as a possible precursor for the *m/z* 213 organosulfates.

There was written in the Surratt et al. (2008) paper: "It should be noted that the *m/z* 213 compounds were not detected by Gómez-González et al. (2008) in the aerosol collected from an isoprene/NO_x/SO_2 EPA photooxidation experiment."

5. The authors should not use relative abundance to compare m/z 229 formation between 2-pentenal to hexenal, as this depends on the response of other components of the sample. Any quantitative comparison should be done using absolute abundance normalized to the amount of organic carbon extracted.

Response: The sentence has been rephrased as follows: "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 of the Supplement."

6. The OS formulas in Table 2 and in the results and discussion are anionic and should be indicated as such with a superscripted negative symbol.

Response: The suggested corrections have been made.

7. Does the MS data (e.g. base peak chromatogram) support that the later-eluting *m/z* 229 peaks in the 2-E-hexenal SOA have a molecular ion of *m/z* 229, such that these are isomers (as suggested on page 29567, line 6)? It is also plausible that *m/z* 229 may be a fragment ion of later-eluting compounds.

Response: It was confirmed that the later-eluting *m/z* 229 peaks in 2-*E*-hexenal and 3-*Z*-hexenal SOA (Fig. S1) have a deprotonated molecule at *m/z* 229 and were not due to fragment ions of other species. As this is quite a standard practice in MS analysis to perform checks like this, we did not consider it necessary to mention this in the manuscript.

8. The first line of section 3.3 appears erroneous. The chromatogram shows only one *m/z* 229 peak for 2-E-pentanal, while the text suggests “stereoisomeric forms.”

Response: For clarity, we have deleted the adjective “stereoisomeric” here; however, it should be realized that there are several stereoisomeric forms possible, theoretically eight, which cannot or only partially be chromatographically separated. This feature is discussed earlier in the manuscript (Page 29567, lines 10-15).

9. The structures proposed in Table 2 and described in the text are “tentatively identified” based on MS data and should be clearly noted as such. These structures may only be unequivocally confirmed using structurally-matched standards.

Response: We concur with this criticism and have made appropriate changes in several places in the text and in the heading of Table 2.

10. Figure 4 and section 3.4. The author’s results and conclusions from the quantum chemical calculations are not clear. In particular, the meaning of “accommodated” in the statement in the caption “the negative charge can be accommodated by the carboxyl group” is not clear. Please use chemical terminology and free energies to explain the different behavior of these ions. Without more thorough discussion and clarification, these results have very limited value and should be removed.

Response: Section 3.4 has been thoroughly revised, as suggested. See our reply to the comment made by reviewer #1.

11. Technical comments on Table 1 a. Sample codes should be removed as these are not of use to the scientific community. b. The seed type and concentration should be presented as “AS:SA (1/1, w/w)” as done in the text, instead of 1 2 + 1 2 . c. The footnote should be revised to account for the NO2 contaminant (0.3%).

Response: The sample codes (experiment numbers) have been kept, but the other suggested corrections have been made. The experiment numbers may be meaningless to the average reader, but if a reader wants to request additional information about the experiments, those numbers make it far easier for us to address that request quickly and accurately. Also, if these same experiments are analyzed again and used in another paper, the experiment numbers make it much easier to make connections between the papers.

12. Presentation of Figures a. The MS/MS spectra shown in Figures 2 and 3 may be moved to the supplement, as the relevant data are summarized in Table 2. b. Figure 1 should be removed, as chromatograms in Figure 1c, 1d, 1e are duplicated in Figure 2, 3, and 4. Unique parts of Figure 1 a and b are not discussed in detail and may also be moved to the supplement, or removed.

Response: We prefer to keep all figures. For example, Figure 1 is useful to get an idea about the peak areas of the targeted organosulfates compared to those of the isoprene SOA-related 2-methyltetrol sulfates (*m/z* 215), which is clearly mentioned in the text, while the base peak chromatogram, shown at the top, also shows all compounds, including unretained material eluting in the solvent front and sulfuric acid. The latter information has been mentioned in the legend to Figure 1 of the revised text. With respect to removing Figures 2 and 3, we also prefer to keep them, because we already present the data obtained for 2-*E*-hexenal and 3-*Z*-hexenal in the supplement. Table 2 only provides limited MS/MS information, only *m/z* values of product ions but no relative abundances.

13. Abstract (page 29557, line 22) “sulfoxy” should be “sulfooxy” 14. Section 3.3 (page 29567, line 27) “is also a” should be “is also an”

Response: The corrections have been made.

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

Comment [MC1]: Revised version

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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 weigths (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 two 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, and 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*-hexenylacetate. 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)~~, which occur at substantial concentrations in fine ambient aerosol (PM$_{2.5}$) from a forested site in Belgium (Gómez-González et al., 2012)~~. 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~~presented~~ substantial concentrations of a *m/z* 225 organosulfate, originating from 3-Z-hexenal, i.e., 6.8-±-10.1 ng m^{-3} versus 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 ~~with~~ of sulfuric acid ~~of~~ with epox~~y~~ide-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). Futhermore~~In addition~~, 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, not only formed 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~~s~~ of organosulfates to organic mass for twelve sites in the Unites States was found to be 5-10% using a S-estimation method, and was higher during warm months when photochemical oxidation chemistry is most active (Tolocka and Turpin, 2012). ~~As to K-puszta, Hungary, it~~ 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 2-hydroxy-2-methyl-3-sulfooxypropanic acid from methacrolein in the presence of NO_x ($NO + NO_2$), which, as 2-*E*-pent~~a~~enal, 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, ambient monitoring studies can 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~~ with 2-*E*-pentenal, 3-*Z*-hexenal and 2-*E*-hexenal~~, 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 ~~resorting to~~using reversed-phase LC using a trifunctionally-bonded C_{18} stationary phase (Safi Shalamzari et al., 2013).~~ As to mass spectrometric techniques, u~~Use was made of high-resolution MS to infer the elemental composition, while ion trap 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 ~~prepared~~ 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 ~~selected~~ biogenic VOC ~~(i.e., 2-*E*-pentenal, 2-*E*-hexenal and 3-*Z*-hexenal)~~ 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 1,500 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 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 3 times with 10 mL of methanol in an ultrasonic bath for 10 min. ~~As to the use of methanol for extraction, i~~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 type of 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 in two portions, which were dried under nitrogen, and one of the ~~residues~~ portions was stored at –20 °C until use, because not all analyses could be performed at the same time. ~~The residue~~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.

[Table 1]

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 ~~reaction time at which the~~ 2-*E*-pentenoic acid reaction products were sampled ~~was~~ 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, ~~and~~ 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 night-time sample and the work-up 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 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 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 a HSS T3 column (2.1 x 100 mm; 1.8 µm particle size; Waters), which, as 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: 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; 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-hydroxy~~-3-sulfooxy~~pentanoic acid and 2-sulfooxy-3-hydroxy~~-2-sulfooxy~~pentanoic 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 chromatogram (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). The *m/z* 229, 213 and 169 compounds will be ~~structurally characterized~~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 ~~relative abundance~~ peak area compared to that of the *m/z* 215 compounds in ambient fine aerosol, which correspond to isoprene SOA compounds, i.e., sulfate esters of the 2-methyltetrols, formed by sulfation of intermediary C_5-epoxydiols (Surratt et al., 2007a, 2008, 2010). The structures of the ~~BVOC precursors 2-*E*-pentenal, 2-*E*-hexenal and 3-*Z*-hexenal, and 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.

[Figure 1]

[Table 2]

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

Figure 2a-f 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 ~~although at a lower relative abundance than for 2-*E*-pentenal SOA~~, 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~~a and b~~. 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 are consistent with an organosulfate, whereas the losses of H_2O (18 u) and CO_2 (44 u), affording *m/z* 211 and *m/z* 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 further fragmentation of *m/z* 185 (Fig. S2~~a~~) at *m/z* 167, 153, 141, and 123 (Scheme 1). Ions formed by further fragmentation of *m/z* 211 (Fig. S2~~b~~) 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.

[Figure 2]

[Scheme 1]

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 although 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-methylpropanic acid from methacrolein, which, as 2-*E*-pentanal, is also an α,β-unsaturated aldehyde (Lin et al., 2013). Reaction~~s~~ (1) ~~are~~ is 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. Reaction~~s~~ (2) introduces a nitrate group at the C-4 position, which hydrolyzes in the particle phase in the presence of sulfuric acid. Peroxyradicals (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 medium (Boschan et al., 1955; Sato, 2008). Reactions (3) and (4) are similar to those established for the formation of 3-sulfooxy-2-hydroxy-2-methylpropanic 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).

[Scheme 2]

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*-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, ~~and~~ differs in retention time from the same *m/z* 213 isomer (with the same MS characteristics) occuring 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. These calculations provide insight why in the case of the isomer with the sulfate group located at C-3 loss of SO_3 is observed, while this fragmentation is absent for the other isomer with the sulfate group located at C-2. It can be seen from the optimized geometries presented in Figure 4 that for 2-hydroxy-3-sulfooxypentanoic acid (A) the negative charge, following elimination of SO_3, can be accomodated by the carboxyl group, which is in close proximity to the C-3~~

~~oxygen atom (Scheme 3), whereas for 3-hydroxy-2-sulfooxypentanoic acid (B) this process is unlikely.~~ The distinctly different fragmentation behavior of the two isomers was addressed through quantum chemical calculations. Figures 4a and 4b 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 Figs. 4c and 4d, respectively. However, the energetics of both processes are different: while for the C-3 isomer (Figs. 4a and 4c) this is accompanied by an energy increase of 85.30 $kJ.mol^{-1}$, the corresponding value for the C-2 isomer (Figs. 4b and 4d) 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.

[Figure 3]

[Scheme 3]

[Figure 4]

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. Figure 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; Shalamzari et al., 2013; Hettiyadura et al., 2015). ~~However, since no authentic standard was available, this assignment should be regarded as tentative.~~ 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 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 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-methylpropanic acid.

[Figure 5]

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 (Sect. 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~~, which, as 2-*E*-pentenal, is also a α,β-unsaturated aldehyde~~ (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.

[Scheme 4].

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 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, and 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, as 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 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 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.

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Supplement available

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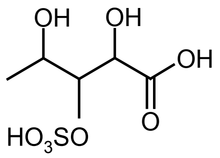
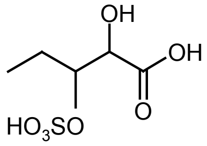
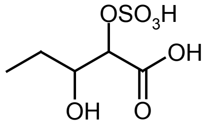
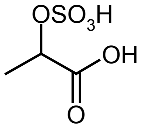
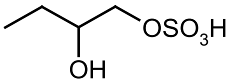
Table 1. Chamber conditions for experiments used for the structural characterization of unknown organosulfates related to 2-*E*-pentenal, 2-*E*-hexenal, and 3-*E*-hexenal SOA. Abbreviations: AS, ammonium sulfate; SA, sulfuric acid; RH, relative humidity.

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
		Steady State:	1.1 ppmC	178 ppb	207 ppb	4.9 µg m^{-3}	28 µg m^{-3}	516 nmol 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
		Steady state:	0.3 ppmC	200 ppb	280 ppb	5 µg m^{-3}	30 µg m^{-3}	439 nmol 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
		Steady State:	4.3 ppmC	195 ppb	207 ppb	20.1 µg m^{-3}	26 µg m^{-3}	587 nmol m^{-3} [H^{+}]air RH: 30%

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

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

Figures and schemes

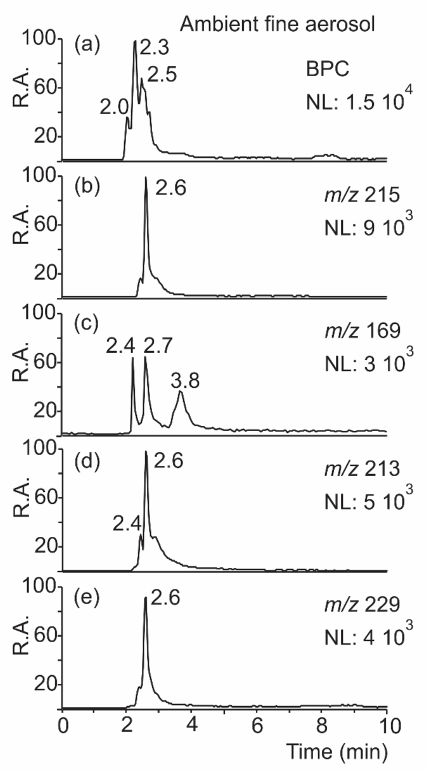


Figure 1. Selected LC/MS chromatographic data using regular RP-LC obtained for ambient fine aerosol, including a base peak chromatogram (BPC) and extracted ion chromatograms (EICs) at *m/z* 215, 169, 213 and 229, corresponding to organosulfates related to isoprene (*m/z* 215; 2-sulfooxy-1,3,4-trihydroxy-2-methylbutane) 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 [panel **(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.

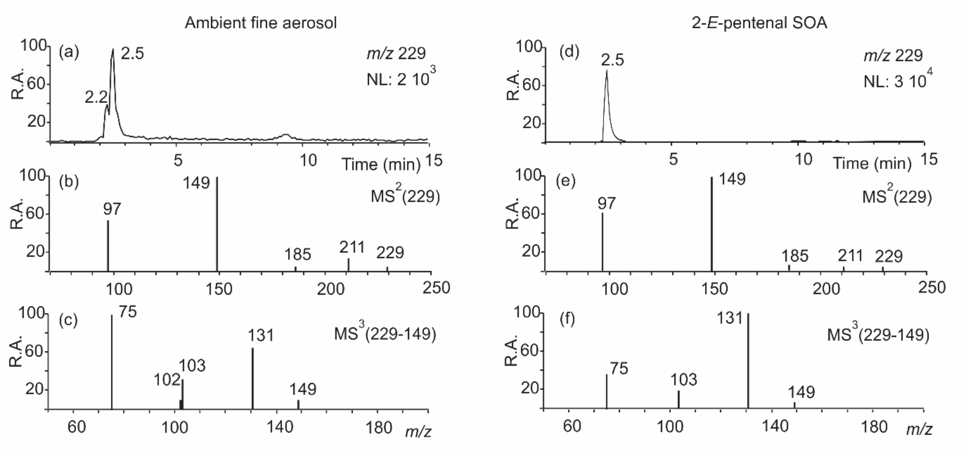
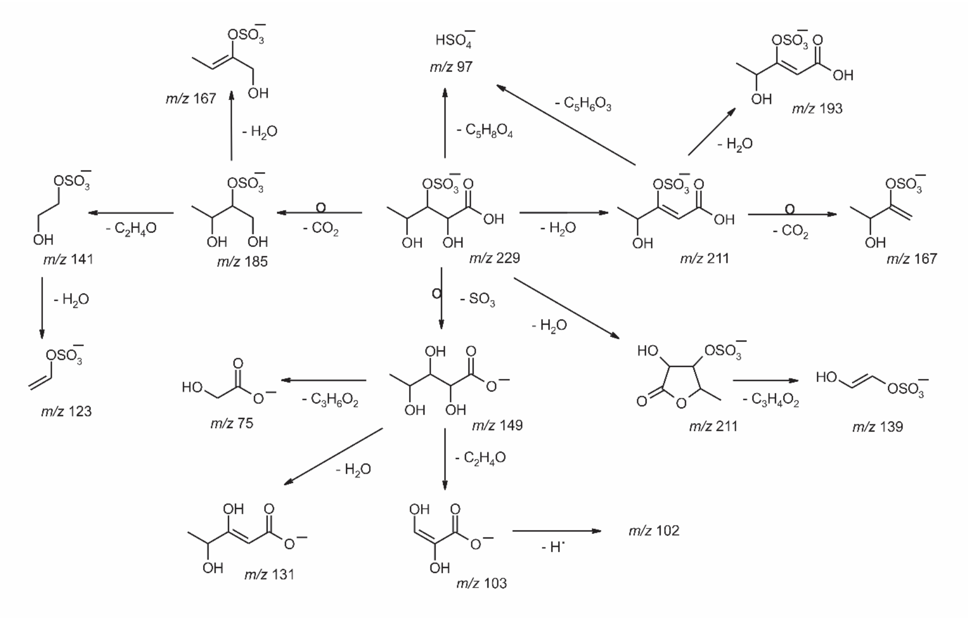
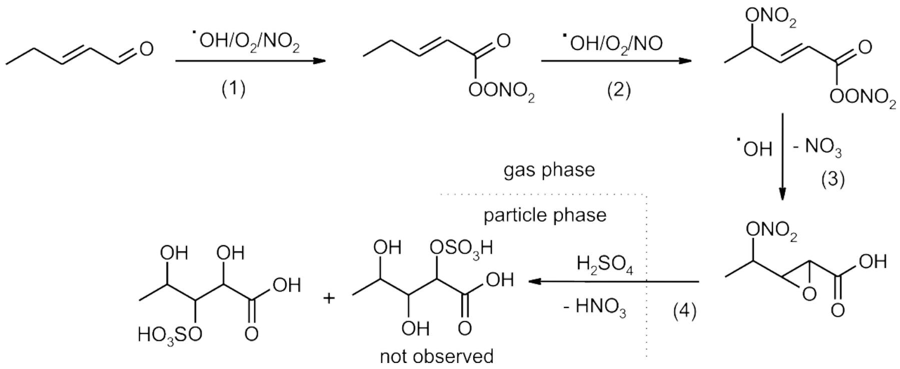


Figure 2. Selected LC/MS chromatographic data (*m/z* 229 EICs) for **(a)** ambient fine aerosol and **(d)** SOA generated from 2-*E*-pentenal in the presence of acidic seed aerosol, as well as selected MS data (MS^2 or MS^3 product ion spectra) for the peak eluting at 2.5 min in **(b** and **c)** ambient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



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.



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).

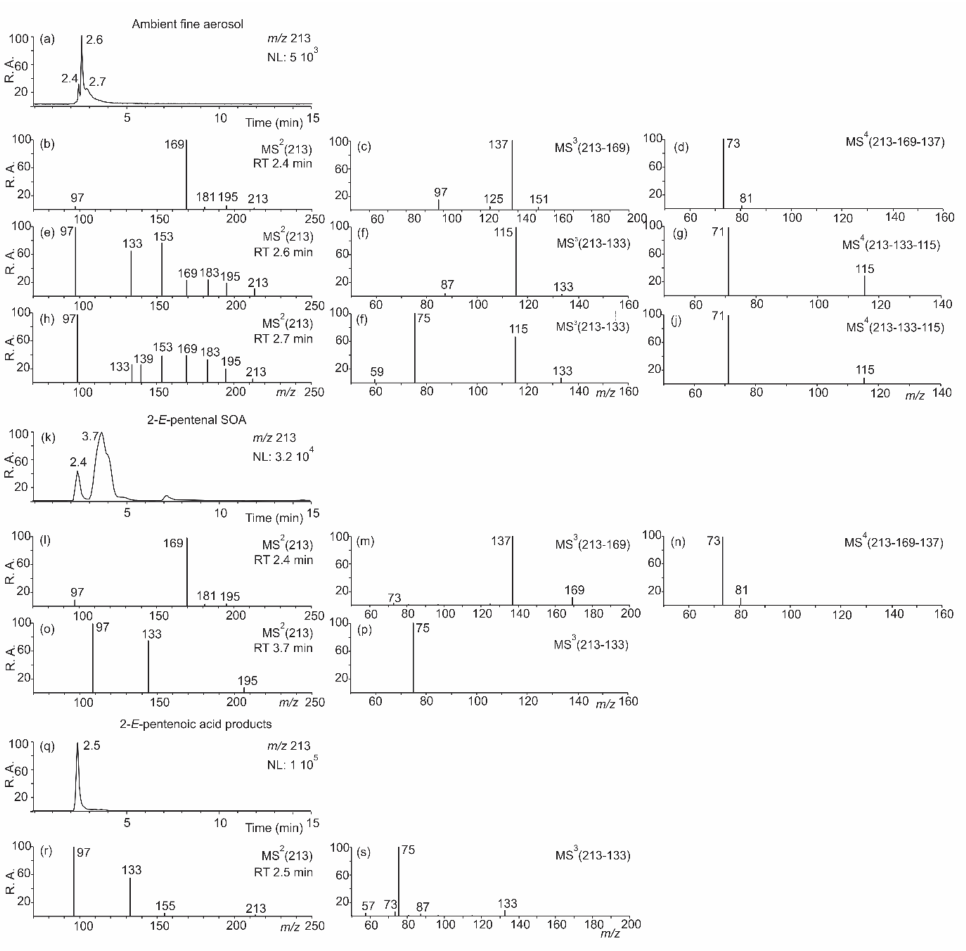
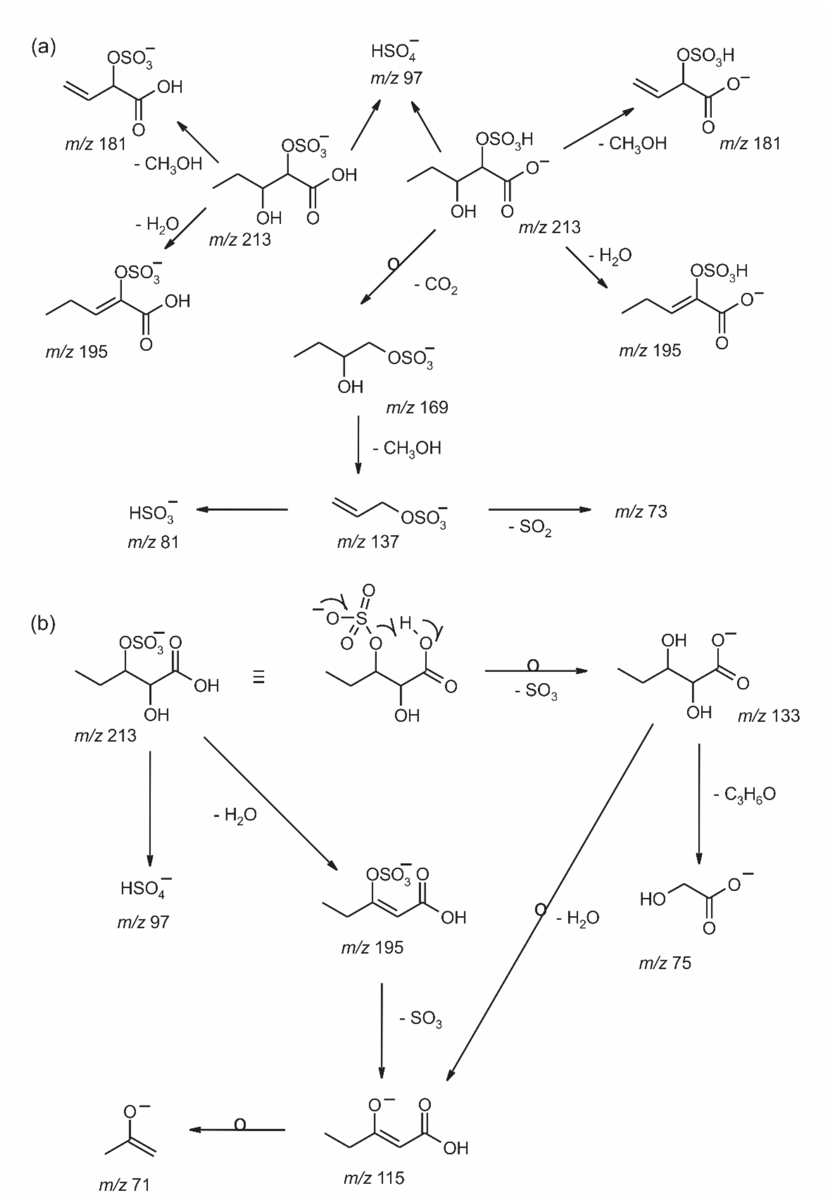


Figure 3. Selected LC/MS chromatographic data (*m/z* 213 EICs) and selected MS data (MS^2, MS^3 and MS^4 product ion spectra) for ambient fine aerosol **(a-j)**, 2-*E*-pentenal smog chamber SOA **(k-p)**, and 2-*E*-pentenoic acid aqueous-phase reaction products **(q-s)**. Abbreviation: NL, normalization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



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 panel **(a)**.

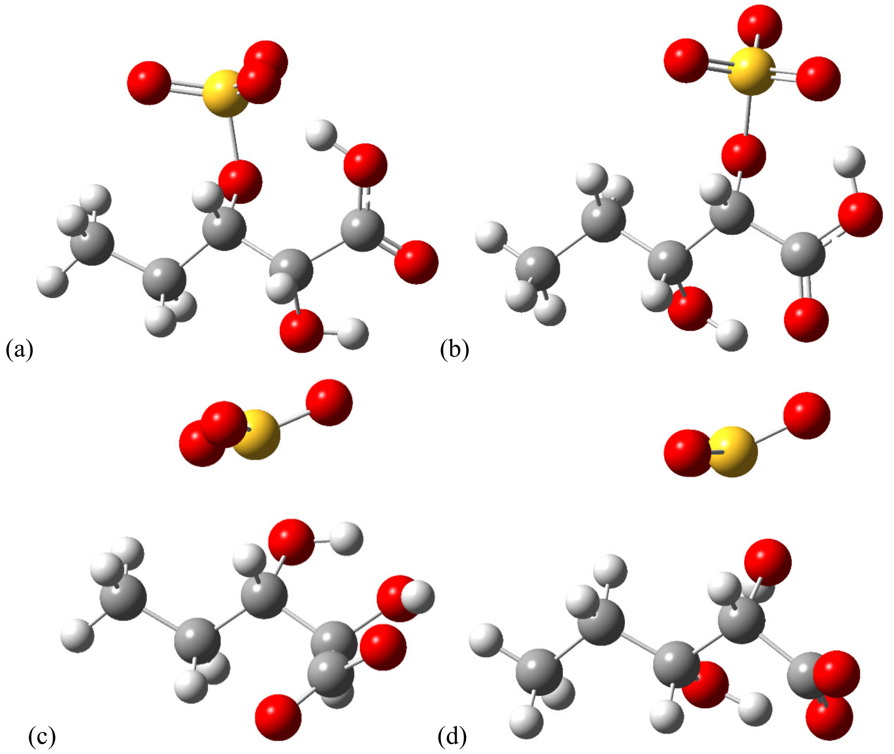


Figure 4. Optimized gas-phase geometries of the lowest-energy conformers of the MW 214 sulfate derivatives of 2,3-dihydroxypentanoic acid with the sulfate group located at **(a)** C-3 and **(b)** C-2, and the associated optimized structures [**(c)** and **(d)**, respectively] after transfer of the carboxyl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

~~Optimized geometries in the gas-phase using ab-initio methods for **(a)** 3-sulfooxy-2-hydroxypentanoic acid and **(b)** 2-sulfooxy-3-hydroxypentanoic acid. After loss of SO_3, the negative charge can be accommodated by the carboxyl group in the case of panel **(a)** (see also Scheme 3b).~~

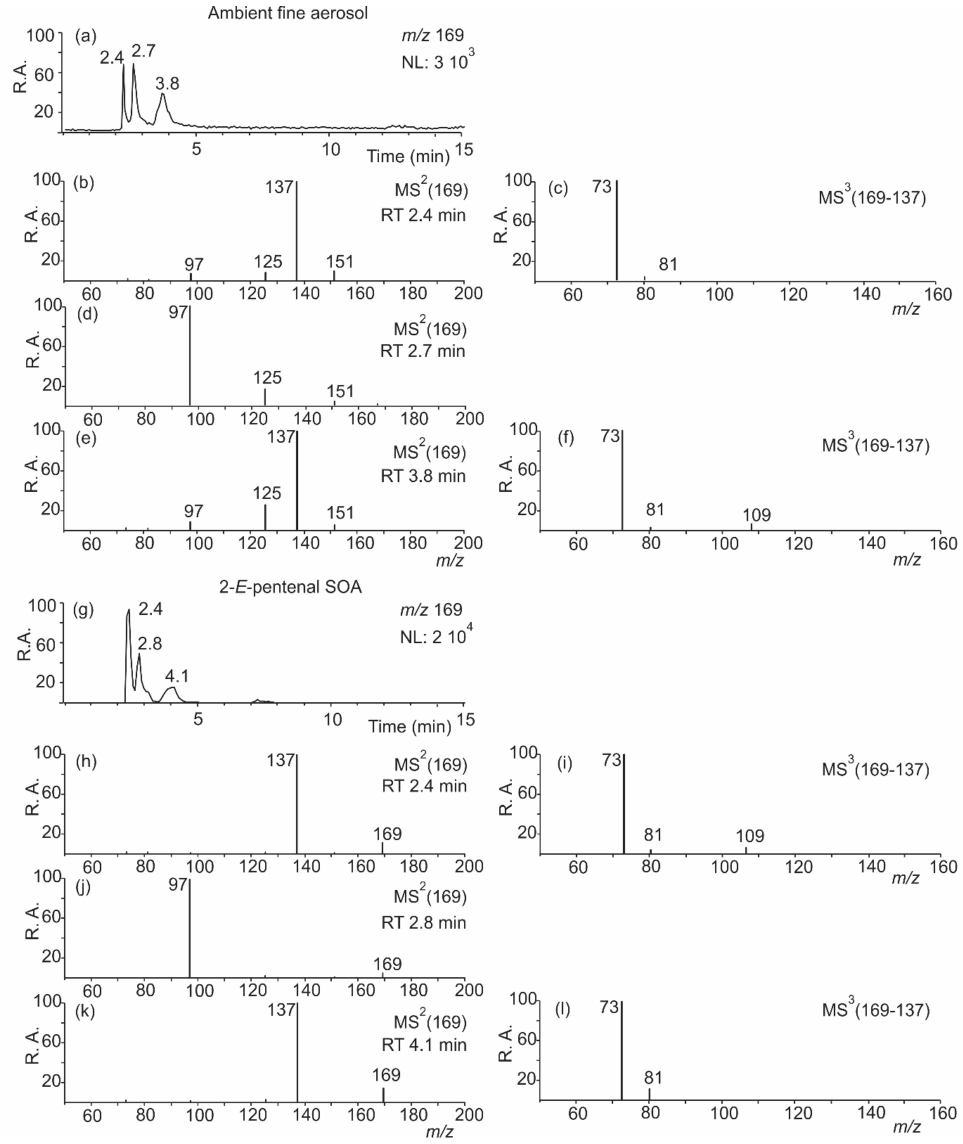
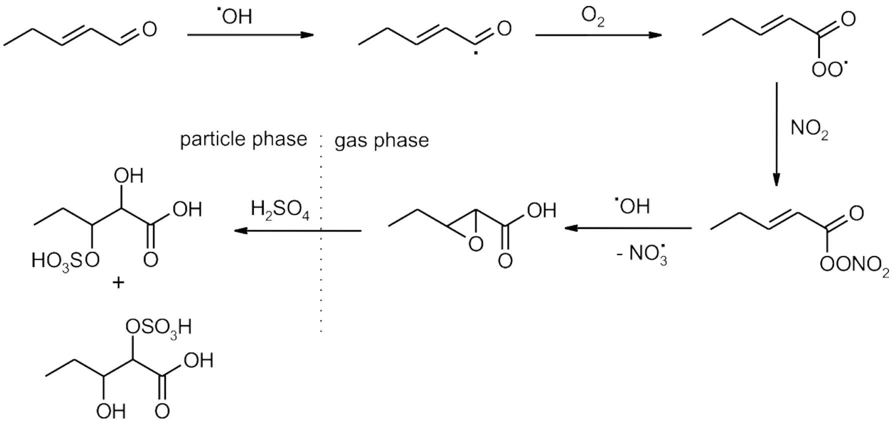


Figure 5. Selected LC/MS chromatographic data (*m/z* 169 EICs) and selected MS data (MS^2 or MS^3 product ion spectra) for ambient fine aerosol **(a-f)** and 2-*E*-pentenal SOA **(g-l)**. Abbreviation: NL, normalization level.



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).

Supplement for:

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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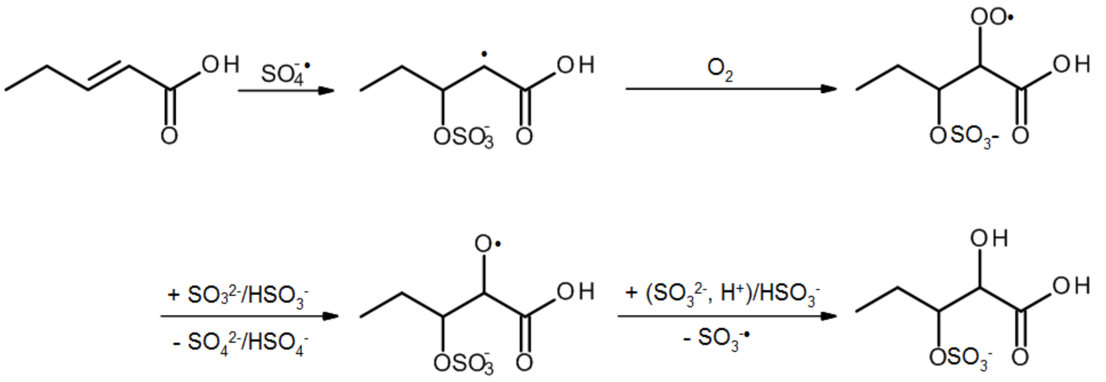
This supplement contains 1 scheme and 4 figures.



Scheme S1. Formation mechanism for 3-sulfoxy-2-hydroxypentanoic acid through reaction of 2-*E*-pentenoic acid with the sulfate radical anion in aqueous solution.

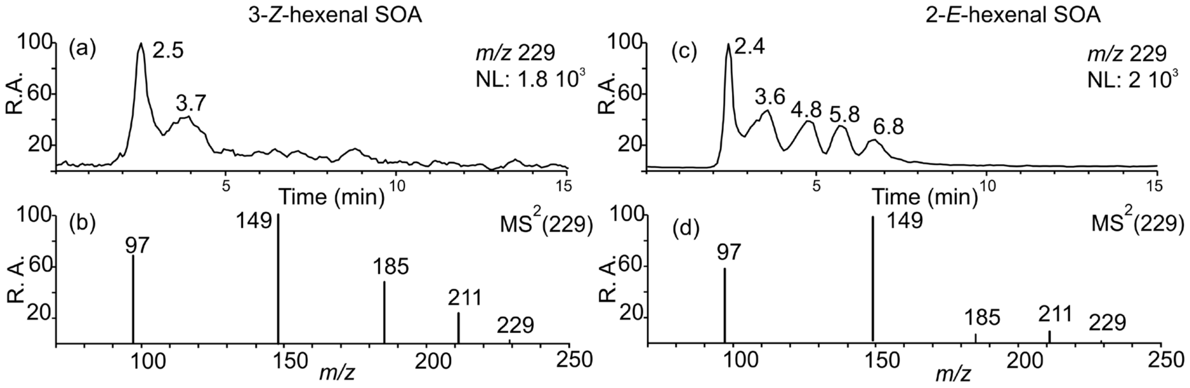


Figure S1. Selected LC/MS extracted ion chromatographic data (*m/z* 229) for the selected filters containing 3-*Z*-hexenal and 2-*E*-hexenal SOA, as well as a MS^2 product ion spectrum for the peak eluting at 2.5 min and 2.4 min, respectively.

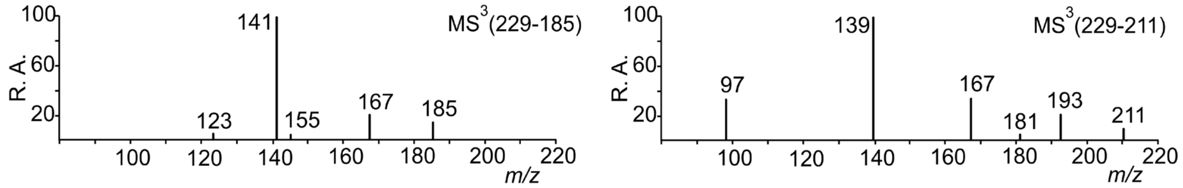


Figure S2. Additional MS^3 product ion data for the peak at 2.5 min present in ambient fine aerosol (Fig. 2a).

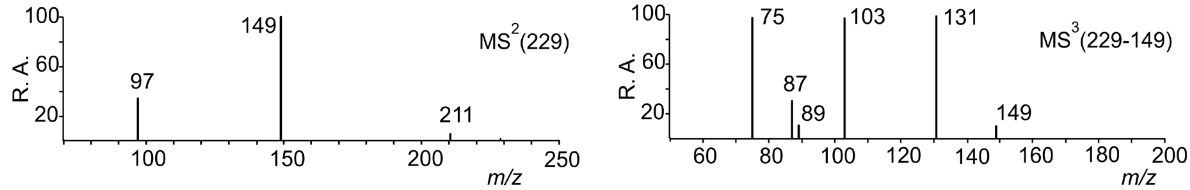


Figure S3. Selected MS data (MS^2 or MS^3 product ion spectra) for the peak eluting at 2.2 min in ambient aerosol (Fig. 2a).

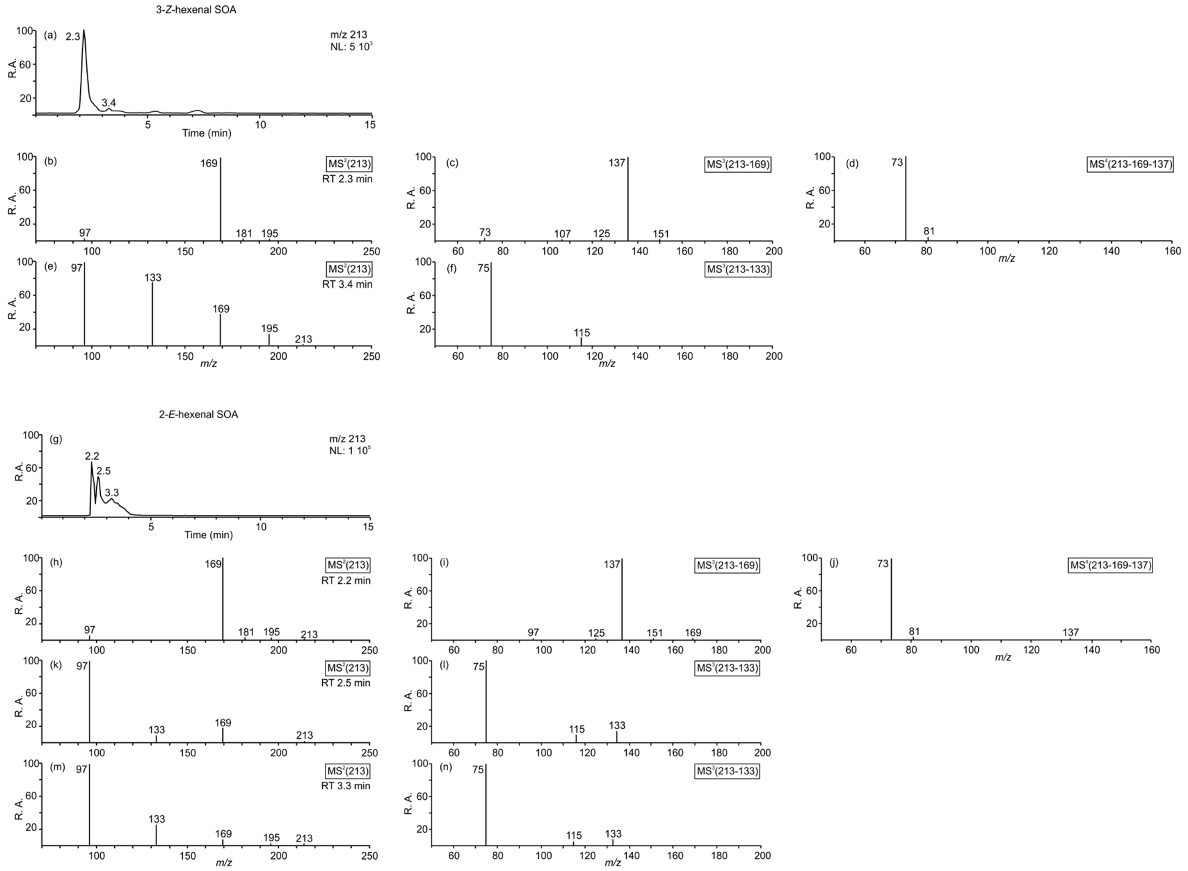


Figure S4. Selected LC/MS chromatographic data (*m/z* 213 EICs) and MS data (MS^2, MS^3 and MS^4 product ion spectra) for 3-*Z*-hexenal **(a-f)** and 2-*E*-hexenal SOA **(g-n)**. Abbreviation: NL, normalization level.

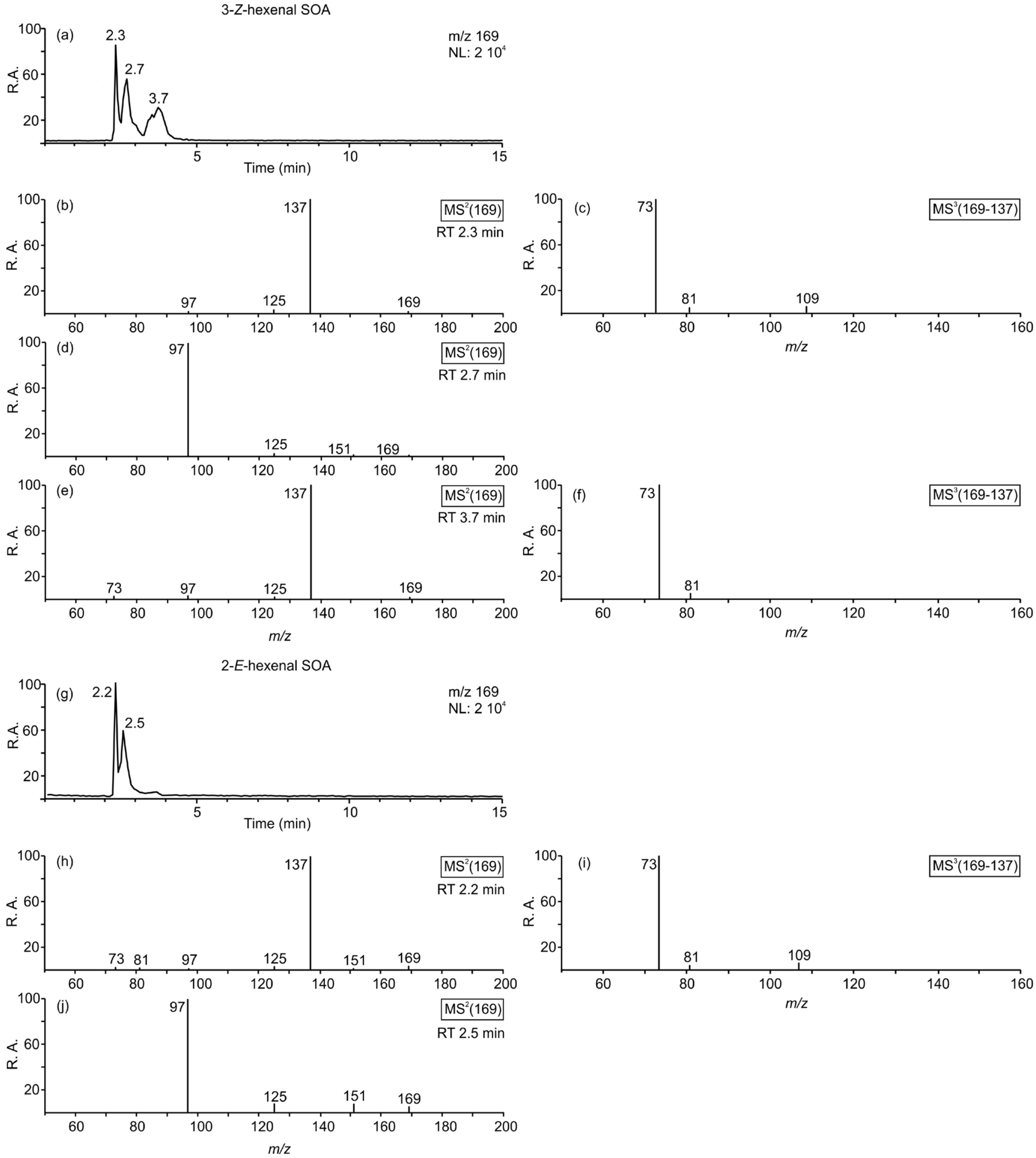


Figure S5. Selected LC/MS chromatographic data (*m/z* 169 EICs) and MS data (MS^2 and MS^3 product ion spectra) for 3-*Z*-hexenal SOA **(a-f)**, and 2-*E*-hexenal SOA **(g-j)**. The peak at RT 3.7 min in 2-*E*-hexenal SOA **(g)** is minor, but detailed analysis shows that the same *m/z* 169 compound as in 3-*Z*-hexenal SOA **(a)** is present. Abbreviation: NL, normalization level.