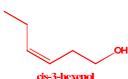
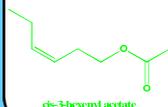


Introduction

Green leaf volatiles (GLVs) are an important group of chemicals released by vegetation which have emission fluxes that can be significantly increased when plants are damaged or stressed. A series of simulation chamber experiments has been conducted at the European Photoreactor (EUPHORE) in Valencia, Spain, to investigate secondary organic aerosol (SOA) formation from the atmospheric oxidation of the major GLVs *cis*-3-hexenylacetate and *cis*-3-hexen-1-ol. The results are used to obtain mechanistic details on SOA forming reactions and to assess the potential importance of GLVs as a global source of SOA.



Experimental Conditions and Results

The EUPHORE chamber is a hemisphere (200,000 L) made of FEP foil surrounded by a retractable steel housing. Ozonolysis of the GLVs was performed in the absence of radical scavenger and seed aerosol at a relative humidity ca. 6%. The decay of the hydrocarbons was monitored by FTIR spectroscopy and gas chromatography and the formation and evolution of SOA was measured using a scanning mobility particle sizer. Samples of SOA were collected onto quartz filter papers when the particle concentration in the chamber had reached a maximum, approximately 4 h after the start of the reaction. The filters were taken at 81.2 L min⁻¹ (at 25C) and stored in a freezer at -4C before analysis.



Fig 1. EUPHORE Atmospheric Simulation Chamber

Table 1. Details of the simulation chamber experiments.

Experiment	[O ₃] (ppbv)	[HONO] ₀ (ppbv)	[HC] ₀ (ppbv)	Δ[HC] ^a (ppbv)	Aerosol Mass ^b (μg m ⁻³)	Aerosol Yield ^c (%)
<i>cis</i> -3-hexenylacetate ozonolysis	1460		1602	1335	800	8.5
<i>cis</i> -3-hexen-1-ol ozonolysis	1600		1580	1404	854	9.6
<i>cis</i> -3-hexenylacetate photooxidation		105	498	489	9.7	0.9
<i>cis</i> -3-hexen-1-ol photooxidation		103	449	434	43.2	3.1
isoprene photooxidation		100	511	511	18.5	1.2

^a Amount of parent hydrocarbon (HC) reacted, corrected for dilution. ^b Determined at the time of measured maximum particle volume concentration, corrected for wall loss, assuming a density of 1.0 g cm⁻³. ^c Calculated from aerosol mass/Δ[HC].

Filter samples were extracted into high purity water, filtered and reduced to 1 ml using a vacuum solvent evaporator. Liquid chromatography-ion trap mass spectrometry was carried out using HCT Plus ion trap mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany) equipped with an Eclipse ODS-C18 column with 5 μm particle size (Agilent, 4.6 mm×150 mm). Experiments to determine the yield of SOA produced from the hydroxyl radical initiated oxidation of *cis*-3-hexen-1-ol, *cis*-3-hexenyl acetate and isoprene were performed using nitrous acid (HONO, 100 ppbv) as the OH precursor and a VOC mixing ratio of 500 ppbv.

Oligomer Formation

Oligomers identified by LC-ESI-MS/MS

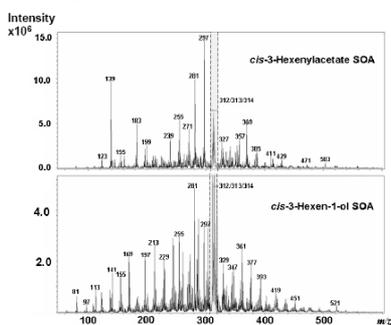


Fig. 2. Average mass spectrum (in positive ionisation mode) of the water extract of secondary organic aerosol formed during the ozonolysis of *cis*-3-hexenylacetate and *cis*-3-hexen-1-ol. All species are displayed as their [M+Li]⁺ adducts (e.g. the peak at 113 Da is due to a compound with a molecular mass of 106). The features at 312–314 Da in both spectra were also present in blank filter samples and are probably due to low-level contaminants in the chamber.

Table 2. Oligomers identified in SOA produced from the atmospheric oxidation of *cis*-3-hexen-1-ol.

Name	Structure	Name in paper	MW (g mol ⁻¹)	[M+Li] ⁺
2-ethyl-1,3-dioxan-4-ol		HPA + propanal	132	139
3-(2-hydroxy ethoxy) propanoic acid			134	141
3-(2-hydroxyethyl)-1,3-dioxan-4-ol		HPA dimer	148	155
3-(3-hydroxy propanoyloxy) propanoic acid		HPAacid dimer	162	169
3-(3-(2-hydroxyethyl) propoxyloxy) propanoic acid			206	213
3-(3-(2-hydroxy ethoxy)-3-oxopropanoyloxy) propanoic acid			220	227
5-(3-hydroxy-5-(2-hydroxy ethoxy) propoxyloxy) propanoic acid			222	229
1-(2-(4-hydroxy-1,3-dioxan-2-yl) ethoxy) propanoic acid		HPA trimer	222	229
1,3-bis(2-(3-(2-hydroxy ethoxy) propoxyloxy) propanoic acid			224	231
3-(3-(2-hydroxy propanoyloxy) propoxyloxy) propanoic acid		HPAacid trimer	234	241
3-(3-(2-hydroxy ethoxy) propoxyloxy) propanoic acid		HPA trimer	236	243
3-(3-(3-(2-hydroxy propanoyloxy) propoxyloxy) propoxyloxy) propanoic acid		HPAacid tetramer	306	313

^a Tentative identification.

The mass spectrum of *cis*-3-hexenylacetate SOA contained small molecules (e.g., 3-acetoxypropanal, [M+Li]⁺ = 123 Da) and oligomers with ester and ether linkages, produced from chemical reactions in the particle-phase. However, oligomer growth beyond dimers and trimers appeared to be blocked by the low reactivity of the acetate group.

The *cis*-3-hexen-1-ol SOA produced a very strong oligomeric pattern. Fragmentation of SOA products yielded ions corresponding to 3-hydroxypropanal (3-HPA) and 3-hydroxypropanoic acid (3-HPAacid). 3-HPA is a major gas phase product from *cis*-3-hexen-1-ol ozonolysis and in the presence of water, is known to undergo reversible hydration and dimerization, as shown in Fig. 4. Ions matching the dimer, trimer and tetramer masses ([M+Li]⁺=155, 229, 303 Da) were found in the spectrum. Hydrated 3-HPA can also react with propanal, to form a cyclic ether, [M+Li]⁺=139 Da. 3-HPAacid forms linear polyesters with peaks due to *n*=2, 3, 4 and 5 at [M+Li]⁺=169, 241, 313, 385 Da, respectively.

The ability to form oligomers is therefore strongly linked to the reactivity of the oxidation products in the particle phase.

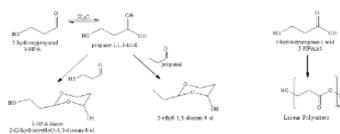


Fig. 4. Formation of oligomers from reactions of the atmospheric oxidation products of *cis*-3-hexen-1-ol.

GLVs as a Global Source of SOA

A series of simulation chamber experiments was performed to compare the yields of SOA generated from the atmospheric oxidation of isoprene, *cis*-3-hexen-1-ol and *cis*-3-hexenyl acetate under identical conditions. The following aerosol mass yields were obtained; *cis*-3-hexen-1-ol (3.1%), *cis*-3-hexenyl acetate (0.9%) and isoprene (1.2%). Assuming that these SOA yields can be scaled according to the value typically used for isoprene (3%, Henze and Seinfeld, 2006), the relative yields of SOA produced from *cis*-3-hexen-1-ol and *cis*-3-hexenyl acetate in the atmosphere are 7.75% and 2.25% respectively. This leads to an estimated global SOA source of 1–5 TgC yr⁻¹ from the OH-initiated oxidation of these two GLVs, up to a third of that from isoprene. The SOA yields from ozonolysis (at initial concentrations of 1600 ppbv) were 9.5% for *cis*-3-hexen-1-ol and 8.6% for *cis*-3-hexenyl acetate, indicating that ozonolysis is likely to be an additional SOA production route for these GLVs.

A recent estimate of global SOA production based on VOC fluxes indicated that there may be significant missing SOA precursors that are currently unknown (Goldstein and Galbally, 2007). The results obtained in this study indicate that GLVs may be an important part of this unidentified global source of SOA, which have been overlooked as a consequence of their volatile first generation oxidation products. Here only 2 compounds have been considered, but there are a number of other GLV species emitted into the atmosphere (e.g. *trans*-3-hexenal, *cis*-2-hexenal, *cis*-2-hexenol) indicating that the SOA potential of green leaf volatiles may be considerably higher than estimated here. Clearly, considerable further work on emission fluxes, simulation chamber studies, field measurements and modelling is required to fully evaluate the importance of GLVs to the SOA budget. Future scenarios may also be considered, where higher emissions of GLVs could arise from plant stress induced by extreme temperatures or high ozone concentrations, or from the use of plants for biofuels (GLV emissions are major emission from oil seed rape).