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Campholenic aldehyde ozonolysis: a mechanism leading to specific biogenic secondary organic aerosol constituents

A. Kahnt[1,2], **Y. Iinuma**[1], **A. Mutzel**[1], **O. Böge**[1], **M. Claeys**[2], **and H. Herrmann**[1]

[1]Leibniz-Institut für Troposphärenforschung (TROPOS), Permoserstr. 15, Leipzig, 04318, Germany
[2]Department of Pharmaceutical Sciences, University of Antwerp (Campus Drie Eiken), 2610 Antwerp, Belgium

Correspondence to: H. Herrmann (herrmann@tropos.de)

Abstract. In the present study, campholenic aldehyde ozonolysis was performed to investigate pathways leading to specific biogenic secondary organic aerosol (SOA) marker compounds. Campholenic aldehyde, a known α-pinene oxidation product, is suggested to be a key intermediate in the formation of terpenylic acid upon α-pinene ozonolysis. It was reacted with ozone in the presence and absence of an OH radical scavenger, leading to SOA formation with a yield of 0.75 and 0.8, respectively. The resulting oxidation products in the gas and particle phases were investigated employing a denuder/filter sampling combination. Gas-phase oxidation products bearing a carbonyl group, which were collected by the denuder, were derivatised by 2,4-dinitrophenylhydrazine (DNPH) followed by liquid chromatography/negative ion electrospray ionisation time-of-flight mass spectrometry analysis and were compared to the gas-phase compounds detected by online proton-transfer-reaction mass spectrometry. Particle-phase products were also analysed, directly or after DNPH derivatisation, to derive information about specific compounds leading to SOA formation. Among the detected compounds, the aldehydic precursor of terpenylic acid was identified and its presence was confirmed in ambient aerosol samples from the DNPH derivatisation, accurate mass data, and additional mass spectrometry (MS^2 and MS^3 fragmentation studies). Furthermore, the present investigation sheds light on a reaction pathway leading to the formation of terpenylic acid, involving α-pinene, α-pinene oxide, campholenic aldehyde, and terpenylic aldehyde. Additionally, the formation of diaterpenylic acid acetate could be connected to campholenic aldehyde oxidation. The present study also provides insights into the source of other highly functionalised oxidation products (e.g. m/z 201, $C_9H_{14}O_5$ and m/z 215, $C_{10}H_{16}O_5$), which have been observed in ambient aerosol samples and smog chamber-generated monoterpene SOA. The m/z 201 and 215 compounds were tentatively identified as a C_9- and C_{10}-carbonyl-dicarboxylic acid, respectively, based on reaction mechanisms of campholenic aldehyde and ozone, as well as detailed interpretation of mass spectral data, in conjunction with the formation of corresponding DNPH derivatives.

1 Introduction

Biogenic volatile organic compounds (BVOCs) are important secondary organic aerosol (SOA) precursor compounds, owing to their significant global emission and their reactivity towards atmospheric oxidants. Reactions with the OH radical, the nitrate radical and ozone result in multifunctional oxidation products that impact particle formation and contribute to aerosol growth. In the Northern Hemisphere where mixed and boreal forests dominate, monoterpenes such as α-pinene, β-pinene and Δ^3-carene are the prevailing BVOCs. In addition, other BVOCs likely serve as SOA precursors, as the observed global SOA burden cannot be explained from bottom-up approaches using laboratory-derived SOA yields from the oxidation of monoterpenes (e.g. Hallquist et al., 2009, and references therein).

Another indication for other yet unidentified and reactive BVOCs results from ozone flux measurements at boreal forest sites (Wolfe et al., 2011). Furthermore, missing sinks for OH radicals between 50 % (Sinha et al., 2010) and 58 % (Nölscher et al., 2012) have been reported for OH

Table 1. Experimental conditions and results for the performed chamber experiments for campholenic aldehyde, α-pinene, and α-pinene oxide.

Experiment	Initial HC	Initial O_3 [ppb]	CO [ppm]	Seed particles	Seed particle pH	RH [%]	T [°C]	Reaction time [min]	ΔHC [ppb]	ΔO_3 [ppb]	ΔM [µg m^{-3}]	SOA yield
25/11/2010	100 ppb campholenic aldehyde	57	105	30 mM $(NH_4)_2SO_4$/10 mM H_2SO_4	2	50	21	204	58	45	267	0.75
26/11/2010	100 ppb campholenic aldehyde	62	–	30 mM $(NH_4)_2SO_4$/10 mM H_2SO_4	2	50	21	204	68	45	342	0.8
29/09/2010	100 ppb campholenic aldehyde	62	–	–	–	49	21	210	69	40	273	0.63
01/03/2011	100 ppb α-pinene	60	–	30 mM $(NH_4)_2SO_4$/10 mM H_2SO_4	2	53	20	210	70	52	108	0.34
25/02/2009	100 ppb α-pinene oxide	60	–	30 mM $(NH_4)_2SO_4$ / 10 mM H_2SO_4	0	47	22	122	–	–	37.1	–

reactivity measurements in boreal forests. In this context, higher molecular weight aldehydes have been suggested to be an important sink for OH radicals in the boreal forest (Hellén et al., 2004). For these reasons, campholenic aldehyde, a known oxidation product of α-pinene, is an interesting candidate to be further investigated with regard to its reaction products and its SOA formation potential. The compound was first reported as an unknown $C_{10}H_{16}O$ ketone in α-pinene ozonolysis by Alvarado et al. (1998), and was later confirmed as campholenic aldehyde by Schrader et al. (1999). It has been reported to form from different types of oxidations, including α-pinene reaction with O(^{3}P) atoms with a yield of 0.06 ± 0.02 (Alvarado et al., 1998), and from α-pinene ozonolysis in the presence of NO_x with reported carbon yields in the gas and particle phases of 0.8–1.0 % (Jaoui and Kamens, 2003). Campholenic aldehyde formation was also described from the α-pinene OH reaction (Van den Bergh et al., 2000, 2004), from its NO_3-radical initiated oxidation (Berndt and Böge, 1997), as well as from Lewis acid-catalysed isomerisation reactions of α-pinene oxide in the aqueous phase (Bleier and Elrod, 2013). Furthermore, campholenic aldehyde formation was recently identified during the acid-catalysed rearrangement of α-pinene oxide, where the subsequent gas-phase ozonolysis of campholenic aldehyde could be related to a significant formation of SOA mass (Iinuma et al., 2013). The existence of campholenic aldehyde in ambient samples was reported from filter measurements (Pio et al., 2001; Anttila et al., 2005; Kallio et al., 2006); however, it is most likely also present in the gas phase owing to its high vapour pressure (Bleier and Elrod, 2013). Campholenic aldehyde has been reported as a wood odour compound (Weissbecker et al., 2004) and is also known as a natural constituent of essential oils (e.g. Gogus et al., 2006; Ali et al., 2008; Samaneh et al., 2010); hence, direct emission from plants might be possible as well.

Based on the results of a previous study (Iinuma et al., 2013), which identified campholenic aldehyde as a potentially important SOA precursor, the ozonolysis of campholenic aldehyde was further investigated in the present study. Gas- and particle-phase products were characterised in detail, thereby resorting to mass spectrometric approaches. A derivatisation technique for carbonyl group-containing compounds was applied, and the resulting derivatives were analysed by liquid chromatography coupled to high-resolution mass spectrometry (MS). Additional MS^2 and MS^3 fragmentation studies of specific compounds and comparison of the MS data to those of ambient filter samples were performed to derive the structures of campholenic aldehyde SOA components.

2 Experimental

2.1 Chamber experiments

Campholenic aldehyde was synthetically prepared according to the procedure by Castro et al. (2005) and was obtained in a purity of about 98 %, as determined by gas chromatography/mass spectrometry. Its ozonolysis was carried out in the Leipziger Aerosol Chamber (LEAK), which has a volume of 19 m^3 and a S / V ratio of 2 m^{-1}. The polytetrafluoroethylene (PTFE) aerosol chamber is equipped to control temperature and humidity. All experiments were performed at a temperature of about 21 °C and at 50 % relative humidity (RH). Ozone was generated from a stream of oxygen (5 L min^{-1}) passing an UV lamp. Initial ozone concentrations in the chamber were about 60 ppb and were monitored during the whole experiment using an ozone monitor (Monitor Labs ML 9812). Seed particles were added to facilitate the condensation of oxidation products during the experiment. The composition of the inorganic salt solutions used, which were nebulised in the chamber, is given in Table 1. The

following chemicals were used to produce the inorganic seed aerosol: $(NH_4)_2SO_4$ ($\geq 99\%$; Sigma-Aldrich) and H_2SO_4 (95–98 %; Sigma-Aldrich). Corresponding seed particle pH values for the experimental conditions (RH and T) were calculated using the extended thermodynamic E-AIM model II (Clegg et al., 1998).

The formation of secondary organic aerosol during the experiment was monitored using a differential mobility particle sizer (DMPS, 3–900 nm). A density of $1 \, \text{g cm}^{-3}$ was assumed to calculate the aerosol mass from the measured difference between the initial seed aerosol volume and formed organic aerosol volume during the course of the experiment. No wall loss correction was applied to the derived SOA yield data. The ozonolysis of campholenic aldehyde was performed in the presence and absence of 105 ppm CO as an OH radical scavenger.

The consumption of campholenic aldehyde during the ozonolysis was determined using a proton-transfer-reaction mass spectrometer (PTR-MS, IONICON Analytik, Innsbruck, Austria). For selected experiments, the PTR-MS measurements were also performed in the scan mode using an m/z range 58–215 and a dwell time of 2 s. These measurements made it possible to obtain additional information about gas-phase compounds which can be compared to detailed chemical information obtained from a denuder sampling technique with 2,4-dinitrophenylhydrazine (DNPH) derivatisation followed by a liquid chromatography/negative ion electrospray ionisation time-of-flight mass spectrometry (LC/($-$)ESI-MS) analysis. Five-channel annular denuder tubes (URG-2000-30B5, Chapel Hill, NC, USA) were used in the present study. The inner denuder surface was coated with non-polar XAD-4 resin (Sigma-Aldrich), a divinyl styrene derivative, based on the procedure described by Kahnt et al. (2011). The derivatisation reagent DNPH was also applied on the inner denuder surface to examine oxidation products bearing carbonyl group(s). The DNPH reagent ($\geq 99\%$, HPLC grade) was purchased from Sigma-Aldrich as a 50 % solution in water and was recrystallised twice in acetonitrile (HPLC grade, Sigma-Aldrich) before usage. The DNPH solution used for the denuder coating procedure consisted of 10 mM DNPH and 90 mM phosphoric acid (85 wt. % in water, Riedel-de Haën) in acetonitrile. After the experiments, the denuder tubes were directly extracted using 50 mL acetonitrile and 1 mL of the internal standard (cyclohexanon-DNPH 100 μM) was added. The flask containing the denuder extract was sealed and was left overnight at room temperature to ensure complete derivatisation. After concentration by a rotary evaporator, the derivatised extract was purified using solid-phase extraction (SPE) cartridges (Oasis HLB, 30 mg adsorbent, Waters, Milford, MA, USA). After elution from the SPE cartridge, the carbonyl-hydrazones were dissolved in 10 mL acetonitrile and stored in a freezer at $-18 \, °C$ until analysis. This sampling preparation procedure was evaluated with various carbonyl compounds in a previous study and showed acceptable reproducibility and recoveries (Kahnt et al., 2011).

The simultaneously collected filter samples were also stored at $-18 \, °C$ until further sample preparation. One half of the filters was directly extracted according to the procedure described by Iinuma et al. (2013), whereas the other half was derivatised using the DNPH reagent. For the latter derivatisation step, the cut filter pieces were immersed in a solution of 10 mM DNPH and 1.5 M phosphoric acid in acetonitrile. A simultaneous derivatisation and extraction was performed under ultrasonic agitation for 15 min. The filter extract was purified by a PTFE syringe filter (15–17 mm diameter, Phenomenex, Torrance, CA, USA) and the remaining filter pieces were flushed again using 500 μL acetonitrile and further ultrasonication. The same SPE procedure as used for the denuder extracts was applied to the derivatised filter extracts. The solution obtained from the elution of the SPE cartridge was dried and reconstituted in 250 μL acetonitrile/water (50/50 v/v) for LC/($-$)ESI-TOFMS analysis.

2.2 Ambient filter samples

Ambient filter samples were analysed to confirm the relevance of selected oxidation products detected from the campholenic aldehyde/O_3 chamber experiments. The atmospheric filter samples were collected during summer 2008 at a rural background site in Seiffen, Saxony, Germany ($50°38'50''$ N, $13°27'80''$ E, 647 m above sea level (a.s.l.)). Summer samples were chosen as a higher biogenic VOC emission was expected since a forest surrounds the village. The ambient aerosol was collected on pre-heated (105 °C, 24 h) quartz fibre filters (Munktell Filter AB, Falun, Sweden) using a Digitel-80 high volume sampler (Digitel Elektronik AG, Hegnau, Switzerland). The samples were collected using a PM_{10} inlet for a sampling duration of 24 hours (from midnight to midnight) at a flow rate of $30 \, \text{m}^3 \, \text{h}^{-1}$. The following filter samples from Seiffen were analysed using LC/($-$)ESI-TOFMS: 19, 27, 28 and 31 August 2008.

In addition, archived $PM_{2.5}$ filter samples collected from K-puszta, Hungary ($46°58'$ N, $19°35'$ E, 125 m a.s.l.) from a 2006 summer campaign were used for a further detailed mass spectrometric analysis. These ambient aerosol samples were collected during the BIOSOL (Formation mechanisms, marker compounds, and source apportionment for BIOgenic atmospheric aeroSOLs) campaign, which took place from 24 May to 29 June 2006 at K-puszta, Hungary, a rural site located on the Great Hungarian Plain, 15 km northwest from the nearest town Kecskemét, and 80 km southeast from Budapest. The surroundings of the site are dominated by mixed forest (62 % coniferous and 28 % deciduous) and grassland (10 %). The site is characterised by intensive solar radiation during summer. The composition of atmospheric particulate matter during the BIOSOL campaign was studied and it was observed that the campaign time could be divided into two periods: from the start of the campaign until

11 June 2006 when it was unusually cold with daily maximum temperatures between 12 and 23 °C, and from 12 June 2006 onward when the temperatures were considerably higher with daily maxima ranging from 24 to 36 °C (Maenhaut et al., 2008). Sections of quartz fibre filters from different days and/or nights of the warm period of the campaign were extracted three times for 30 min in an ultrasonic bath with 20 mL of methanol. The extracts were combined and concentrated in a rotary evaporator at 35 °C and 200 mbar to approximately 1 mL and filtered through a PTFE filter (0.45 µm), then evaporated to dryness under a nitrogen stream. The residue was redissolved in 1 mL of methanol and divided into five portions, which were dried under nitrogen, after which the residues were stored at −20 °C until use on different experimental days. A fraction containing 570 µg of organic carbon, as determined with a thermal–optical method (Birch and Cary, 1996), was redissolved in 1.5 mL of methanol/water (1/4, v/v) by first dissolving the fraction in 0.3 mL of methanol and then adding 1.2 mL of water.

The filter samples were treated in the same manner as described for the chamber samples. For specific MS^2 and MS^3 fragmentation studies, 100 µL of the K-puszta sample was derivatised with a 10 µL DNPH solution that contained 10 mM of the derivatisation reagent and 1.5 M acetic acid (ULC/MS grade, Biosolve, The Netherlands) in 2.5 mL acetonitrile. No further sample purification using SPE was performed to minimise material loss for the chemical analysis. For these samples the analysis was carried out using LC/(−)ESI-ITMS (ion trap mass spectrometry).

2.3 Method for the LC/(−)ESI-TOFMS analysis

The derivatised and purified denuder and filter samples were analysed using an Agilent 1100 series HPLC system (Agilent Technologies, Santa Clara, CA, USA). The chromatographic separation of the carbonyl-hydrazones was carried out using a Pursuit XRs Ultra 2.8 Diphenyl column (100 × 2.0 mm, 2.8 µm, Varian, Palo Alto, CA, USA) and was performed at 30 °C with a flow rate of 0.4 mL min^{-1}. The eluents used were (A) 1 % acetic acid in Milli-Q water, (B) acetonitrile and (C) Milli-Q water. The gradient was programmed as follows: 5 % (A), 30 % (B) and 65 % (C) were held constant for the first 4 min. After 20 min, (B) was increased to 95 % with 5 % (A). Afterwards, (B) was further increased to 100 % and was held constant for 5 min. Then the eluents were set back to their initial conditions and held for 5 min to re-equilibrate the column. The system was coupled to an UV-DAD (ultraviolet diode array detector) followed by a time-of-flight (TOF) mass analyser. This setup enabled the combination of two detection modes, using UV light – as most of the carbonyl-hydrazones absorb light in the range of 360–380 nm, and a mass spectrometer to determine their elemental composition using TOFMS.

2.4 High resolution fragmentation study using UPLC/(−)ESI-IMS-QTOFMS

For a specific mono-DNPH-derivatised compound (m/z 335), the MS^2 fragmentation was carried out using a TOF high-resolution mass spectrometer to elucidate its possible structure. To this end, the DNPH-derivatised filter sample was analysed using a Waters Acquity ultra performance liquid chromatography coupled to a Synapt HDMS electrospray ionisation ion mobility spectrometer and quadrupole time-of-flight mass spectrometer (UPLC/(−)ESI-IMS-QTOFMS). The chromatographic separation was carried out using an Acquity UPLC HSS T3 column (2.1 × 100 mm, 1.8 µm particle size, Waters) and the analysis was performed using an acetonitrile gradient programme as follows: 95 % (A, 0.1 % acetic acid in Milli-Q water) and 5 % (B, acetonitrile) were held constant for the first 2 min, followed after 8 min by 100 % (B) and held constant for 2 min. Then the eluents were set back to their initial conditions and held for 2 min to re-equilibrate the column. The eluent flow rate was 0.5 mL min^{-1} and the column temperature was kept at 40 °C. The details for the MS operating parameters can be found in Iinuma et al. (2009b).

2.5 Method for the LC/(−)ESI-ITMS analysis for selected fragmentation studies

Selected compounds, which were detected from the campholenic aldehyde ozonolysis, were further investigated in terms of fragmentation studies to propose possible structures. For this approach, an LC system consisting of a Surveyor Plus system (pump and autosampler) (Thermo Scientific, San Jose, CA, USA) with an Atlantis T3 column (2.1 × 150 nm, 3 µm particle size, Waters) was employed. The mobile phase was (A) 50 mM ammonium formate buffer pH 3 and (B) methanol. A 65 min gradient was applied as follows: (B) was kept at 3 % for 5 min, increased to 95 % in 15 min and kept for 25 min, followed by the reconditioning to 3 % in 10 min and keeping (B) at 3 % for 10 min. The samples were injected using a volume of 10 µL and the flow rate was 0.2 mL min^{-1}. A linear ion trap mass spectrometer (LXQ, Thermo Scientific) was used as the mass analyser. The mass spectrometer was operated under the following conditions: sheath gas flow (N$_2$), 50 arbitrary units; auxiliary gas flow (N$_2$), 5 arbitrary units; ion source voltage −4.5 kV; capillary temperature 350 °C; and maximum ion injection time of 200 ms. The mass spectrometer was optimised using a *cis*-pinonic acid standard solution, which was directly injected into the instrument at a concentration of 50 µg mL^{-1} together with the LC eluent mixture of ammonium formate buffer (pH 3) and methanol (40/60, v/v). For the MS^2 and MS^3 experiments a target mass isolation width of 2 m/z units and a normalised collision energy level of 35 % were applied.

Under these conditions, the ambient filter samples (K-puszta) and other chamber filters were analysed (α-pinene/O_3, α-pinene oxide/O_3/acidic seed) to compare the observed fragmentation behaviours and confirm their presence in both the laboratory-generated SOA samples and ambient samples. For the unambiguous identification of specific oxidation products, MS^2 and MS^3 fragmentation studies were also carried out with authentic standards. These compounds were terpenylic acid (m/z 171) and diaterpenylic acid acetate (m/z 231), which were prepared based on the procedure described by Claeys et al. (2009) and Iinuma et al. (2009a), respectively.

Detailed chamber experimental conditions for the α-pinene/O_3 and α-pinene oxide/O_3/acidic seed particle studies are given in Table 1.

3 Results and discussions

3.1 Aerosol formation and the effect of an OH radical scavenger

All the performed ozone reactions of campholenic aldehyde resulted in SOA yields greater than 0.6, showing the high SOA formation potential of the precursor compound. A SOA yield of about 0.8 was determined in the absence of the OH radical scavenger (CO), whereas in the presence of CO a somewhat lower SOA yield of 0.75 was observed (Fig. 1, top). It should be noted that, as no wall loss corrections were applied to the gas and particle phase data, the SOA yield data represent only lower limit values. Further studies are necessary to evaluate the wall losses for particles and vapours for this system to better estimate true SOA yield data. However, the results imply that the OH radical side reactions during the campholenic aldehyde ozonolysis contribute to SOA formation only to a small extent. It is interesting to note that the campholenic aldehyde ozonolysis resulted in significantly higher SOA yields in comparison to values published on α-pinene/O_3 that range between 0.022 and 0.543 (Hoffmann et al., 1997; Griffin et al., 1999; Yu et al., 1999; Cocker et al., 2001; Presto and Donahue, 2006; Na et al., 2007; Pathak et al., 2007; Song et al., 2007; Shilling et al., 2008; Saathoff et al., 2009; Hao et al., 2011; Hatfield and Hartz, 2011; Henry and Donahue, 2011; Amin et al., 2013), which also shows the large variation and sensitivity to experimental conditions in one system. Campholenic aldehyde itself is a first-generation α-pinene oxidation product (Fig. 2a), which is still volatile and is expected not to influence SOA growth in α-pinene ozonolysis. Nevertheless, the present study demonstrates that campholenic aldehyde is a highly reactive compound towards ozone and an effective SOA precursor. Consequently, it is likely to be an important contributor to BSOA formation in the α-pinene oxidation under certain conditions. The formation of campholenic aldehyde can result from different pathways, as described in the introduction; also, a di-
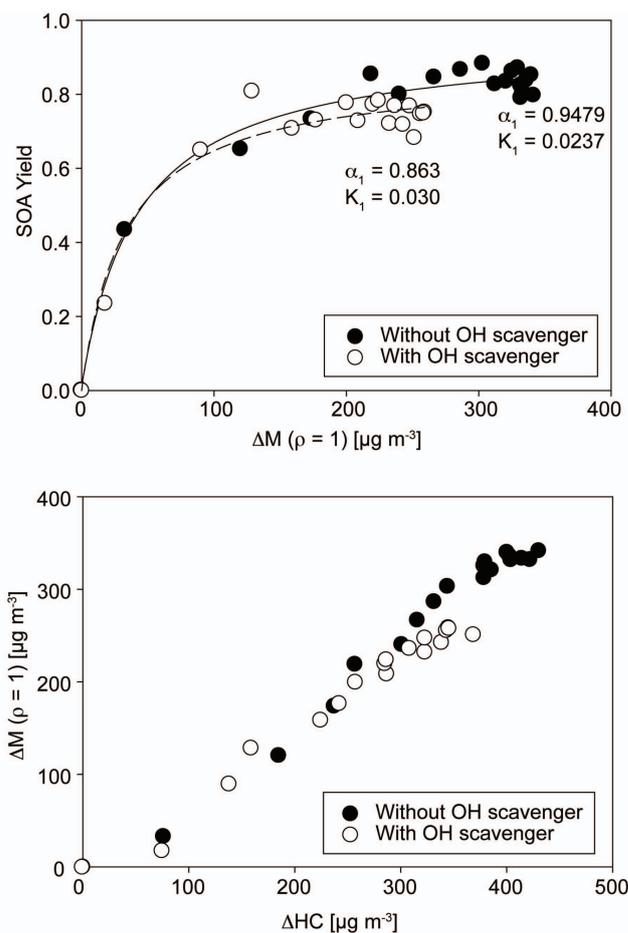

Fig. 1. SOA yield curves (top) and aerosol growth curves (bottom) for the campholenic aldehyde ozonolysis in the presence and absence of CO as an OH radical scavenger.

rect formation via not yet identified reactions, such as radical decomposition as proposed from the NO_3-initiated α-pinene oxidation (Berndt and Böge, 1997), may be involved.

In the campholenic aldehyde ozonolysis, the SOA growth curves did not change significantly with the application of CO (105 ppm) as an OH radical scavenger. A linear relationship between the organic mass formation and the reacted campholenic aldehyde (Fig. 1, bottom) is in line with the behaviour of other SOA precursors bearing one double bond (Ng et al., 2006). For such compounds it was concluded that the first oxidation process is rate-limiting for the aerosol formation as low-volatility products originating from the first-generation oxidation products contribute dominantly to SOA growth. Based on the significant amount of aerosol mass formed during the experiment, highly oxidised low-vapour pressure products were expected in the resulting SOA. In order to obtain more information about the SOA formation mechanisms in campholenic aldehyde oxidation, the resulting product distribution in both the gas and particle phases were investigated.
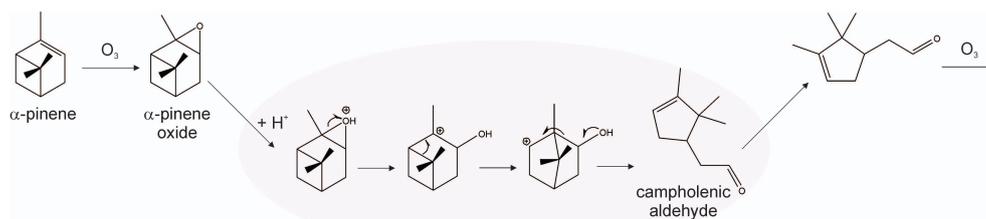
Fig. 2a. Formation of campholenic aldehyde during α-pinene ozonolysis. The shaded area represents a particle.
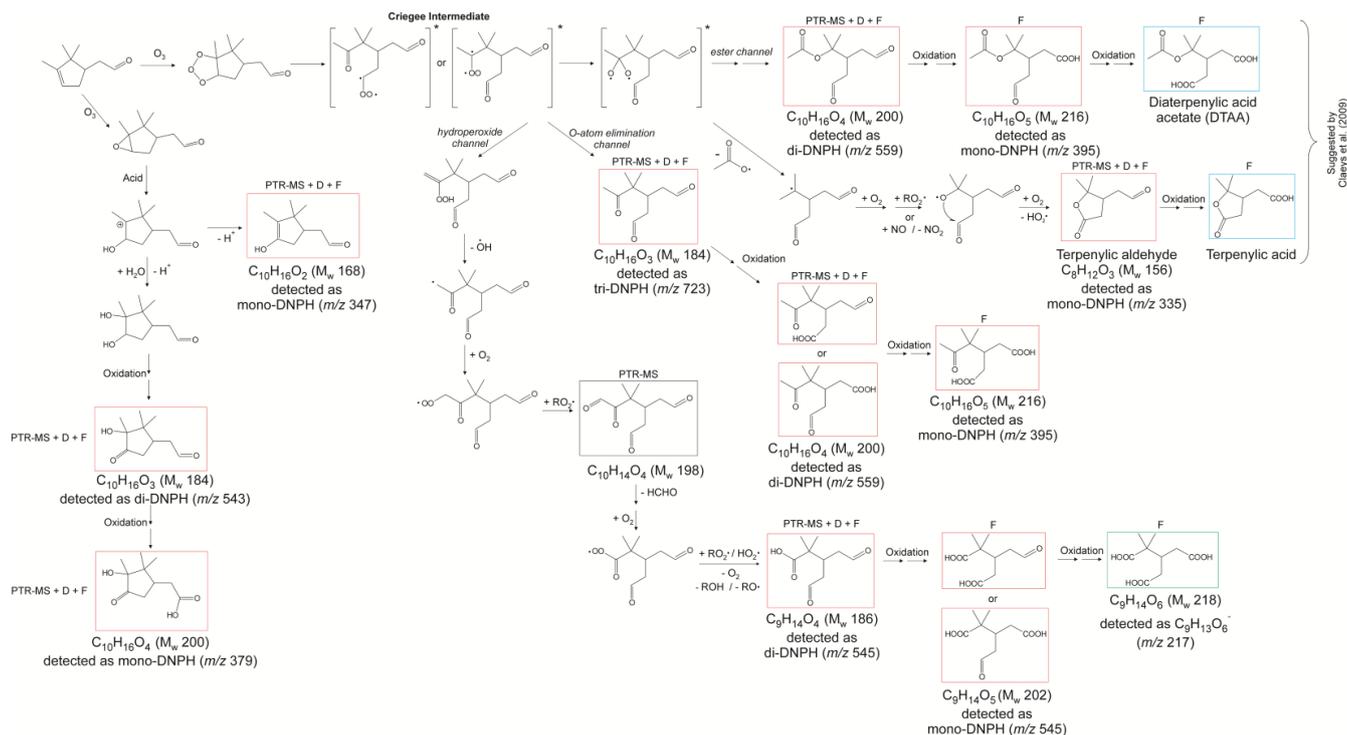
Fig. 2b. Proposed ozonolysis pathways from campholenic aldehyde leading to the detected compounds. The oxidation products identified with authentic standards are shown in blue boxes, those detected by the DNPH method are shown in red boxes, the compound shown in the black box was solely detected by PTR-MS measurements in its protonated form, and the proposed tricarboxylic acid in the green box was detected from direct filter extract analysis. (Abbreviations: D = detected from denuder analysis; F = detected from filter analysis.)

3.2   Oxidation products detected in the gas and particle phases: O₃ and OH reactions

The reaction of campholenic aldehyde with ozone and possible further reactions of formed products are depicted in Fig. 2b. The first step leads to the formation of a primary ozonide resulting from the 1,3-cycloaddition of ozone to the C=C double bond. Its decomposition leads to the excited Criegee intermediate (CI) that reacts further, owing to its high internal energy. Different reaction channels are possible after this initial step, including an unimolecular rearrangement/decomposition of the CI or a collisional stabilisation that leads to the so-called stabilised Criegee intermediate (sCI).

Table 2 summarises the detected oxidation products in the gas phase by PTR-MS. Only a few gas-phase prod-

ucts were affected by the presence or absence of the OH radical scavenger. The combination of PTR-MS measurements and the sampling of gaseous products using a denuder, which enabled an off-line analysis of oxidation products using LC/(−)ESI-TOFMS, led to a better characterisation of carbonyl-containing compounds compared to the use of PTR-MS alone. Based on the results obtained from TOFMS analysis, the number of hydrazone groups and hence the number of carbonyl groups in the molecule were identified (Table 3). Tentative structures were proposed based on the elemental composition and known oxidation pathways. As an unambiguous identification can only be achieved from the comparison to authentic reference compounds, the proposed structures are only tentative.

Table 2. Summary of detected gas-phase oxidation products from the performed campholenic aldehyde experiments using PTR-MS (differences in detected products are shown in bold).

Experiment	PTR-MS $[M+H]^+$
campholenic aldehyde / O_3	59, 61, 71, 73, 75, 77, 81, 85, 87, 97, 99, 101, 113, 115, 123, 125, 127, **137**, 139, 141, 143, **149**, **151**, 155, 157, 165, 167, 169, 171, 173, 181, 183, 185, 187, 199, 201, 213, 215
campholenic aldehyde / O_3 / CO	59, 61, **65**, 71, 73, 75, 77, 81, 85, 87, 97, 99, 101, **105**, 113, 115, 123, 125, 127, **129**, 139, 141, 143, 155, 157, 165, 167, 169, 171, 173, 181, 183, 185, 187, 199, 201, 213, 215

Table 3. Detected gas-phase compounds in the campholenic aldehyde ozonolysis using DNPH derivatisation and parallel PTR-MS measurements.

m/z hydrazone $[M-H]^-$	Measured mass	RT [min]	Elemental composition hydrazone	Error [ppm]	Elemental composition carbonyl	Number of carbonyl groups	MW [g mol^{-1}]	Detected by PTR-MS $[M+H]^+$	Suggested structure
335	335.0996	7.4	$C_{14}H_{15}N_4O_6$	−0.2	$C_8H_{12}O_3$	1	156	157	
347a	347.1351	10.5	$C_{16}H_{19}N_4O_5$	2.8	$C_{10}H_{16}O_2$	1	168	Σ169	
347b	347.1350	11.5	$C_{16}H_{19}N_4O_5$	3.2	$C_{10}H_{16}O_2$	1	168	Σ169	
379	379.1249	12.9	$C_{16}H_{19}N_4O_7$	2.7	$C_{10}H_{16}O_4$	1	200	Σ201	
517	517.1420	13.4	$C_{20}H_{21}N_8O_9$	3.3	$C_8H_{14}O_3$	2	158	−	
529	529.1801	16.0	$C_{22}H_{25}N_8O_8$	1.5	$C_{10}H_{18}O_2$	2	170	Σ171	
531	531.1588	14.4	$C_{21}H_{23}N_8O_9$	0.9	$C_9H_{16}O_3$	2	172	173	
541	541.1419	12.6	$C_{22}H_{21}N_8O_9$	3.3	$C_{10}H_{14}O_3$	2	182	183	
543	543.1585	12.7	$C_{22}H_{23}N_8O_9$	1.5	$C_{10}H_{16}O_3$	2	184	Σ185	
545	545.1386	13.5	$C_{21}H_{21}N_8O_{10}$	−0.2	$C_9H_{14}O_4$	2	186	187	
553	553.1791	16.7	$C_{24}H_{25}N_8O_8$	1.8	$C_{12}H_{18}O_2$	2	170	Σ171	
559a	559.1555	11.3	$C_{22}H_{23}N_8O_{10}$	−2.2	$C_{10}H_{16}O_4$	2	200	Σ201	
559b	559.1557	11.5	$C_{22}H_{23}N_8O_{10}$	−2.5	$C_{10}H_{16}O_4$	2	200	Σ201	
559c	559.1556	12.2	$C_{22}H_{23}N_8O_{10}$	−2.5	$C_{10}H_{16}O_4$	2	200	Σ201	
559d	559.1558	12.7	$C_{22}H_{23}N_8O_{10}$	−2.7	$C_{10}H_{16}O_4$	2	200	Σ201	
559e	559. 1562	13.4	$C_{22}H_{23}N_8O_{10}$	−3.4	$C_{10}H_{16}O_4$	2	200	Σ201	
723	723.1807	16.4	$C_{28}H_{27}N_{12}O_{12}$	9.7	$C_{10}H_{16}O_3$	3	184	Σ185	
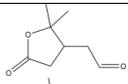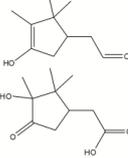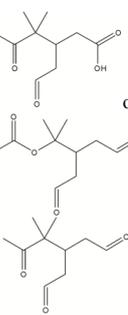
The LC/MS analysis of the DNPH-derivatised denuder extracts showed only a marginal difference in the product distribution between the campholenic aldehyde/O_3 and campholenic aldehyde/O_3/CO experiments. In addition, the product distribution from the filter analysis revealed no differences between the two types of experiments for both the direct filter extract analysis and the method using the DNPH derivatisation. This indicates that the SOA-forming compounds are mainly formed from the reaction of campholenic aldehyde with ozone while the OH radical side reaction in the ozonolysis experiments only contributes to a minor extent to product formation and associated SOA increase. This is in line with the results obtained from the SOA growth behaviour as described in the previous section.

3.3 Individual compounds

For compounds that were observed both from the campholenic aldehyde ozonolysis SOA and the ambient filter, further efforts were done to derive structural information. A summary of oxidation products in the filter samples that could be detected as DNPH derivatives is given in Table 4, together with their elemental composition and tentative structures.

For selected compounds also MS^2 and MS^3 studies were performed and an overview of the performed experiments is provided in Table 5. The individual product ion spectra are shown in the Supplement but selected oxidation products will be discussed in this section.

Table 4. Detected particle-phase compounds in the campholenic aldehyde ozonolysis using DNPH derivatisation.

m/z hydrazone [M-H]⁻	Measured mass	RT [min]	Elemental composition hydrazone	Error [ppm]	Elemental composition carbonyl	Number of carbonyl groups	MW [g mol⁻¹]	Suggested structure
335	335.0974	7.6	$C_{14}H_{15}N_4O_6$	7.0	$C_8H_{12}O_3$	1	156	
347	347.1337	11.5	$C_{16}H_{19}N_4O_5$	7.0	$C_{10}H_{16}O_2$	1	168	
379	379.1249	2.7	$C_{16}H_{19}N_4O_7$	2.6	$C_{10}H_{16}O_4$	1	200	
381a	381.1043	2.4	$C_{15}H_{17}N_4O_8$	2.4	$C_9H_{14}O_5$	1	202	
381b	381.1036	3.5	$C_{15}H_{17}N_4O_8$	4.2	$C_9H_{14}O_5$	1	202	
381c	381.1033	4.4	$C_{15}H_{17}N_4O_8$	4.8	$C_9H_{14}O_5$	1	202	or
395	395.1195	4.6	$C_{16}H_{19}N_4O_8$	3.3	$C_{10}H_{16}O_5$	1	216	
409a	409.0997	2.6	$C_{16}H_{17}N_4O_9$	1.0	$C_{10}H_{14}O_6$	1	230	
409b	409.0991	3.0	$C_{16}H_{17}N_4O_9$	2.5	$C_{10}H_{14}O_6$	1	230	
409c	409.0989	3.6	$C_{16}H_{17}N_4O_9$	2.9	$C_{10}H_{14}O_6$	1	230	
409d	409.0995	4.3	$C_{16}H_{17}N_4O_9$	1.4	$C_{10}H_{14}O_6$	1	230	
541	541.1416	12.7	$C_{22}H_{21}N_8O_9$	3.9	$C_{10}H_{14}O_3$	2	182	
543a	543.1550	12.7	$C_{22}H_{23}N_8O_9$	8.1	$C_{10}H_{16}O_3$	2	184	
543c	543.1567	14.9	$C_{22}H_{23}N_8O_9$	4.9	$C_{10}H_{16}O_3$	2	184	
543d	543.1568	15.4	$C_{22}H_{23}N_8O_9$	4.7	$C_{10}H_{16}O_3$	2	184	
543b	543.1210	14.2	$C_{21}H_{19}N_8O_{10}$	3.6	$C_9H_{12}O_4$	2	184	
545a	545.1358	9.2	$C_{21}H_{21}N_8O_{10}$	5.1	$C_9H_{14}O_4$	2	186	
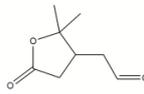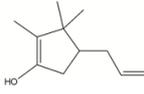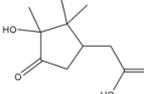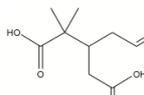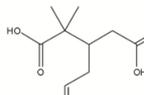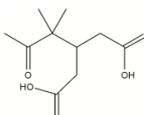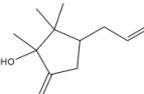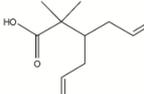
3.3.1 MW 184 compound (detected as tri-DNPH derivative m/z 723)

A tri-carbonyl compound with an elemental composition of $C_{10}H_{16}O_3$ and an m/z value of 723 for the tri-DNPH derivative and of 183 for the non-derivatised compound was de-tected from both the denuder and filter samples. This compound can be explained via the O-atom elimination channel from the CI and represents a first-generation oxidation product in the campholenic aldehyde ozonolysis (Fig. 2b). It is likely to partition into the particle phase as well, where further oxidation is expected to lead to even more functionalised

Table 4. Continued.

m/z hydrazone $[M-H]^-$	Measured mass	RT [min]	Elemental composition hydrazone	Error [ppm]	Elemental composition carbonyl	Number of carbonyl groups	MW [g mol^{-1}]	Suggested structure
545b	545.1352	9.8	$C_{21}H_{21}N_8O_{10}$	6.3	$C_9H_{14}O_4$	2	186	
545c	545.1376	11.4	$C_{21}H_{21}N_8O_{10}$	1.9	$C_9H_{14}O_4$	2	186	
545d	545.1430	12.0	$C_{21}H_{21}N_8O_{10}$	−11	$C_9H_{14}O_4$	2	186	
545e	545.1356	12.5	$C_{21}H_{21}N_8O_{10}$	5.6	$C_9H_{14}O_4$	2	186	
545f	545.1364	13.1	$C_{21}H_{21}N_8O_{10}$	4.0	$C_9H_{14}O_4$	2	186	
545g	545.1403	13.5	$C_{21}H_{21}N_8O_{10}$	−3.1	$C_9H_{14}O_4$	2	186	
557	557.1383	11.7	$C_{22}H_{21}N_8O_{10}$	0.5	$C_{10}H_{14}O_4$	2	198	
559a	559.1552	9.1	$C_{22}H_{23}N_8O_{10}$	−1.7	$C_{10}H_{16}O_4$	2	200	
559b	559.1526	11.3	$C_{22}H_{23}N_8O_{10}$	3.1	$C_{10}H_{16}O_4$	2	200	
559c	559.1537	11.5	$C_{22}H_{23}N_8O_{10}$	1.0	$C_{10}H_{16}O_4$	2	200	
559d	559.1557	12.0	$C_{22}H_{23}N_8O_{10}$	−2.5	$C_{10}H_{16}O_4$	2	200	
559e	559.1541	12.3	$C_{22}H_{23}N_8O_{10}$	0.3	$C_{10}H_{16}O_4$	2	200	
559f	559.1542	12.7	$C_{22}H_{23}N_8O_{10}$	0.1	$C_{10}H_{16}O_4$	2	200	
559g	559.1534	13.4	$C_{22}H_{23}N_8O_{10}$	1.5	$C_{10}H_{16}O_4$	2	200	
573a	573.1311	11.2	$C_{22}H_{21}N_8O_{11}$	4.3	$C_{10}H_{14}O_5$	2	214	
573b	573.1305	12.4	$C_{22}H_{21}N_8O_{11}$	5.2	$C_{10}H_{14}O_5$	2	214	
589	589.1293	12.0	$C_{22}H_{21}N_8O_{12}$	−0.3	$C_{10}H_{14}O_6$	2	230	
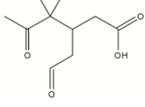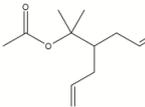
products. Such functionalised species were indeed detected in the filter samples at m/z 171, 187, 199, 201, 215, 229, and 231. Considering these highly functionalised species, the proposed tri-carbonyl compound ($C_{10}H_{16}O_3$, m/z 183) might constitute an intermediate during the formation of the latter functionalised species in later oxidation steps.

3.3.2 Terpenylic acid (MW 172) and diaterpenylic acid acetate (MW 232)

As shown in Fig. 2b, the formation of terpenylic acid and diaterpenylic acid acetate (DTAA) has been suggested to proceed from the further reaction of campholenic aldehyde, which can be formed during the α-pinene ozonolysis from α-pinene oxide (Claeys et al., 2009; Iinuma et al., 2013). The comparison of filter samples from campholenic aldehyde/O_3, α-pinene oxide/O_3/acidic seed particles, α-pinene/O_3 chamber experiments and ambient aerosol samples confirmed the proposed pathway as both terpenylic acid (m/z 171) and DTAA (m/z 231) could be unambiguously identified in all of the investigated filter samples (Figs. S2 and S24). This confirmation was based on matching retention times (RTs) and the same mass spectral fragmentation behaviour as those of authentic standard compounds. As the identification of terpenylic acid from campholenic aldehyde ozonolysis has recently been discussed by Iinuma et al. (2013), only the MS^2 and MS^3 data from the compound that was unambiguously identified as DTAA are shown in Fig. 3. The additional

m/z 231 compound eluting at 22.4 min is not identified at the present stage, but its fragmentation is shown in the Supplement related to this article (Fig. S25; see URL at end). Based on the results obtained in the present study, valuable information about chemical formation pathways of important BSOA constituents could be obtained.

3.3.3 MW 156 compound (detected as mono-DNPH derivative m/z 335)

Both the denuder and filter samples showed the presence of a mono-DNPH derivative at m/z 335. This oxidation product was also observed in α-pinene ozonolysis samples and in ambient filter samples collected in Seiffen, Germany (Fig. 4). Due to its atmospheric relevance further efforts were made to characterise the m/z 335 compound. MS^2 experiments with a high-resolution mass spectrometer enabled the determination of the elemental composition of certain product ions (Fig. 5). The product ions at m/z 179, 163, 152 and 120 are commonly observed DNPH fragments and have been described in the literature (Brombacher et al., 2001; Kölliker et al., 2001). As can be seen in Fig. 5, the MS^2 product ion spectrum is dominated by DNPH-related product ions though other specific ions could also be observed. Among those, the m/z 171 was the most abundant product ion and, therefore, it was further investigated by additional MS^3 experiments using ion trap mass spectrometry (ITMS). For these MS^n studies the filter samples were freshly

Table 5. List of products with matching RT observed from campholenic aldehyde/O_3, α-pinene oxide/O_3/acidic seed, α-pinene/O_3 and a K-puszta filter sample, including their corresponding DNPH derivatives (when appropriate). The table summarises all the mass spectral data recorded in the present study.

m/z [M-H]$^-$	Elemental composition	RT (min)	Product ion spectra	Corresponding DNPH derivative m/z [M-H]$^-$	RT (min)	Product ion spectra
–	$C_8H_{12}O_3$			335 (mono-DNPH)	27.3	MS^2 335; MS^3 335→171
171	terpenylic acid	19.1	MS^2 171 MS^3 171→127	–		
187	$C_8H_{12}O_5$	16.9	MS^2 187 MS^3 187 → 125			
		17.7	MS^2 187 MS^3 187 → 125			
		19.5	MS^2 187 MS^3 187 → 143			
199	$C_{10}H_{16}O_4$	20.8	MS^2 199; MS^3 199→181	379 (mono-DNPH)	27.1	MS^2 379
		22[a]	MS^2 199; MS^3 199→181	559 (di-DNPH)	28.4	MS^2 559
201	$C_9H_{14}O_5$	20.8	MS^2 201; MS^3 201 → 157	381 (mono-DNPH)	27.4	MS^2 381
215	$C_{10}H_{16}O_5$	21.1	MS^2 215; MS^3 215 → 171	395 (mono-DNPH)	28.2	MS^2 395
229	$C_{10}H_{14}O_6$	20.0	MS^2 229; MS^3 229 → 185	409 (mono-DNPH)	25.4[b] 25.8[b]	MS^2 409
				589 (di-DNPH)	24.0[b]	MS^2 589
231	DTAA[c]	22	MS^2 231; MS^3 231→171	–		
	$C_{10}H_{16}O_6$	22.4	MS^2 231; MS^3 231→199			

[a] only detected in campholenic aldehyde/O_3 and the ambient SOA sample;
[b] in campholenic aldehyde/O_3 and α-pinene oxide/O_3/acidic seed;
[c] DTAA = diaterpenylic acid acetate.
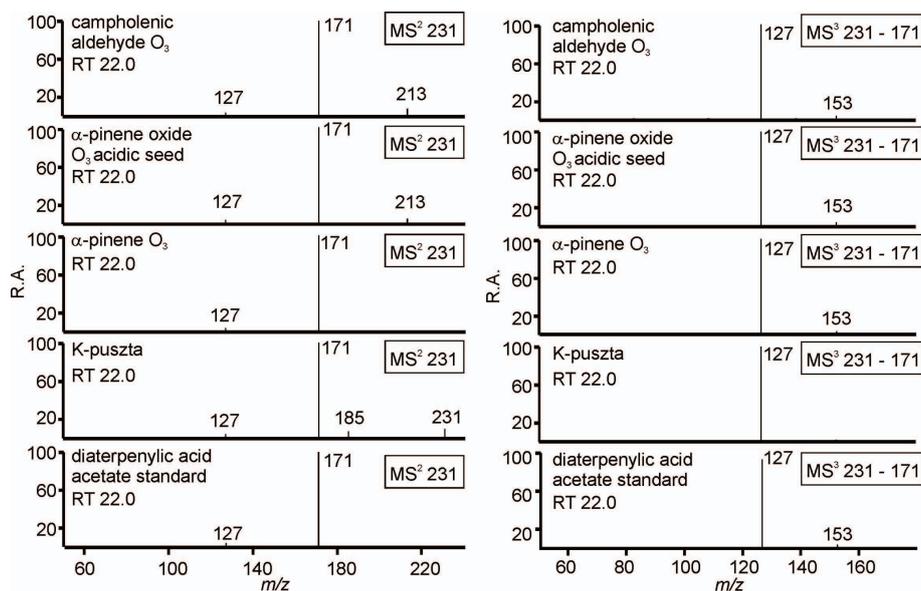
Fig. 3. MS^2 and MS^3 product ion spectra for the m/z 231 compound (RT 22 min) unambiguously identified as DTAA.
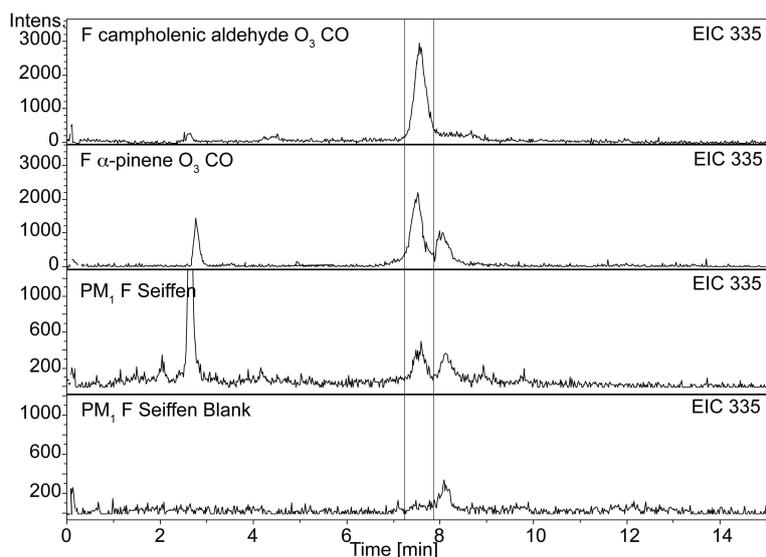
Fig. 4. Extracted ion chromatograms (EICs) of a mono-DNPH-derivatised compound (m/z 335) detected in campholenic aldehyde ozonolysis, α-pinene ozonolysis and an ambient filter sample (Seiffen, Germany).
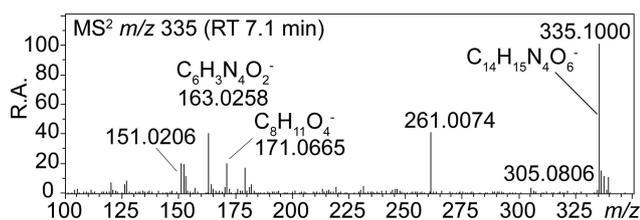

Fig. 5. High-resolution MS^2 data for the m/z 335 compound.

derivatised with DNPH and acetic acid, and no further sample purification was performed to ensure that sufficient material mass was available for the MS^3 experiments. It is noted that in the LC/($-$)ESI-ITMS analysis, with its different analytical conditions, more m/z 335 isobaric isomer peaks were detected in comparison to the UPLC/($-$)ESI-IMS-TOFMS analysis (Fig. S1). The peak with the RT 27.2 min was detected from all the investigated filter samples, including the chamber aerosol from campholenic aldehyde, α-pinene/O$_3$, α-pinene oxide/O$_3$/acidic seed and an ambient filter sample (K-puszta). Almost identical MS^2 and MS^3 patterns were observed for this peak (Fig. 6), demonstrating that the same m/z 335 compound is present in all of the filter samples and also has atmospheric relevance.

In comparison to the obtained fragmentation pattern from the high resolution MS^2 experiment using the Synapt instrument, slightly different product ions were observed from the ITMS analysis. This can be explained by different operational parameters between the two instruments used for the fragmentation studies.

A diagnostic product ion was m/z 171 for which the high resolution data suggested an elemental composition of C$_8$H$_{11}$O$_4$. This specific product ion was observed only from one of the various m/z 335 isomers in the ITMS analysis with matching retention time and confirmed the presence of the same compound from all of the investigated filter samples. The further fragmentation (m/z 335 $\rightarrow$ m/z 171) showed a strong product ion at m/z 127, pointing to a further CO$_2$ loss ($-$44 amu). Other product ions (m/z 153, 109, and 83) showed low abundances but could also be explained. All of the observed product ions showed a pattern that is similar to that reported for terpenylic acid (C$_8$H$_{12}$O$_4$, MW 172). As both the elemental composition of the m/z 171 product ion from the high resolution MS^2 data and the fragmentation pattern from MS^3 experiments (m/z 335 $\rightarrow$ m/z 171) matched with reported fragmentation behaviour of terpenylic acid (Yasmeen et al., 2010, 2011), the m/z 171 was attributed to deprotonated terpenylic acid. The proposed fragmentation of the m/z 335 compound is shown in Fig. 7. The formation of deprotonated terpenylic acid represents a quite unusual behaviour and might be explained by an intramolecular transfer of oxygen from the nitro group. The migration of an oxygen atom from the *ortho* nitro group to the –CH=N– substructure, followed by rearrangements, has been known for long from hydrazones and was described for derivatised aromatic and aliphatic aldehydes and ketones (Djerassi and Sample, 1965; Goldsmith and Djerassi, 1966; Kleipool and Heins, 1964; Seibl, 1970; Seibl and Völlmin, 1968). Based on the observed fragmentation in the present study, the m/z 335 was assigned as the DNPH derivative of terpenylic aldehyde.

The identification of terpenylic aldehyde is an important finding which enables us to explain a possible pathway leading to terpenylic acid in the atmosphere. Terpenylic acid, which is an abundant BSOA tracer compound,
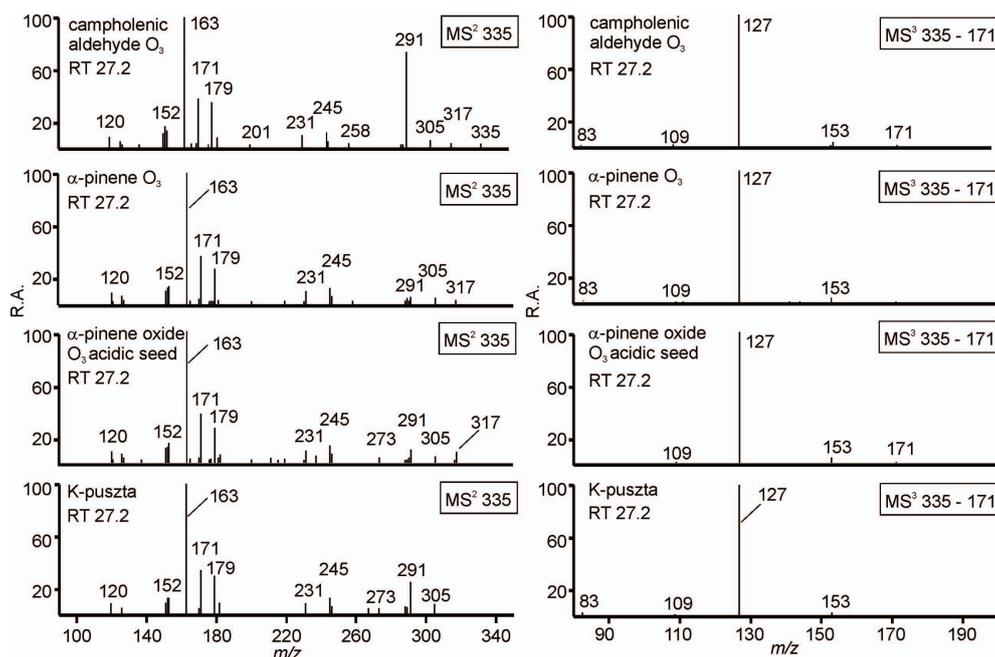
Fig. 6. MS^2 and MS^3 data for the m/z 335 compound from different SOA filter samples and an ambient sample.

is an important early-generation product in α-pinene SOA and represents a major monoterpene tracer in atmospheric aerosol (Claeys et al., 2009). Reported concentrations of terpenylic acid are comparable to commonly reported monoterpene oxidation products such as *cis*-pinic acid and *cis*-pinonic acid, ranging up to $20\,\mathrm{ng\,m^{-3}}$ in PM$_{10}$ samples (Iinuma and Herrmann, 2013), and significant concentrations also have been reported in PM$_{2.5}$ (Gómez-González et al., 2012; Kristensen et al., 2013) and PM$_1$ filter samples (Kristensen and Glasius, 2011). In the present study, a precursor of terpenylic acid could be characterised on the basis of mass spectrometric data, which previously had only been proposed in the literature (Claeys et al., 2009). As the aldehydic precursor of terpenylic acid was observed from filter samples of campholenic aldehyde/O$_3$, α-pinene/O$_3$, α-pinene oxide/O$_3$/acidic seed, and ambient filter samples (Fig. S1), a reaction pathway suggested in the literature (Claeys et al., 2009; Iinuma et al., 2013), which explains the formation of terpenylic acid from α-pinene ozonolysis, could be supported. According to this mechanism, the reaction between α-pinene and ozone leads to the formation of α-pinene oxide, which can rearrange on acidic seed particles, leading to campholenic aldehyde. As campholenic aldehyde contains a double bond it can react further with ozone to form terpenylic aldehyde, which can be further oxidised in the particle phase to terpenylic acid. This pathway was recently corroborated by laboratory experiments (Iinuma et al., 2013) and additional evidence is provided within the present study.

Terpenylic aldehyde can be regarded as a semi-volatile compound and connects gas- and particle-phase processes to explain certain SOA constituents such as terpenylic acid

and related compounds (e.g. DTAA). The applied sampling device in this study was optimised for the collection of carbonyl compounds from the gas phase in chamber studies; it is unlikely that these particulate constituents mainly result from the adsorption of gaseous species on the PTFE filter used. However, as no authentic standard was available for terpenylic aldehyde, its DNPH derivatisation efficiency and possible losses during the sample preparation procedure could not be considered. Based on these uncertainties, it was not quantified from the atmospheric aerosol samples in the present study. Nevertheless, further studies are warranted to shed light on the formation of terpenylic aldehyde in the gas phase, and its subsequent phase transition and the reactions leading to terpenylic acid.

3.3.4 MW 202 and 216 compounds

The compounds at m/z 201 (MW 202, C$_9$H$_{14}$O$_5$) and 215 (MW 216, C$_{10}$H$_{16}$O$_5$) both appeared as a single peak from the campholenic aldehyde SOA sample (Fig. S15 and S17, respectively). Based on possible reaction pathways, their chemical structures were proposed, and taking into account the detailed interpretation of the MS data as well as the detection of corresponding DNPH derivatives, their structures were tentatively identified. These compounds (MW 202 and MW 216) have been reported in the literature from α-pinene ozonolysis SOA (Winterhalter et al., 2003; Iinuma et al., 2005; Venkatachari and Hopke, 2008; Camredon et al., 2010; Putman et al., 2012) but only little is known about their structure. Peroxidic substructures have been proposed for these compounds in previous studies; the m/z 201 compound was
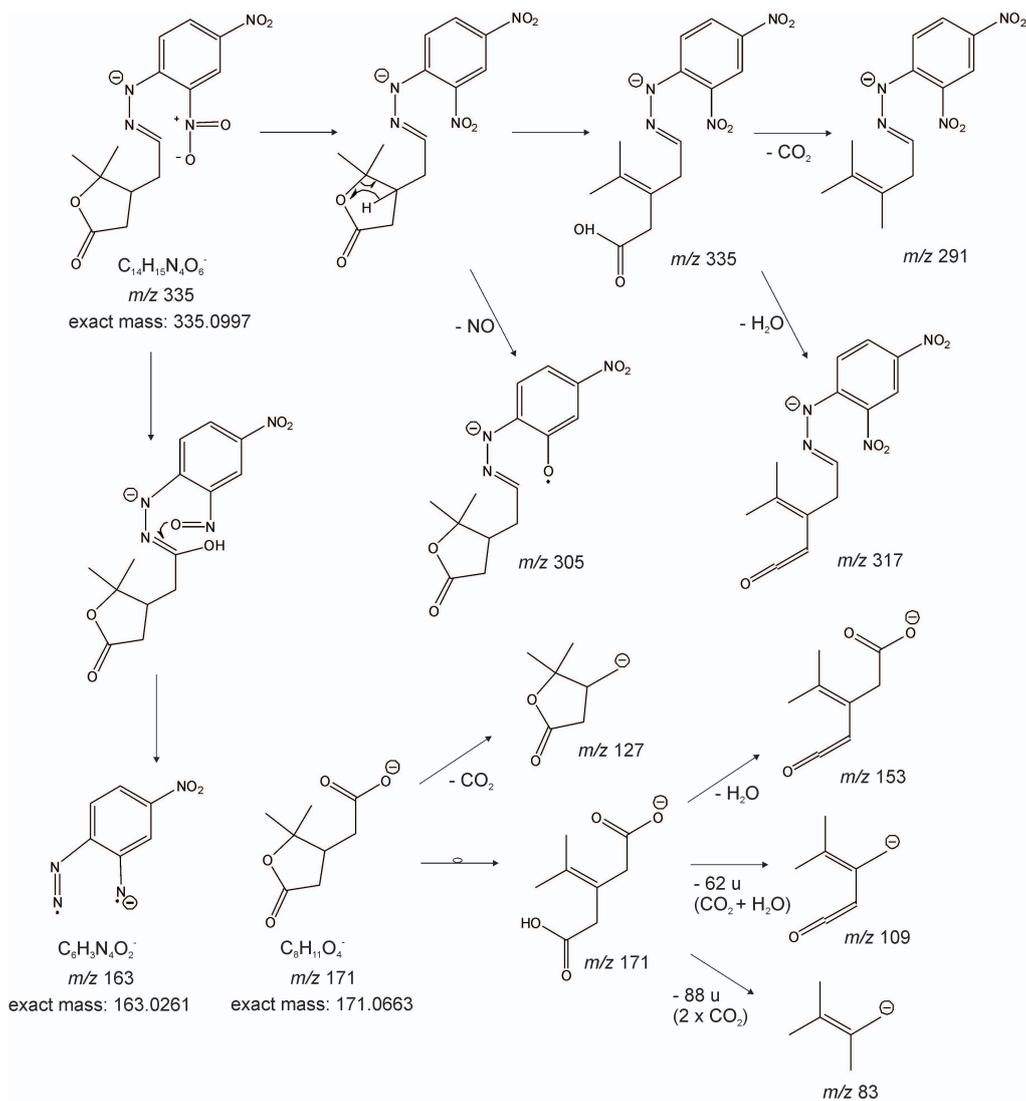
Fig. 7. Proposed fragmentation mechanism for the m/z 335 compound showing MS^2 and MS^3 (m/z 335 → m/z 171) product ions.
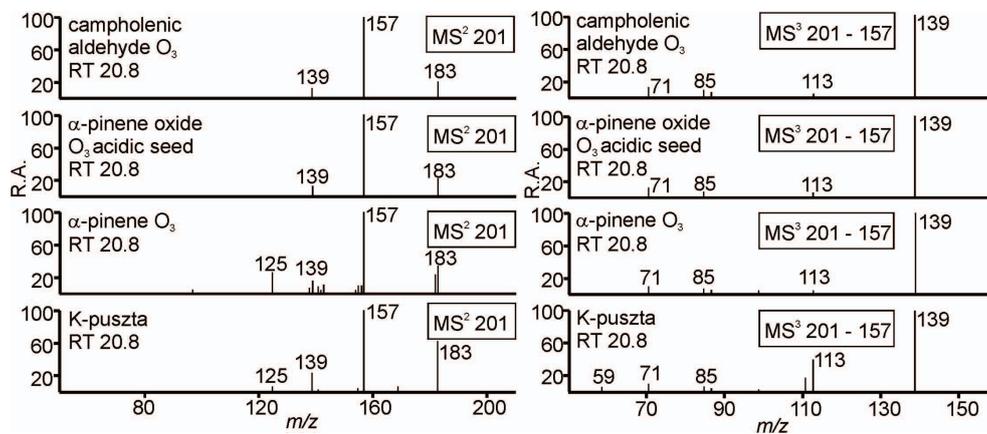

Fig. 8. MS^2 and MS^3 product ion spectra for the m/z 201 compound.
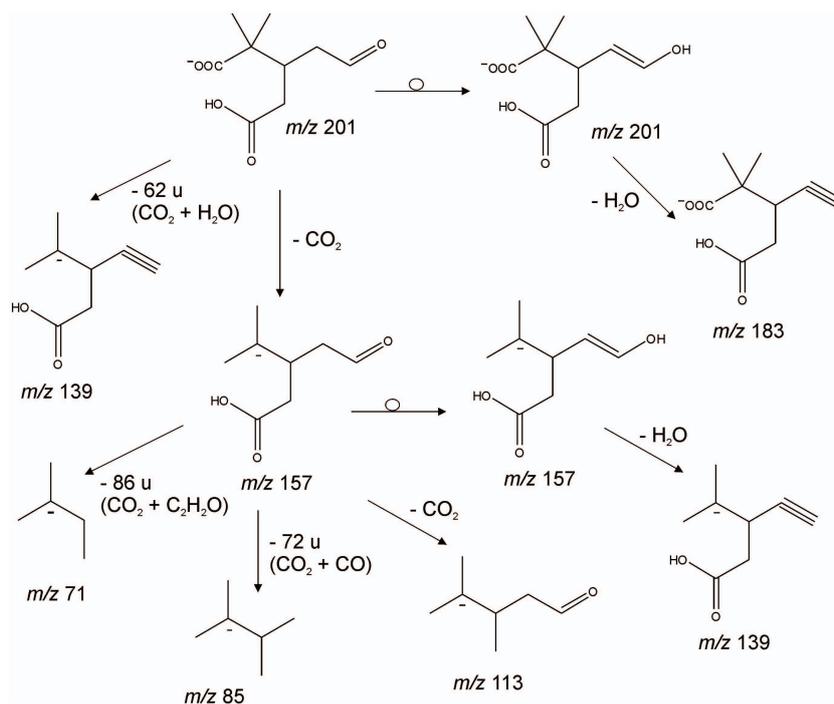
**Fig. 9.** Proposed structure of the m/z 201 compound and its fragmentation mechanism.
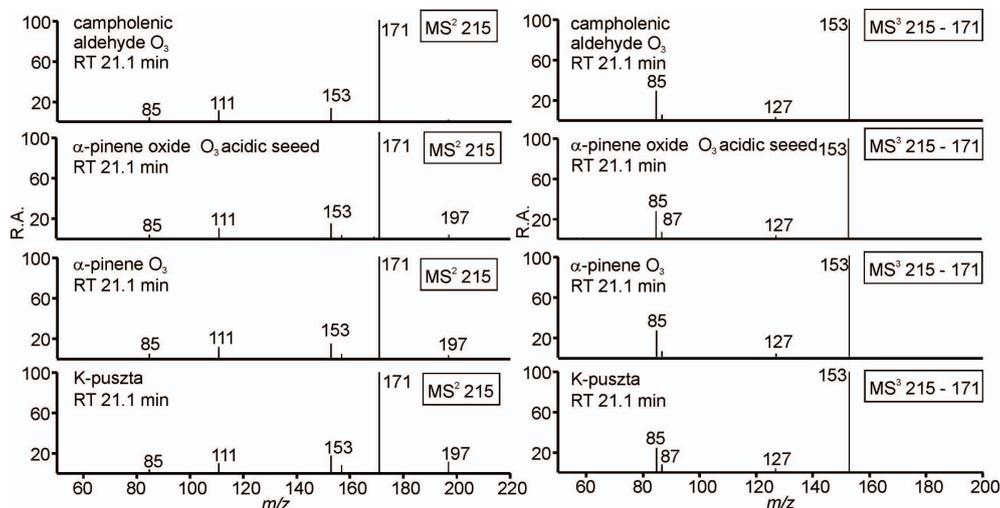
Fig. 10. MS^2 and MS^3 product ion spectra for the m/z 215 compound.

assigned to peroxo-pinic acid by Winterhalter et al. (2003), whereas a tricarbonyl group-containing hydroperoxide was suggested by Camredon et al. (2010) for the m/z 215 compound.

In this study, several isomers were detected in the α-pinene/O$_3$ SOA sample for the m/z 201 compound but only one peak was observed from the campholenic aldehyde ozonolysis (Fig. S15). Based on its fragmentation mechanism, a peroxidic substructure could not be confirmed as the main product ions resulted from the loss of water (-18 amu),

CO$_2$ (-44 amu) and the combination of both (-62 amu), as shown in the MS^2 data (Fig. 8, left), whereas the MS^3 (m/z 201 $\rightarrow$ m/z 157) spectrum was dominated by the loss of water (Fig. 8, right). These product ions can be explained with a mono-aldehydic dicarboxylic acid structure, as shown in Fig. 9. The corresponding mono-DNPH derivative of the MW 202 compound (m/z 381) together with its resulting MS data are given in Fig. S16.

For the m/z 215 compound, several isomers were also detected from the α-pinene ozonolysis and the ambient SOA
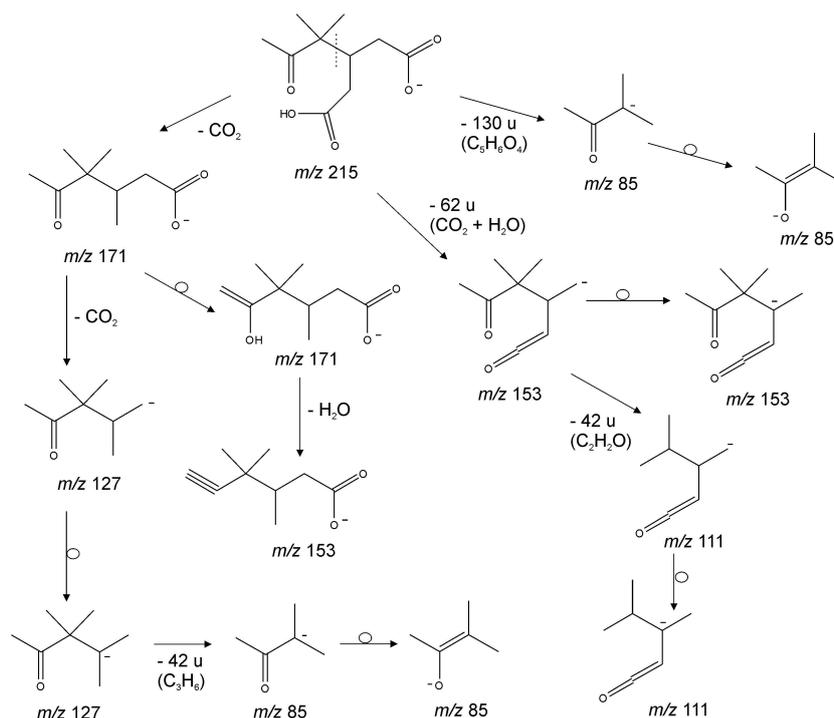
Fig. 11. Proposed structure of the m/z 215 compound and its fragmentation mechanism.

sample but the compound eluting at 21.1 min could be clearly associated with a campholenic aldehyde oxidation product (Fig. S17). Based on the MS^2 and MS^3 product ion spectra (Fig. 10), a mono-carbonyl group-containing dicarboxylic acid and its fragmentation mechanism could be proposed (Fig. 11). Similarly, for the MW 216 compound a corresponding mono-DNPH derivative (m/z 395) was detected; its fragmentation behaviour is given in Fig. S18.

The current study enabled the identification of campholenic aldehyde as a possible precursor compound for specific biogenic aerosol constituents, which are commonly observed in ambient aerosol. Other, yet unknown formation routes or pathways that could be favoured under chamber conditions can explain the observed differences in abundances for some of the oxidation products detected in the atmospheric and the chamber SOA samples.

4 Conclusions and atmospheric implications

The present study demonstrates that the ozonolysis of campholenic aldehyde leads to highly functionalised oxidation products, which are responsible for its high SOA formation potential. These highly functionalised compounds explain the enhanced degree of functionality of organic aerosol constituents and the oxidation state of atmospheric aerosol, which usually cannot be reached under normal aerosol chamber experimental conditions.

Campholenic aldehyde was shown to be a possible precursor compound for important aerosol constituents commonly observed in ambient aerosol samples. These oxidation products include terpenylic acid and DTAA, and a suggested pathway reported in the literature could be confirmed. Furthermore, the direct precursor of terpenylic acid, i.e. terpenylic aldehyde ($C_8H_{12}O_3$), could be identified and was characterised by detailed interpretation of its mass spectral data. Among other highly oxidised particle-phase products, information about the structures of the MW 202 ($C_9H_{14}O_5$) and MW 216 ($C_{10}H_{16}O_5$) compounds was obtained from detailed MS^2 and MS^3 experiments. As these compounds were demonstrated to be of atmospheric relevance, their structures were characterised as carbonyl-dicarboxylic acids based on their mass spectral fragmentation patterns and those of corresponding DNPH derivatives. Their formation from campholenic aldehyde oxidation highlights the importance of campholenic aldehyde as an intermediate and could be used to explain α-pinene SOA products, whose structures do not retain an α-pinene or cyclobutane skeleton.

Supplementary material related to this article is available online at http://www.atmos-chem-phys.net/14/719/2014/acp-14-719-2014-supplement.pdf.

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