The Coupling of a High-efficiency Aerosol Collector with Electrospray Ionisation/Orbitrap Mass Spectrometry as a novel tool for Real-time Chemical Characterisation of Fine and Ultrafine Particles

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Supporting Information

Sensitivity and limit of detection (LOD) calculations:

The sensitivity of a certain compound in the HEAC/ESI/Orbitrap-MS system is determined by finding the slope of the best-fit line of the calibration curve. To find the best-fit line of the calibration curve, the generalised least-squares estimation algorithm by York et al. (2004) was used due to uncertainties in both x- and y-directions. After obtaining the slope, the limit of detection (LOD) of the compound by the HEAC/ESI/Orbitrap-MS was determined using equation (1) shown below:

$$\frac{S}{N} = \frac{k_i \times LOD}{\sigma} \qquad (1)$$

where k_i is the sensitivity for the specific compound (given by the slope of the best-fit line), σ is the standard deviation of the background signal for the particular compound (in the blank sample), and S/N is the signal-to-noise ratio of the instrument (Zhang et al., 2016).

Data analysis:

All data analyses were done using Rstudio version 4.2.3 (R Development Core Team, 2023). The York-fit algorithm used in sensitivity and LOD calculation was run by the "IsoplotR" package (Vermeesch, 2018), and figures were created by the "ggplot2" package (Wickham, 2016). SMPS data was exported by Aerosol Instrument Manager (AIM) software (version 9.0.0.0), developed by TSI incorporated. Orbitrap-MS data was initially processed by the Thermo Xcalibur software (Thermo Fisher, USA). When necessary, the raw data was converted into mzXML format by RawConverter (He et al., 2015) and analysed using the "xcms" package in Rstudio (Smith et al., 2006).

α-pinene ozonolysis product identification

The identification of α-pinene ozonolysis products were done by MZmine (ver. 3.9.0). The raw data in .raw (Thermo Fisher) format was directly imported to MZmine. After importing the raw data, “Mass detection” was carried out to identify all the ion present in every mass spectrum. The parameters set for mass detection are as follows:

Retention time: 0 to 115 minutes (Full range)
Polarity: negative
Mass detector: Exact mass
Noise level: 1.0
m/z tolerance: 5.0E-4 m/z or 1 ppm

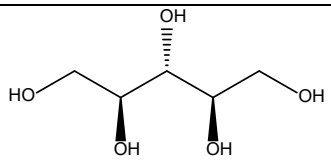
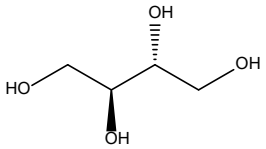
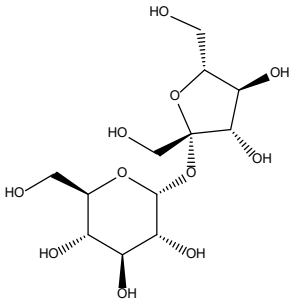
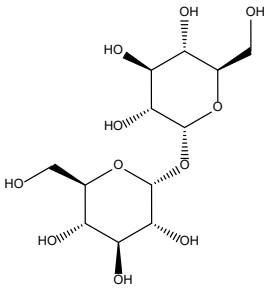
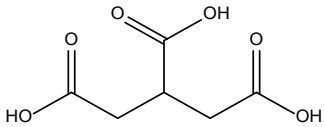
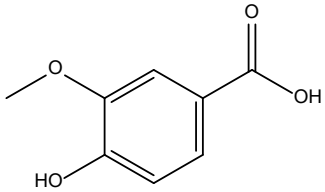
In particular, the noise level was set to 1 to capture all possible ion signals. A mass list of around 200,000 ions with unique exact mass was generated. After that, A “feature detection” algorithm was applied to the raw data to construct the time series of all ions in the mass list that fulfill the criteria set in the algorithm. The parameters set in the feature detection algorithm are as follow:

Retention time: 0 to 115 minutes (full range)
Polarity: negative
Minimum consecutive scans: 2
Minimum intensity for consecutive scans: 0
Minimum absolute height: 5.0
m/z tolerance (scan-to-scan): 0.002 m/z or 5.0 ppm

The current setting screened out a large amount of noise ions (~90%) in the mass list, and a feature list containing the time series of 20004 ions was generated. These time series were then individually inspected. Ions were assigned as “product ions” if their signals showed an increase when the HEAC was sampling from the reaction bottle. The above workflow

identified over three hundred product ions in the fast α-pinene injection experiment, including isotope signals of some product ions.

Table S1. Details and selected physical properties of compounds used for the sensitivity and LOD characterisation experiment.

Compound	Structure	Chemical formula	Exact mass	m/z $[M–H]^-$	Water solubility	Vapor pressure (Pa at 25°C)*
Adonitol		$C_5H_{12}O_5$	152.0685	151.0612	6.42 x 10^5mg/L	1.51
Erythritol		$C_4H_{10}O_4$	122.0579	121.0506	6.1x10^5 mg/L	6.36x10^{-4}
Sucrose		$C_{12}H_{22}O_{11}$	342.1162	341.1089	2.1x10^6 mg/L	2.24 x 10^{-12}
Trehalose		$C_{12}H_{22}O_{11}$	342.1162	341.1089	6.89x10^6 mg/L	2.23x10^{-12}
Tricarballylic acid		$C_6H_8O_6$	176.0321	175.0248	500 mg/ml	3.88 x 10^{-3}
Vanillic acid		$C_8H_8O_4$	168.0423	167.0350	1500 mg/L	1.89 x 10^{-2}

* Vapor pressure estimation was carried out by EPI Suite software using the AEROWIN v1.00 programme.

Table S2. Sensitivity and LOD of the chemical compounds analysed in the current study. Uncertainties reported in the table refer to the standard errors of the results.

Compound	Sensitivity (10^4 counts m^3 μg^{-1})	LOD (ng m^{-3})
Adonitol	0.64 ± 0.10	14 ± 2.3
Erythritol	0.62 ± 0.078	1.1 ± 0.14
Sucrose	0.68 ± 0.14	4.5 ± 0.91
Trehalose	0.53 ± 0.11	1.9 ± 0.38
Tricarballylic acid	1.9 ± 0.21	65 ± 7.4
Vanillic acid	1.8 ± 0.18	36 ± 3.6

Table S3. Sensitivity and LOD of vanillic acid, TCA and adonitol in different working fluids.

Compound	Working fluid	Sensitivity (10^4 counts m^3 μg^{-1})	LOD (ng m^{-3})
Adonitol	H_2O	0.86 ± 0.097	17 ± 1.9
	MeOH	0.38 ± 0.023	20 ± 1.2
	ACN	0.50 ± 0.030	42 ± 2.6
TCA	H_2O	1.6 ± 0.12	22 ± 1.7
	MeOH	0.65 ± 0.048	26 ± 1.9
	ACN	4.7 ± 0.30	12 ± 0.75
Vanillic acid	H_2O	2.6 ± 0.25	5.9 ± 0.58
	MeOH	2.7 ± 0.25	7.1 ± 0.67
	ACN	6.6 ± 0.60	2.1 ± 0.19

Table S4. The list of products identified in the α-pinene ozonolysis experiments.

Molecular Mass	No.C	No.H	No.O	Formula	DBE*
74.001	2	2	3	C2H2O3	2
58.043	3	6	1	C3H6O	1
72.022	3	4	2	C3H4O2	2
74.038	3	6	2	C3H6O2	1
88.017	3	4	3	C3H4O3	2
104.012	3	4	4	C3H4O4	2
70.043	4	6	1	C4H6O	2
72.059	4	8	1	C4H8O	1
84.022	4	4	2	C4H4O2	3
86.038	4	6	2	C4H6O2	2
100.017	4	4	3	C4H4O3	3
102.033	4	6	3	C4H6O3	2
118.028	4	6	4	C4H6O4	2
120.044	4	8	4	C4H8O4	1
82.043	5	6	1	C5H6O	3
84.059	5	8	1	C5H8O	2
86.075	5	10	1	C5H10O	1
96.022	5	4	2	C5H4O2	4
98.038	5	6	2	C5H6O2	3
100.054	5	8	2	C5H8O2	2
112.017	5	4	3	C5H4O3	4
114.033	5	6	3	C5H6O3	3
128.012	5	4	4	C5H4O4	4
130.028	5	6	4	C5H6O4	3
132.044	5	8	4	C5H8O4	2
144.007	5	4	5	C5H4O5	4
146.023	5	6	5	C5H6O5	3
148.039	5	8	5	C5H8O5	2
162.018	5	6	6	C5H6O6	3
164.034	5	8	6	C5H8O6	2
96.059	6	8	1	C6H8O	3
98.075	6	10	1	C6H10O	2
110.038	6	6	2	C6H6O2	4
112.054	6	8	2	C6H8O2	3
114.070	6	10	2	C6H10O2	2
126.033	6	6	3	C6H6O3	4
128.049	6	8	3	C6H8O3	3
142.028	6	6	4	C6H6O4	4
144.044	6	8	4	C6H8O4	3
146.060	6	10	4	C6H10O4	2
108.059	7	8	1	C7H8O	4
110.075	7	10	1	C7H10O	3
112.091	7	12	1	C7H12O	2
124.054	7	8	2	C7H8O2	4
126.070	7	10	2	C7H10O2	3

128.086	7	12	2	C7H12O2	2
138.033	7	6	3	C7H6O3	5
140.049	7	8	3	C7H8O3	4
142.065	7	10	3	C7H10O3	3
144.081	7	12	3	C7H12O3	2
146.097	7	14	3	C7H14O3	1
154.028	7	6	4	C7H6O4	5
156.044	7	8	4	C7H8O4	4
158.060	7	10	4	C7H10O4	3
160.076	7	12	4	C7H12O4	2
162.092	7	14	4	C7H14O4	1
174.055	7	10	5	C7H10O5	3
176.071	7	12	5	C7H12O5	2
190.050	7	10	6	C7H10O6	3
192.066	7	12	6	C7H12O6	2
122.075	8	10	1	C8H10O	4
124.091	8	12	1	C8H12O	3
126.107	8	14	1	C8H14O	2
138.070	8	10	2	C8H10O2	4
140.086	8	12	2	C8H12O2	3
142.102	8	14	2	C8H14O2	2
154.065	8	10	3	C8H10O3	4
156.081	8	12	3	C8H12O3	3
170.060	8	10	4	C8H10O4	4
172.076	8	12	4	C8H12O4	3
174.092	8	14	4	C8H14O4	2
186.055	8	10	5	C8H10O5	4
188.071	8	12	5	C8H12O5	3
190.087	8	14	5	C8H14O5	2
202.050	8	10	6	C8H10O6	4
204.066	8	12	6	C8H12O6	3
206.082	8	14	6	C8H14O6	2
220.061	8	12	7	C8H12O7	3
222.077	8	14	7	C8H14O7	2
136.091	9	12	1	C9H12O	4
138.107	9	14	1	C9H14O	3
140.123	9	16	1	C9H16O	2
152.086	9	12	2	C9H12O2	4
154.102	9	14	2	C9H14O2	3
168.081	9	12	3	C9H12O3	4
170.097	9	14	3	C9H14O3	3
184.076	9	12	4	C9H12O4	4
186.092	9	14	4	C9H14O4	3
188.108	9	16	4	C9H16O4	2
198.055	9	10	5	C9H10O5	5
200.071	9	12	5	C9H12O5	4
202.087	9	14	5	C9H14O5	3
204.103	9	16	5	C9H16O5	2

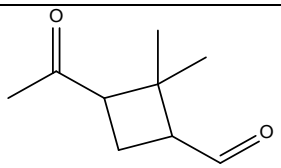
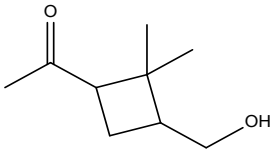
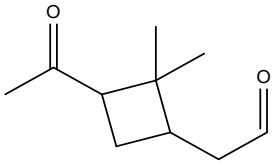
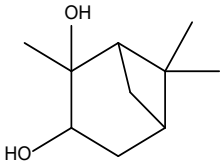
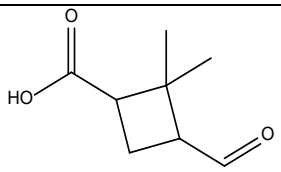
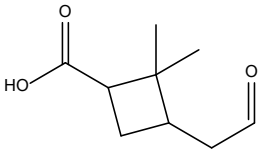
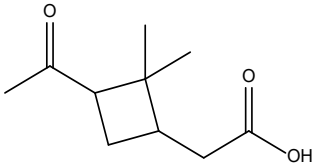
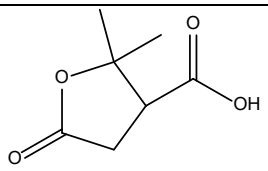
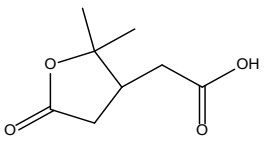
218.082	9	14	6	C9H14O6	3
220.098	9	16	6	C9H16O6	2
234.077	9	14	7	C9H14O7	3
164.086	10	12	2	C10H12O2	5
168.118	10	16	2	C10H16O2	3
180.081	10	12	3	C10H12O3	5
182.097	10	14	3	C10H14O3	4
184.113	10	16	3	C10H16O3	3
196.076	10	12	4	C10H12O4	5
198.092	10	14	4	C10H14O4	4
200.108	10	16	4	C10H16O4	3
202.124	10	18	4	C10H18O4	2
212.071	10	12	5	C10H12O5	5
216.103	10	16	5	C10H16O5	3
218.119	10	18	5	C10H18O5	2
228.066	10	12	6	C10H12O6	5
230.082	10	14	6	C10H14O6	4
232.098	10	16	6	C10H16O6	3
234.114	10	18	6	C10H18O6	2
248.093	10	16	7	C10H16O7	3
264.088	10	16	8	C10H16O8	3
212.108	11	16	4	C11H16O4	4
214.124	11	18	4	C11H18O4	3
226.087	11	14	5	C11H14O5	5
228.103	11	16	5	C11H16O5	4
230.119	11	18	5	C11H18O5	3
280.120	11	20	8	C11H20O8	2
210.129	12	18	3	C12H18O3	4
222.092	12	14	4	C12H14O4	6
226.124	12	18	4	C12H18O4	4
238.087	12	14	5	C12H14O5	6
242.119	12	18	5	C12H18O5	4
238.124	13	18	4	C13H18O4	5
254.119	13	18	5	C13H18O5	5
252.140	14	20	4	C14H20O4	5
270.151	14	22	5	C14H22O5	4
282.151	15	22	5	C15H22O5	5
284.167	15	24	5	C15H24O5	4
298.146	15	22	6	C15H22O6	5
278.156	16	22	4	C16H22O4	6
294.151	16	22	5	C16H22O5	6
296.167	16	24	5	C16H24O5	5
310.146	16	22	6	C16H22O6	6
312.162	16	24	6	C16H24O6	5
314.178	16	26	6	C16H26O6	4
326.141	16	22	7	C16H22O7	6
328.157	16	24	7	C16H24O7	5

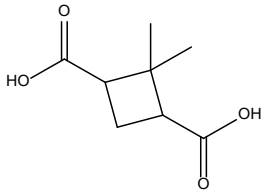
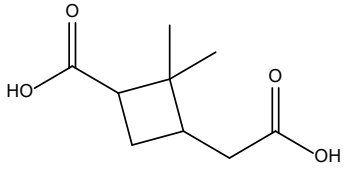
330.173	16	26	7	C16H26O7	4
344.152	16	24	8	C16H24O8	5
346.168	16	26	8	C16H26O8	4
312.199	17	28	5	C17H28O5	4
324.162	17	24	6	C17H24O6	6
326.178	17	26	6	C17H26O6	5
328.194	17	28	6	C17H28O6	4
340.157	17	24	7	C17H24O7	6
342.173	17	26	7	C17H26O7	5
344.189	17	28	7	C17H28O7	4
346.205	17	30	7	C17H30O7	3
356.152	17	24	8	C17H24O8	6
358.168	17	26	8	C17H26O8	5
360.184	17	28	8	C17H28O8	4
362.200	17	30	8	C17H30O8	3
374.163	17	26	9	C17H26O9	5
376.179	17	28	9	C17H28O9	4
378.195	17	30	9	C17H30O9	3
390.158	17	26	10	C17H26O10	5
308.204	18	28	4	C18H28O4	5
322.183	18	26	5	C18H26O5	6
324.199	18	28	5	C18H28O5	5
326.215	18	30	5	C18H30O5	4
336.162	18	24	6	C18H24O6	7
338.178	18	26	6	C18H26O6	6
340.194	18	28	6	C18H28O6	5
342.210	18	30	6	C18H30O6	4
354.173	18	26	7	C18H26O7	6
356.189	18	28	7	C18H28O7	5
358.205	18	30	7	C18H30O7	4
370.168	18	26	8	C18H26O8	6
372.184	18	28	8	C18H28O8	5
374.200	18	30	8	C18H30O8	4
388.179	18	28	9	C18H28O9	5
390.195	18	30	9	C18H30O9	4
404.174	18	28	10	C18H28O10	5
406.190	18	30	10	C18H30O10	4
420.169	18	28	11	C18H28O11	5
422.185	18	30	11	C18H30O11	4
320.204	19	28	4	C19H28O4	6
322.220	19	30	4	C19H30O4	5
336.199	19	28	5	C19H28O5	6
338.215	19	30	5	C19H30O5	5
350.178	19	26	6	C19H26O6	7
352.194	19	28	6	C19H28O6	6
354.210	19	30	6	C19H30O6	5
364.157	19	24	7	C19H24O7	8
368.189	19	28	7	C19H28O7	6

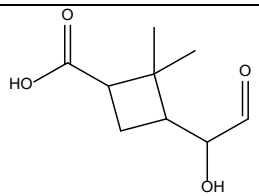
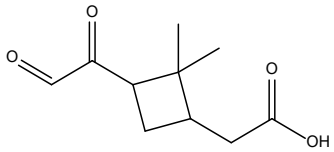
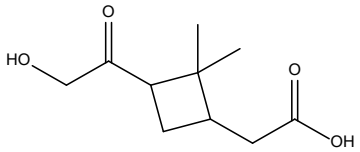
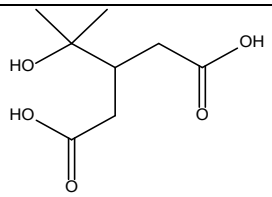
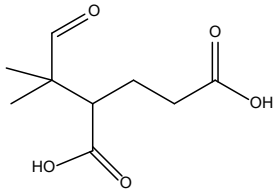
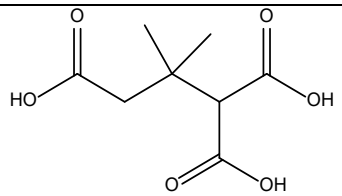
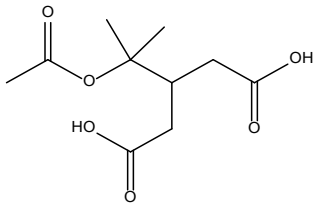
370.205	19	30	7	C19H30O7	5
378.136	19	22	8	C19H22O8	9
380.152	19	24	8	C19H24O8	8
384.184	19	28	8	C19H28O8	6
386.200	19	30	8	C19H30O8	5
388.216	19	32	8	C19H32O8	4
396.147	19	24	9	C19H24O9	8
400.179	19	28	9	C19H28O9	6
400.179	19	28	9	C19H28O9	6
402.195	19	30	9	C19H30O9	5
404.211	19	32	9	C19H32O9	4
416.174	19	28	10	C19H28O10	6
350.215	20	30	5	C20H30O5	6
352.231	20	32	5	C20H32O5	5
366.210	20	30	6	C20H30O6	6
368.226	20	32	6	C20H32O6	5
370.242	20	34	6	C20H34O6	4
378.173	20	26	7	C20H26O7	8
382.205	20	30	7	C20H30O7	6
384.221	20	32	7	C20H32O7	5
386.237	20	34	7	C20H34O7	4
394.168	20	26	8	C20H26O8	8
398.2	20	30	8	C20H30O8	6
400.216	20	32	8	C20H32O8	5
402.232	20	34	8	C20H34O8	4
416.211	20	32	9	C20H32O9	5
390.173	21	26	7	C21H26O7	9
420.199	26	28	5	C26H28O5	13
422.215	26	30	5	C26H30O5	12
438.21	26	30	6	C26H30O6	12

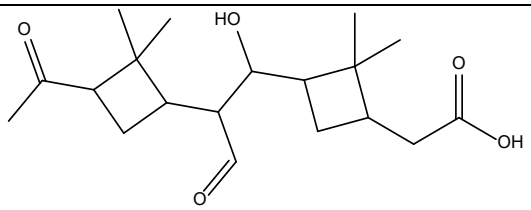
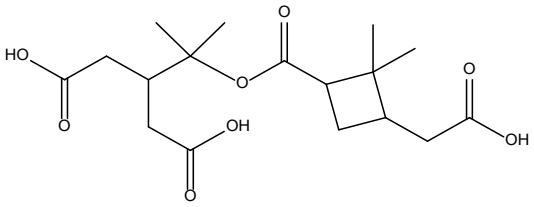
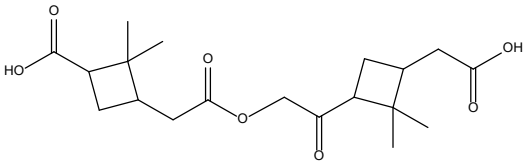
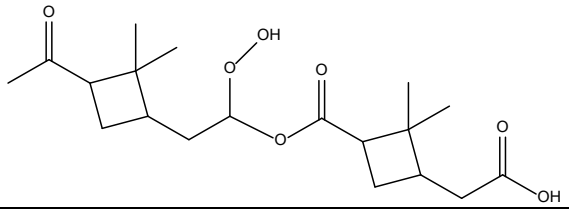
*** DBE = double bond equivalent**

Table S5. Products identified in the mass spectrum were obtained from the fast α-pinene ozonolysis experiment.

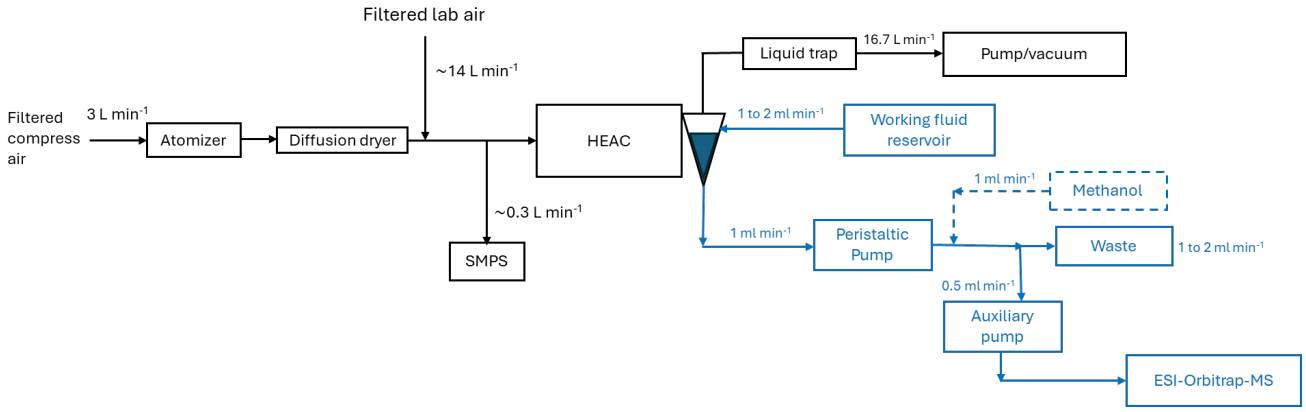
Name	No. of C atom	Chemical formula	m/z	Proposed structure	Reference
O2					
Norpinoaldehyde	9	C9H14O2	153.09		Witkowski and Gieczak, 2014
C96OH	9	C9H16O2	155.11		MCM
Pinaldehyde	10	C10H16O2	167.11		Witkowski and Gieczak, 2014
Pinanediol	10	C10H18O2	169.12		MCM
O3					
Norpinalic acid	8	C8H12O3	155.07		Ma and Marston, 2008
Pinalic acid	9	C9H14O3	169.09		Witkowski and Gieczak, 2014
Pinonic acid	10	C10H16O3	183.10		Jenkin et al., 2000
O4					
Terebic acid	7	C7H10O4	157.05		Yasmeen et al., 2010
Terpenylic acid	8	C8H12O4	171.06		Claeys et al., 2009

Norpinic acid	8	C8H12O4	171.06		Ma and Marston, 2008
Pinic acid	9	C9H14O4	185.08		Ma and Marston, 2008

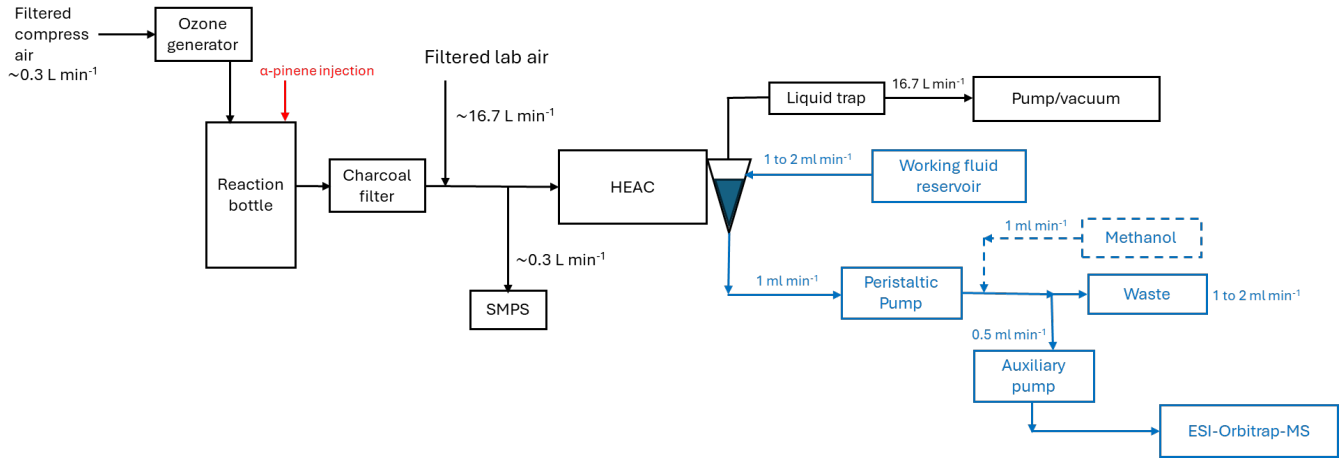
Name	**No. of C atom**	**Chemical formula**	**m/z**	**Proposed structure**	**Reference**
4-hydroxy-pinalic-3-acid	9	C9H14O4	185.08		Ma and Marston, 2008
Oxopinonic acid	10	C10H14O4	197.08		Zhang et al., 2015
OH-pinonic acid	10	C10H16O4	199.09		Jenkin et al., 2000
O5					
Diaterpenylic acid	8	C8H14O5	189.07		Yasmeen et al., 2010
C9-Carbonyl dicarboxylic acid	9	C9H14O5	201.07		Sato et al., 2016
O6					
3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)	8	C8H12O6	203.06		Claeys et al., 2009
Diaterpenylic acid acetate	10	C10H16O6	231.09		Yasmeen et al., 2010

Dimer	m/z	structure	Reference
Aldol reaction products of pinonic acid and pinonaldehyde	337.21		Witkowski and Gieczak, 2014
Dimer ester of pinic acid and diaterpenylic acid	357.16		Yasmeen et al., 2010
Dimer ester of pinic acid and 10-hydroxypinonic acid	367.18		Yasmeen et al., 2010
Dimer ester of pinic acid and SCI	369.20		Witkowski and Gieczak, 2014

(a)



(b)



(c)

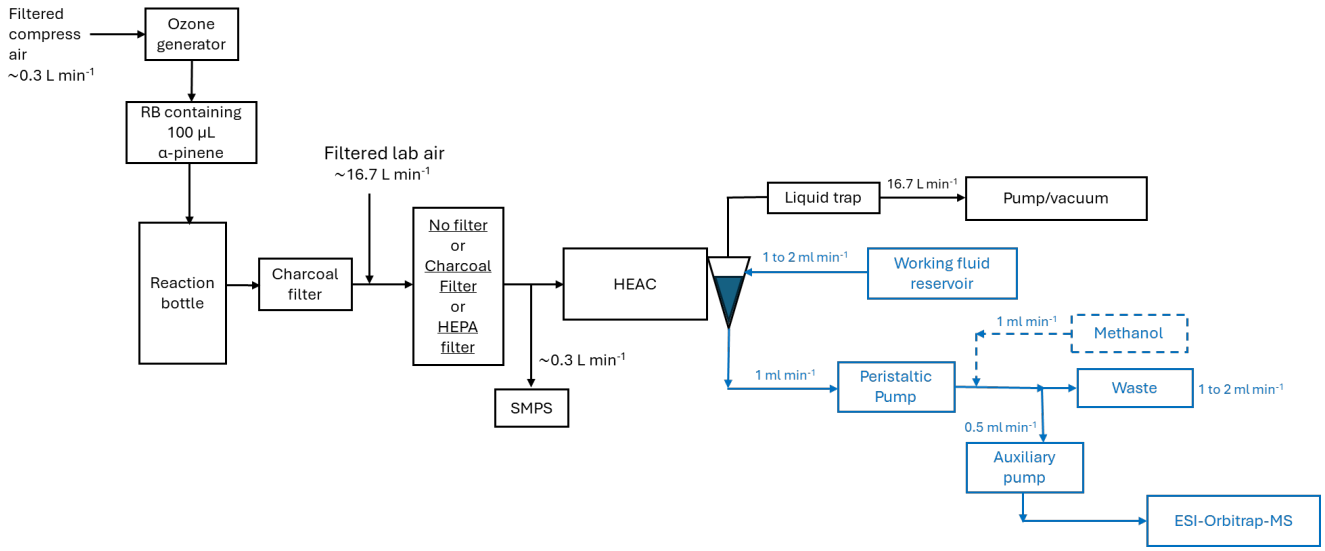


Figure S1. Instrumental setup for (a) sensitivity and LOD characterisation experiments, (b) fast α-pinene injection experiment and (c) slow α-pinene injection experiment. Air supplied to the system was filtered by activated charcoal and HEPA filters. Dash lines indicate the additional setup when using Milli-Q water as the working fluid.

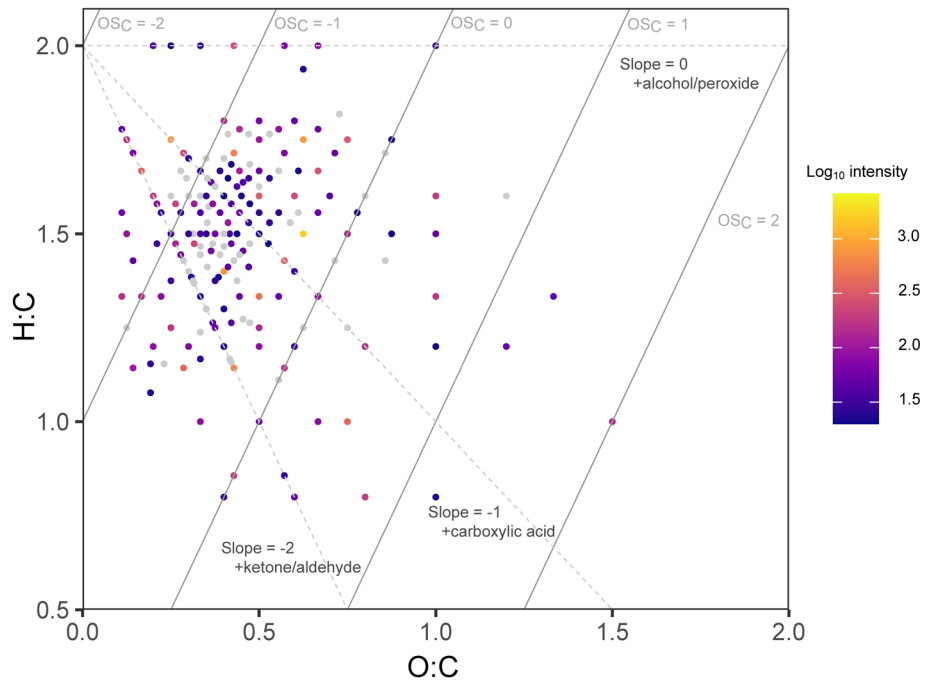


Figure S2. Van Krevelen diagram of the ozonolysis products in the fast α-pinene injection experiment. The data in this figure correspond to the moment when the particle mass concentration peaked. Coloured points represent data with signal intensities > Log 1.5, while light-grey points represent data with a signal intensity < Log 1.5. OS_C corresponds to the averaged oxidation state of a compound as describe in Kroll et al. (2011).

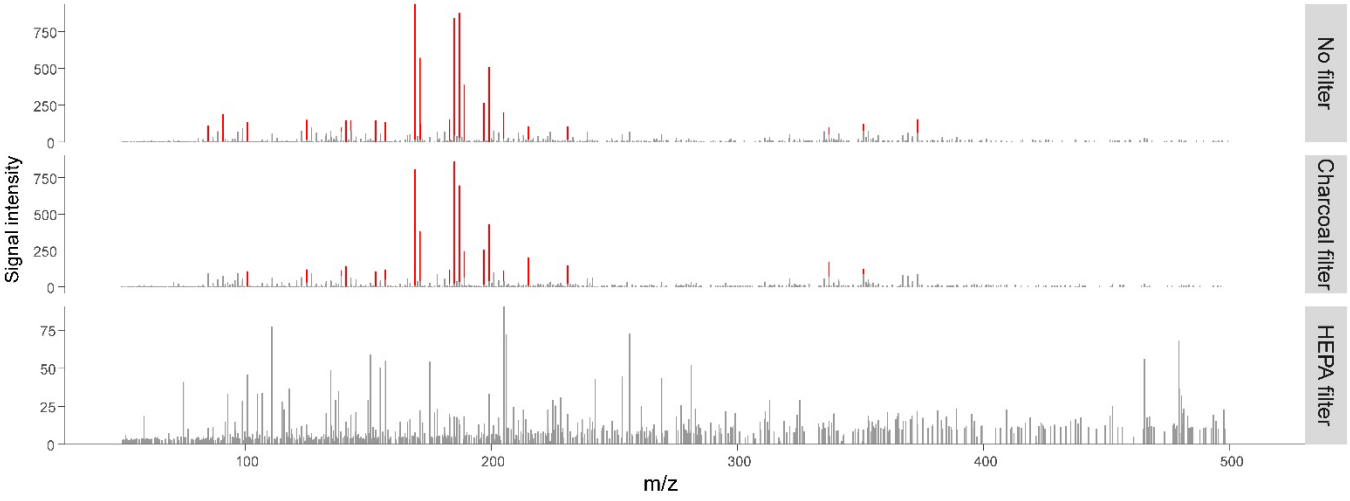


Figure S3. The mass spectrum obtained from the slow α-pinene injection experiment when the particle concentration was the highest. Peaks with signal intensity larger than 100 were highlighted in red. Note that the y-axis scale of HEPA filter is 10 times lower than the other two filters.

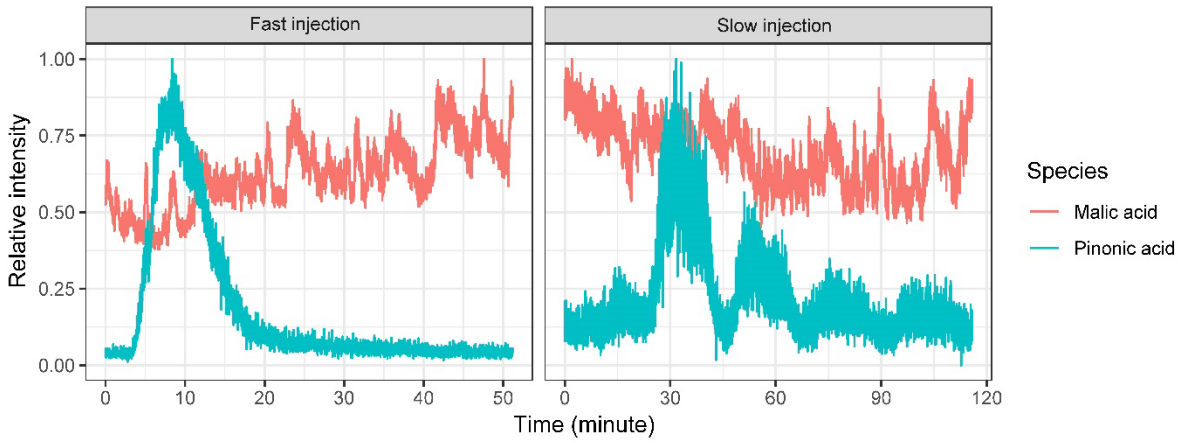


Figure S4. Relative signal intensities of malic acid (internal standard) and pinonic acid (reaction product) in fast and slow α-pinene injection experiments. The relative signal intensity was calculated by normalizing the signal intensity of each data point to the highest signal intensity in the whole experiment.

Reference

HE, L., DIEDRICH, J., CHU, Y.-Y. & YATES, J. R., III 2015. Extracting Accurate Precursor Information for Tandem Mass Spectra by RawConverter. *Analytical Chemistry,* 87**,** 11361-11367.

KROLL, J. H., DONAHUE, N. M., JIMENEZ, J. L., KESSLER, S. H., CANAGARATNA, M. R., WILSON, K. R., ALTIERI, K. E., MAZZOLENI, L. R., WOZNIAK, A. S., BLUHM, H., MYSAK, E. R., SMITH, J. D., KOLB, C. E. & WORSNOP, D. R. 2011. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nature Chemistry,* 3**,** 133-139.

R DEVELOPMENT CORE TEAM 2023. R: A language and environment for statistical computing. R Foundation for Statistical Computing.

SMITH, C. A., WANT, E. J., O'MAILLE, G., ABAGYAN, R. & SIUZDAK, G. 2006. XCMS: Processing Mass Spectrometry Data for Metabolite Profiling Using Nonlinear Peak Alignment, Matching, and Identification. *Analytical Chemistry,* 78**,** 779-787.

VERMEESCH, P. 2018. IsoplotR: A free and open toolbox for geochronology. *Geoscience Frontiers,* 9**,** 1479-1493.

WICKHAM, H. 2016. Data Analysis. *In:* WICKHAM, H. (ed.) *ggplot2: Elegant Graphics for Data Analysis*. Cham: Springer International Publishing.

YORK, D., EVENSEN, N. M., MARTíNEZ, M. L. & DE BASABE DELGADO, J. 2004. Unified equations for the slope, intercept, and standard errors of the best straight line. *American Journal of Physics,* 72**,** 367-375.

ZHANG, X., DALLESKA, N. F., HUANG, D. D., BATES, K. H., SOROOSHIAN, A., FLAGAN, R. C. & SEINFELD, J. H. 2016. Time-resolved molecular characterization of organic aerosols by PILS + UPLC/ESI-Q-TOFMS. *Atmospheric Environment,* 130**,** 180-189.