Supplement of

Molecular transformations of phenolic SOA during photochemical aging in the aqueous phase: competition among oligomerization, functionalization, and fragmentation

Lu Yu et al.

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Section S1: Nano-DESI measurement and data analysis

The nano-DESI analyses were performed using a high-resolution LTQ-Orbitrap mass spectrometer (Thermo Electron, Bremen, Germany) with a resolving power (m/Δm) of 100,000 at m/z = 400. The instrument is equipped with a nano-DESI source assembled from two fused-silica capillaries (150 μm o.d./50 μm i.d.) (Roach et al., 2010). The analysis was performed under the following conditions: spray voltage of 3-5 kV, 0.5-1 mm distance from the tip of the nanospray capillary to the 250 °C heated inlet of the LTQ-Orbitrap, and 0.3-0.9 μL/min flow rate of acetonitrile : water (7:3 volume) solvent. Both positive and negative mode mass spectra were acquired using the Xcalibur software (Thermo Electron, Inc.).

Signals with S/N > 10 were picked out using the Decon2LS software developed at the Pacific Northwest National Laboratory (PNNL) (Jaitly et al., 2009). Data was further processed with Microsoft Excel using a set of built-in macros developed by Roach et al. (2011). The background and sample peaks were first aligned, and the peaks corresponding to 13C isotopes were removed. Peaks in the sample spectra that are at least 10 times bigger than the corresponding peaks in the background spectra were retained for further analysis. Peaks were segregated into different groups using the higher-order mass defect transformation developed by Roach et al. (2011). Molecular formula was assigned with Formula Calculator v. 1.1 (http://www.magnet.fsu.edu/usershub/scientificdivisions/icr/icr_software.html) using the following constraints: C ≥ 0, H ≥ 0, O ≥ 0 for the negative ion mode data and C ≥ 0, H ≥ 0, O ≥ 0, Na ≤ 1 for the positive ion mode data. Approximately 70% of the peaks can be assigned with molecular formula within these constraints.

Section S2: HR-AMS measurement and data analysis

In this study, a High Resolution Time-of-Flight Aerosol Mass Spectrometer (Aerodyne Res. Inc., Billerica, MA; thereafter referred to as AMS) was used to characterize the bulk chemical composition and elemental ratios of the low-volatility substances. The working principles of the AMS have been discussed previously (DeCarlo et al., 2006; Canagaratna et al., 2007). Briefly, the AMS analyzes nonrefractory aerosols that can be evaporated at ~ 600 °C via 70 eV EI mass spectrometry. In this study, the AMS was operated in “V” mode (mass resolutions of ~ 3000) to acquire mass spectra up to m/z 500.

The AMS data were analyzed using the AMS data analysis software (SQUIRREL v1.12 and PIKA v1.53 downloaded from http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/). The V-mode data was analyzed to obtain high resolution mass spectra (HRMS), the atomic ratios of oxygen-to-carbon (O/C), hydrogen-to-carbon (H/C) and the organic mass-to-carbon ratio (OM/OC) (Aiken et al., 2008). The relative humidity measured at the AMS inlet was very low (< 2%), and we assume that contribution from gaseous water molecules was negligible. The H2O+ signal of organics was thus determined as the difference between the measured H2O+ signal and that produced by sulfates (Allan et al., 2004).

A solution composed of equal mass concentrations of ammonium sulfate and sucrose (C12H22O11) was atomized and analyzed using AMS. The measured O/C and H/C ratio is 0.95 and 1.98 respectively. The error for O/C and H/C measurement is 3% and 8% respectively. Thus, the atomization procedure generates nearly equal amount of solutes in complex mixture.
Table S1 Most abundant compounds identified in SYR aqSOA formed during different stages of the \( \bullet \)OH-mediated reactions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula(^a)</th>
<th>Proposed structure</th>
<th>( C^+ (\mu \text{g m}^{-3}) ) at 25 °C, 1 atm(^b)</th>
<th>Relative abundance (ranking)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 °C, 1 atm(^b) at 25 °C, 1 atm(^b)</td>
<td>P1: 0-2 hrs</td>
</tr>
<tr>
<td>1</td>
<td>C(<em>{16})H(</em>{18})O(_8) (306.1103)</td>
<td><img src="image1" alt="Proposed structure" /></td>
<td>3.2E-03</td>
<td>100 (1)</td>
</tr>
<tr>
<td>2</td>
<td>C(<em>{15})H(</em>{18})O(_7) (310.1052)</td>
<td><img src="image2" alt="Proposed structure" /></td>
<td>1.7E-05</td>
<td>56 (2)</td>
</tr>
<tr>
<td>3</td>
<td>C(<em>{15})H(</em>{16})O(_6) (292.0946)</td>
<td><img src="image3" alt="Proposed structure" /></td>
<td>3.4E-04</td>
<td>46 (3)</td>
</tr>
<tr>
<td>4</td>
<td>C(<em>{15})H(</em>{16})O(_8) (340.0794)</td>
<td><img src="image4" alt="Proposed structure" /></td>
<td>3.9E-12</td>
<td>28 (4)</td>
</tr>
<tr>
<td>5</td>
<td>C(<em>{13})H(</em>{14})O(_7) (282.0739)</td>
<td><img src="image5" alt="Proposed structure" /></td>
<td>5.8E-08</td>
<td>19 (5)</td>
</tr>
<tr>
<td>6</td>
<td>C(<em>{15})H(</em>{16})O(_8) (324.0845)</td>
<td><img src="image6" alt="Proposed structure" /></td>
<td>2.8E-09</td>
<td>19 (6)</td>
</tr>
<tr>
<td>7</td>
<td>C(<em>{16})H(</em>{18})O(_7) (322.1052)</td>
<td><img src="image7" alt="Proposed structure" /></td>
<td>1.7E-05</td>
<td>18 (7)</td>
</tr>
<tr>
<td>8</td>
<td>C(<em>{14})H(</em>{12})O(_2) (292.0583)</td>
<td><img src="image8" alt="Proposed structure" /></td>
<td>4.0E-11</td>
<td>17 (8)</td>
</tr>
<tr>
<td>9</td>
<td>C(<em>{15})H(</em>{15})O(_{10}) (358.0900)</td>
<td><img src="image9" alt="Proposed structure" /></td>
<td>1.5E-13</td>
<td>13 (9)</td>
</tr>
<tr>
<td>10</td>
<td>C(<em>{14})H(</em>{14})O(_4) (310.0688)</td>
<td><img src="image10" alt="Proposed structure" /></td>
<td>9.9E-11</td>
<td>12 (10)</td>
</tr>
<tr>
<td></td>
<td>Molecular formula</td>
<td>Proposed structure</td>
<td>Molecular weight (amu)</td>
<td>Estimated saturation concentration ($C^*$, $\mu g m^{-3}$)</td>
</tr>
<tr>
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<td>-------------------</td>
<td>--------------------</td>
<td>------------------------</td>
<td>-------------------------------------------------------------</td>
</tr>
<tr>
<td>11</td>
<td>C$<em>{12}$H$</em>{12}$O$_7$ (268.0583)</td>
<td><img src="image1" alt="Structure 1" /></td>
<td>1.3E-07</td>
<td>11 (13)</td>
</tr>
<tr>
<td>12</td>
<td>C$<em>{13}$H$</em>{16}$O$_8$ (300.0845)</td>
<td><img src="image2" alt="Structure 2" /></td>
<td>3.4E-07</td>
<td>8.1 (22)</td>
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<tr>
<td>13</td>
<td>C$_6$H$_8$O$_6$ (176.0321)</td>
<td><img src="image3" alt="Structure 3" /></td>
<td>3.1E+04</td>
<td>7.2 (27)</td>
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<tr>
<td>14</td>
<td>C$<em>{14}$H$</em>{16}$O$_9$ (328.0794)</td>
<td><img src="image4" alt="Structure 4" /></td>
<td>7.6E-11</td>
<td>6.7 (30)</td>
</tr>
<tr>
<td>15</td>
<td>C$_8$H$_6$O$_5$ (146.0215)</td>
<td><img src="image5" alt="Structure 5" /></td>
<td>2.7E+01</td>
<td>4.6 (48)</td>
</tr>
<tr>
<td>16</td>
<td>C$_4$H$_6$O$_5$ (134.0215)</td>
<td><img src="image6" alt="Structure 6" /></td>
<td>3.3E+00</td>
<td>4.4 (50)</td>
</tr>
<tr>
<td>17</td>
<td>C$_6$H$_6$O$_6$ (162.0164)</td>
<td><img src="image7" alt="Structure 7" /></td>
<td>5.0E-02</td>
<td>4.2 (54)</td>
</tr>
<tr>
<td>18</td>
<td>C$<em>{10}$H$</em>{10}$O$_6$ (174.0164)</td>
<td><img src="image8" alt="Structure 8" /></td>
<td>5.2E-05</td>
<td>3.4 (66)</td>
</tr>
</tbody>
</table>

a Molecular formulas and proposed structures of 18 compounds identified according to (-) nano-DESI spectra. They represent the top 10 most abundant aqSOA compounds observed at each reaction stage. The exact molecular weight of each compound is shown in parentheses.

b Estimated saturation concentrations ($C^*$, $\mu g m^{-3}$) of the compounds at 25 °C, 1 atm, determined using the Nannoolal vapor pressure and extrapolation method.

c Relative abundances (%) of the compounds and, in parentheses, their abundance ranks counted in the sorted relative abundance list of all the compounds identified in the nano-DESI mass spectrum of the specified time period.
Table S2 Most abundant compounds identified in GUA aqSOA formed during different stages of the $^3\text{C}^*$-mediated reactions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula</th>
<th>Proposed structure</th>
<th>$C^*$ (μg m$^{-3}$) at 25 °C, 1 atm$^b$</th>
<th>Relative abundance (ranking)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P1: 0-2 hrs</td>
</tr>
<tr>
<td>1</td>
<td>C$<em>{14}$H$</em>{14}$O$_4$ (246.0892)</td>
<td><img src="image1" alt="Structure 1" /></td>
<td>8.8E-01</td>
<td>100 (1)</td>
</tr>
<tr>
<td>2</td>
<td>C$<em>{14}$H$</em>{14}$O$_6$ (278.0790)</td>
<td><img src="image2" alt="Structure 2" /></td>
<td>2.5E-05</td>
<td>79 (2)</td>
</tr>
<tr>
<td>3</td>
<td>C$<em>{21}$H$</em>{20}$O$_6$ (368.1259)</td>
<td><img src="image3" alt="Structure 3" /></td>
<td>4.1E-11</td>
<td>65 (3)</td>
</tr>
<tr>
<td>4</td>
<td>C$<em>{20}$H$</em>{16}$O$_6$ (354.1103)</td>
<td><img src="image4" alt="Structure 4" /></td>
<td>8.0E-09</td>
<td>28 (4)</td>
</tr>
<tr>
<td>5</td>
<td>C$<em>{13}$H$</em>{12}$O$_4$ (232.0735)</td>
<td><img src="image5" alt="Structure 5" /></td>
<td>8.7E-02</td>
<td>19 (5)</td>
</tr>
<tr>
<td>6</td>
<td>C$<em>{21}$H$</em>{18}$O$_8$ (398.1001)</td>
<td><img src="image6" alt="Structure 6" /></td>
<td>5.7E-14</td>
<td>16 (6)</td>
</tr>
<tr>
<td>7</td>
<td>C$<em>{21}$H$</em>{20}$O$_8$ (400.1158)</td>
<td><img src="image7" alt="Structure 7" /></td>
<td>5.0E-13</td>
<td>14 (7)</td>
</tr>
<tr>
<td>8</td>
<td>C$<em>{14}$H$</em>{12}$O$_6$ (276.0634)</td>
<td><img src="image8" alt="Structure 8" /></td>
<td>3.1E-06</td>
<td>13 (8)</td>
</tr>
<tr>
<td>9</td>
<td>C$<em>{28}$H$</em>{26}$O$_8$ (490.1627)</td>
<td><img src="image9" alt="Structure 9" /></td>
<td>1.8E-15</td>
<td>10 (9)</td>
</tr>
<tr>
<td>10</td>
<td>C$<em>{14}$H$</em>{14}$O$_5$ (262.0841)</td>
<td><img src="image10" alt="Structure 10" /></td>
<td>6.0E-03</td>
<td>9.2 (10)</td>
</tr>
<tr>
<td></td>
<td>Molecular Formulas</td>
<td>Proposed Structures</td>
<td>Estimated Saturation Concentrations</td>
<td>Relative Abundances</td>
</tr>
<tr>
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<td>--------------------</td>
<td>---------------------</td>
<td>-------------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>11</td>
<td>C_{20}H_{16}O_{7} (368.0896)</td>
<td><img src="image" alt="structure1" /></td>
<td>1.6E-12</td>
<td>9.0 (11)</td>
</tr>
<tr>
<td>12</td>
<td>C_{13}H_{10}O_{5} (246.0528)</td>
<td><img src="image" alt="structure2" /></td>
<td>4.7E-05</td>
<td>6.9 (12)</td>
</tr>
<tr>
<td>13</td>
<td>C_{13}H_{12}O_{6} (264.0634)</td>
<td><img src="image" alt="structure3" /></td>
<td>1.1E-06</td>
<td>6.2 (14)</td>
</tr>
</tbody>
</table>

a Molecular formulas and proposed structures of 13 compounds identified according to (-) nano-DESI spectra. They represent the top 10 most abundant aqSOA compounds observed at each reaction stage. The exact molecular weight of each compound is shown in parentheses.

b Estimated saturation concentrations (C\(^*\), μg m\(^{-3}\)) of the compounds at 25 °C, 1 atm, determined using the Nannoolal vapor pressure and extrapolation method.

c Relative abundances (%) of the compounds and, in parentheses, their abundance ranks counted in the sorted relative abundance list of all the compounds identified in the nano-DESI mass spectrum of the specified time period.
Table S3 Most abundant compounds identified in GUA aqSOA formed during different stages of the •OH-mediated reactions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula(^a)</th>
<th>Proposed structure</th>
<th>(C^* (\mu g , m^{-3})) at 25 (^\circ)C, 1 atm(^b)</th>
<th>Relative abundance (ranking)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P1: 0-2 hrs</td>
<td>P2: 2-4 hrs</td>
</tr>
<tr>
<td>1</td>
<td>C(<em>{14})H(</em>{14})O(_6) (278.0790)</td>
<td><img src="image1" alt="Proposed structure" /></td>
<td>2.5E-05</td>
<td>100 (1)</td>
</tr>
<tr>
<td>2</td>
<td>C(<em>{14})H(</em>{14})O(_4) (246.0892)</td>
<td><img src="image2" alt="Proposed structure" /></td>
<td>8.8E-01</td>
<td>52 (2)</td>
</tr>
<tr>
<td>3</td>
<td>C(<em>{21})H(</em>{20})O(_6) (368.1259)</td>
<td><img src="image3" alt="Proposed structure" /></td>
<td>4.1E-11</td>
<td>28 (3)</td>
</tr>
<tr>
<td>4</td>
<td>C(<em>{13})H(</em>{12})O(_4) (232.0735)</td>
<td><img src="image4" alt="Proposed structure" /></td>
<td>8.7E-02</td>
<td>23 (4)</td>
</tr>
<tr>
<td>5</td>
<td>C(<em>{20})H(</em>{18})O(_6) (354.1103)</td>
<td><img src="image5" alt="Proposed structure" /></td>
<td>8.0E-09</td>
<td>19 (5)</td>
</tr>
<tr>
<td>6</td>
<td>C(_{8})H(_6)O(_3) (150.0317)</td>
<td><img src="image6" alt="Proposed structure" /></td>
<td>5.2E+02</td>
<td>15 (6)</td>
</tr>
<tr>
<td>7</td>
<td>C(<em>{14})H(</em>{12})O(_6) (276.0634)</td>
<td><img src="image7" alt="Proposed structure" /></td>
<td>3.1E-06</td>
<td>13 (7)</td>
</tr>
<tr>
<td>8</td>
<td>C(<em>{13})H(</em>{10})O(_5) (246.0528)</td>
<td><img src="image8" alt="Proposed structure" /></td>
<td>4.7E-05</td>
<td>12 (8)</td>
</tr>
<tr>
<td>9</td>
<td>C(<em>{21})H(</em>{18})O(_8) (398.1001)</td>
<td><img src="image9" alt="Proposed structure" /></td>
<td>5.7E-14</td>
<td>9.9 (9)</td>
</tr>
<tr>
<td>10</td>
<td>C(<em>{13})H(</em>{12})O(_6) (264.0634)</td>
<td><img src="image10" alt="Proposed structure" /></td>
<td>1.1E-06</td>
<td>9.7 (10)</td>
</tr>
<tr>
<td></td>
<td>Molecular formula</td>
<td>Proposed structure</td>
<td>Estimated concentration</td>
<td>Relative abundance</td>
</tr>
<tr>
<td>---</td>
<td>-------------------</td>
<td>--------------------</td>
<td>------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>11</td>
<td>C_{13}H_{10}O_{4} (230.0579)</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>1.2E-02</td>
<td>6.2 (16)</td>
</tr>
<tr>
<td>12</td>
<td>C_{13}H_{10}O_{3} (214.0630)</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>2.0E+00</td>
<td>5.5 (19)</td>
</tr>
<tr>
<td>13</td>
<td>C_{7}H_{10}O_{6} (190.0477)</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>4.4E-03</td>
<td>3.7 (21)</td>
</tr>
<tr>
<td>14</td>
<td>C_{4}H_{6}O_{5} (134.0215)</td>
<td><img src="image" alt="Molecular structure" /></td>
<td>5.6E+00</td>
<td>0.0 (N/A)</td>
</tr>
</tbody>
</table>

\(^a\) Molecular formulas and proposed structures of 14 compounds identified according to (-) nano-DESI spectra. They represent the top 10 most abundant aqSOA compounds observed at each reaction stage. The exact molecular weight of each compound is shown in parentheses.

\(^b\) Estimated saturation concentrations (C*, μg m\(^{-3}\)) of the compounds at 25 °C, 1 atm, determined using the Nannoolal vapor pressure and extrapolation method.

\(^c\) Relative abundances (%) of the compounds and, in parentheses, their abundance ranks counted in the sorted relative abundance list of all the compounds identified in the nano-DESI mass spectrum of the specified time period.
Table S4 Most abundant compounds identified in PhOH aqSOA formed during different stages of the \(^3\text{C}^*\)-mediated reactions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula(^a)</th>
<th>Proposed structure</th>
<th>(C^* (\mu g \text{ m}^{-3})) at 25 (^\circ\text{C}, 1 \text{ atm})(^b)</th>
<th>Relative abundance (ranking)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P1: 0-5 hrs</td>
<td>P2: 5-9 hrs</td>
</tr>
<tr>
<td>1</td>
<td>C(<em>{12})H(</em>{10})O(_3) (202.0630)</td>
<td><img src="image1.png" alt="Proposed structure 1" /></td>
<td>9.0E-01</td>
<td>100 (1)</td>
</tr>
<tr>
<td>2</td>
<td>C(<em>{13})H(</em>{14})O(_3) (278.9042)</td>
<td><img src="image2.png" alt="Proposed structure 2" /></td>
<td>6.5E-04</td>
<td>88 (2)</td>
</tr>
<tr>
<td>3</td>
<td>C(<em>{18})H(</em>{14})O(_4) (294.0892)</td>
<td><img src="image3.png" alt="Proposed structure 3" /></td>
<td>2.4E-06</td>
<td>45 (3)</td>
</tr>
<tr>
<td>4</td>
<td>C(<em>{12})H(</em>{10})O(_2) (186.0680)</td>
<td><img src="image4.png" alt="Proposed structure 4" /></td>
<td>9.2E+01</td>
<td>27 (4)</td>
</tr>
<tr>
<td>5</td>
<td>C(<em>{13})H(</em>{10})O(_3) (214.0630)</td>
<td><img src="image5.png" alt="Proposed structure 5" /></td>
<td>2.0E+00</td>
<td>21 (5)</td>
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<td>6</td>
<td>C(<em>{18})H(</em>{12})O(_5) (308.0684)</td>
<td><img src="image6.png" alt="Proposed structure 6" /></td>
<td>4.0E-07</td>
<td>21 (6)</td>
</tr>
<tr>
<td>7</td>
<td>C(<em>{20})H(</em>{14})O(_6) (350.0790)</td>
<td><img src="image7.png" alt="Proposed structure 7" /></td>
<td>1.1E-10</td>
<td>20 (7)</td>
</tr>
<tr>
<td>8</td>
<td>C(<em>{24})H(</em>{18})O(_4) (370.1204)</td>
<td><img src="image8.png" alt="Proposed structure 8" /></td>
<td>9.2E-10</td>
<td>16 (8)</td>
</tr>
<tr>
<td>9</td>
<td>C(<em>{13})H(</em>{10})O(_4) (230.0579)</td>
<td><img src="image9.png" alt="Proposed structure 9" /></td>
<td>1.2E-02</td>
<td>16 (9)</td>
</tr>
<tr>
<td>10</td>
<td>C(<em>{18})H(</em>{12})O(_4) (292.0735)</td>
<td><img src="image10.png" alt="Proposed structure 10" /></td>
<td>6.0E-04</td>
<td>13 (10)</td>
</tr>
<tr>
<td>11</td>
<td>C(<em>{14})H(</em>{10})O(_5) (258.0528)</td>
<td><img src="image11.png" alt="Proposed structure 11" /></td>
<td>1.0E-04</td>
<td>11 (11)</td>
</tr>
<tr>
<td></td>
<td>Molecular formula</td>
<td>Structure</td>
<td>Estimated saturation concentration (C*, μg m⁻³)</td>
<td>Relative abundance (%)</td>
</tr>
<tr>
<td>---</td>
<td>------------------</td>
<td>-----------</td>
<td>-----------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>12</td>
<td>C₈H₆O₅ (182.0215)</td>
<td><img src="image1" alt="Structure" /></td>
<td>8.8E-02</td>
<td>5.3 (18)</td>
</tr>
<tr>
<td>13</td>
<td>C₇H₆O₃ (138.0317)</td>
<td><img src="image2" alt="Structure" /></td>
<td>9.3E+03</td>
<td>4.2 (21)</td>
</tr>
<tr>
<td>14</td>
<td>C₇H₆O₄ (154.0266)</td>
<td><img src="image3" alt="Structure" /></td>
<td>1.6E+01</td>
<td>2.4 (37)</td>
</tr>
<tr>
<td>15</td>
<td>C₄H₄O₄ (116.0110)</td>
<td><img src="image4" alt="Structure" /></td>
<td>1.1E+03</td>
<td>0.6 (95)</td>
</tr>
<tr>
<td>16</td>
<td>C₄H₆O₅ (134.0215)</td>
<td><img src="image5" alt="Structure" /></td>
<td>5.6E+00</td>
<td>0.0 (N/A)</td>
</tr>
<tr>
<td>17</td>
<td>C₄H₆O₄ (118.0266)</td>
<td><img src="image6" alt="Structure" /></td>
<td>2.3E+03</td>
<td>0.0 (N/A)</td>
</tr>
</tbody>
</table>

**a** Molecular formulas and proposed structures of 17 compounds identified according to (-) nano-DESI spectra. They represent the top 10 most abundant aqSOA compounds observed at each reaction stage. The exact molecular weight of each compound is shown in parentheses.

**b** Estimated saturation concentrations (C*, μg m⁻³) of the compounds at 25 °C, 1 atm, determined using the Nannoolal vapor pressure and extrapolation method.

**c** Relative abundances (%) of the compounds and, in parentheses, their abundance ranks counted in the sorted relative abundance list of all the compounds identified in the nano-DESI mass spectrum of the specified time period.
Table S5 Most abundant compounds identified in PhOH aqSOA formed at different stages of the •OH-mediated reactions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula(^a)</th>
<th>Proposed structure</th>
<th>(C^*) ((\mu)g m(^{-3})) at 25 °C, 1 atm(^b)</th>
<th>Relative abundance (ranking)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P1: 0-6 hrs</td>
</tr>
<tr>
<td>1</td>
<td>C(<em>{13})H(</em>{10})O(_4) (230.0579)</td>
<td><img src="image1" alt="Proposed structure 1" /></td>
<td>1.2E-02</td>
<td>100 (1)</td>
</tr>
<tr>
<td>2</td>
<td>C(<em>{13})H(</em>{10})O(_3) (214.0630)</td>
<td><img src="image2" alt="Proposed structure 2" /></td>
<td>2.0E+00</td>
<td>90 (2)</td>
</tr>
<tr>
<td>3</td>
<td>C(<em>{12})H(</em>{10})O(_3) (202.0630)</td>
<td><img src="image3" alt="Proposed structure 3" /></td>
<td>9.0E-01</td>
<td>48 (3)</td>
</tr>
<tr>
<td>4</td>
<td>C(<em>{20})H(</em>{14})O(_6) (350.0790)</td>
<td><img src="image4" alt="Proposed structure 4" /></td>
<td>1.1E-10</td>
<td>47 (4)</td>
</tr>
<tr>
<td>5</td>
<td>C(<em>{14})H(</em>{10})O(_5) (258.0528)</td>
<td><img src="image5" alt="Proposed structure 5" /></td>
<td>1.0E-04</td>
<td>39 (5)</td>
</tr>
<tr>
<td>6</td>
<td>C(<em>{3})H(</em>{5})O(_3) (150.0317)</td>
<td><img src="image6" alt="Proposed structure 6" /></td>
<td>8.5E-08</td>
<td>27 (6)</td>
</tr>
<tr>
<td>7</td>
<td>C(<em>{3})H(</em>{5})O(_3) (158.0215)</td>
<td><img src="image7" alt="Proposed structure 7" /></td>
<td>2.2E-02</td>
<td>19 (7)</td>
</tr>
<tr>
<td>8</td>
<td>C(<em>{3})H(</em>{5})O(_3) (154.0266)</td>
<td><img src="image8" alt="Proposed structure 8" /></td>
<td>1.6E+01</td>
<td>15 (8)</td>
</tr>
<tr>
<td>9</td>
<td>C(<em>{3})H(</em>{5})O(_3) (182.0215)</td>
<td><img src="image9" alt="Proposed structure 9" /></td>
<td>8.8E-02</td>
<td>15 (9)</td>
</tr>
<tr>
<td>10</td>
<td>C(<em>{12})H(</em>{10})O(_4) (218.0579)</td>
<td><img src="image10" alt="Proposed structure 10" /></td>
<td>4.7E-03</td>
<td>14 (10)</td>
</tr>
<tr>
<td>11</td>
<td>C(<em>{4})H(</em>{6})O(_5) (134.0215)</td>
<td><img src="image11" alt="Proposed structure 11" /></td>
<td>5.2E+00</td>
<td>0.0 (N/A)</td>
</tr>
<tr>
<td>12</td>
<td>C(<em>{11})H(</em>{10})O(_8) (270.0376)</td>
<td><img src="image12" alt="Proposed structure 12" /></td>
<td>4.7E-11</td>
<td>0.0 (N/A)</td>
</tr>
<tr>
<td></td>
<td>Molecular Formulas and Proposed Structures of 16 Compounds Identified According to (-) Nano-DESI Spectra. They Represent the Top 10 Most Abundant aqSOA Compounds Observed at Each Reaction Stage. The Exact Molecular Weight of Each Compound Is Shown in Parentheses.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Estimated Saturation Concentrations (C^*, µg m^3) of the Compounds at 25 °C, 1 atm, Determined Using the Nannoolal Vapor Pressure and Extrapolation Method.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Relative Abundances (%) of the Compounds and, in Parentheses, Their Abundance Ranks Counted in the Sorted Relative Abundance List of All the Compounds Identified in the Nano-DESI Mass Spectrum of the Specified Time Period.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>C_4H_6O_4 (118.0266)</td>
<td><img src="image" alt="Proposed Structure" /></td>
<td>2.3E+03</td>
<td>0.0 (N/A)</td>
</tr>
<tr>
<td>14</td>
<td>C_6H_8O_6 (176.0321)</td>
<td><img src="image" alt="Proposed Structure" /></td>
<td>3.1E+04</td>
<td>9.0 (19)</td>
</tr>
<tr>
<td>15</td>
<td>C_4H_4O_4 (116.0110)</td>
<td><img src="image" alt="Proposed Structure" /></td>
<td>1.1E+03</td>
<td>1.6 (48)</td>
</tr>
<tr>
<td>16</td>
<td>C_5H_6O_6 (162.0164)</td>
<td><img src="image" alt="Proposed Structure" /></td>
<td>5.0E-02</td>
<td>1.8 (44)</td>
</tr>
</tbody>
</table>
Table S6 Most abundant compounds identified in SYR aqSOA formed at different stages of the $^{3}$C*-mediated reactions using (+) nano-DESI MS.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula$^{a}$</th>
<th>Proposed structure</th>
<th>$C^*$ ($\mu$g m$^{-3}$) at 25 °C, 1 atm$^{b}$</th>
<th>Relative abundance (%) (ranking)$^{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P1: 0-2 hrs</td>
<td>P2: 2-4 hrs</td>
</tr>
<tr>
<td>1</td>
<td>C$<em>{16}$H$</em>{18}$O$_{6}$ (306.1103)</td>
<td><img src="image1" alt="Proposed structure" /></td>
<td>3.1E-03</td>
<td>100 (1)</td>
</tr>
<tr>
<td>2</td>
<td>C$<em>{15}$H$</em>{18}$O$_{7}$ (310.1052)</td>
<td><img src="image2" alt="Proposed structure" /></td>
<td>1.7E-05</td>
<td>78.1 (2)</td>
</tr>
<tr>
<td>3</td>
<td>C$<em>{10}$H$</em>{8}$O$_{3}$ (176.0473)</td>
<td><img src="image3" alt="Proposed structure" /></td>
<td>2.3E-09</td>
<td>43.2 (3)</td>
</tr>
<tr>
<td>4</td>
<td>C$<em>{12}$H$</em>{14}$O$_{4}$ (222.0892)</td>
<td><img src="image4" alt="Proposed structure" /></td>
<td>2.1E-09</td>
<td>18.7 (4)</td>
</tr>
<tr>
<td>5</td>
<td>C$<em>{14}$H$</em>{16}$O$_{6}$ (278.0790)</td>
<td><img src="image5" alt="Proposed structure" /></td>
<td>2.5E-05</td>
<td>14.5 (5)</td>
</tr>
<tr>
<td>6</td>
<td>C$<em>{13}$H$</em>{16}$O$_{5}$ (250.0841)</td>
<td><img src="image6" alt="Proposed structure" /></td>
<td>2.0E-12</td>
<td>8.7 (6)</td>
</tr>
<tr>
<td>7</td>
<td>C$<em>{13}$H$</em>{14}$O$_{7}$ (282.0740)</td>
<td><img src="image7" alt="Proposed structure" /></td>
<td>5.8E-08</td>
<td>7.2 (7)</td>
</tr>
<tr>
<td>8</td>
<td>C$<em>{16}$H$</em>{18}$O$_{7}$ (322.1053)</td>
<td><img src="image8" alt="Proposed structure" /></td>
<td>1.7E-05</td>
<td>6.2 (8)</td>
</tr>
<tr>
<td></td>
<td>Formula</td>
<td>Molecular Weight</td>
<td>pIC</td>
<td>Design</td>
</tr>
<tr>
<td>---</td>
<td>-----------</td>
<td>------------------</td>
<td>-----</td>
<td>--------</td>
</tr>
<tr>
<td>9</td>
<td>C₁₅H₁₆O₆</td>
<td>292.0946</td>
<td>3.4E-04</td>
<td>5.3 (9)</td>
</tr>
<tr>
<td>10</td>
<td>C₁₅H₁₉O₁₀</td>
<td>358.0900</td>
<td>1.5E-13</td>
<td>4.8 (10)</td>
</tr>
<tr>
<td>11</td>
<td>C₄H₁₀O₆</td>
<td>202.0477</td>
<td>5.9E-02</td>
<td>4.5 (11)</td>
</tr>
<tr>
<td>12</td>
<td>C₃H₁₀O₂</td>
<td>218.0427</td>
<td>4.2E-02</td>
<td>0.8 (42)</td>
</tr>
<tr>
<td>13</td>
<td>C₁₅H₁₈O₉</td>
<td>340.0794</td>
<td>3.9E-12</td>
<td>3.9 (12)</td>
</tr>
<tr>
<td>14</td>
<td>C₈H₁₀O₃</td>
<td>148.0160</td>
<td>7.3E-06</td>
<td>0.0 (N/A)</td>
</tr>
<tr>
<td>15</td>
<td>C₁₅H₁₈O₉</td>
<td>342.0950</td>
<td>6.6E-21</td>
<td>2.3 (17)</td>
</tr>
<tr>
<td>16</td>
<td>C₂H₁₂O₇</td>
<td>208.0583</td>
<td>N/A</td>
<td>1.0 (33)</td>
</tr>
<tr>
<td>17</td>
<td>C₁₄H₁₆O₁₀</td>
<td>344.0743</td>
<td>2.7E-14</td>
<td>0.6 (46)</td>
</tr>
<tr>
<td>18</td>
<td>C₁₄H₁₆O₉</td>
<td>328.0794</td>
<td>7.6E-11</td>
<td>0.8 (39)</td>
</tr>
<tr>
<td>19</td>
<td>C_{14}H_{16}O_{8} (312.0845)</td>
<td>2.5E-08</td>
<td>0.9 (35)</td>
<td>6.2 (22)</td>
</tr>
</tbody>
</table>

*a* Molecular formulas and proposed structures of 19 compounds identified according to (+) nano-DESI spectra. They represent the top 10 most abundant aqSOA compounds observed at each reaction stage. The exact molecular weight of each compound is shown in parentheses.

*b* Estimated saturation concentrations (C*, μg m⁻³) of the compounds at 25 °C, 1 atm, determined using the Nannoolal vapor pressure and extrapolation method.

*c* Relative abundances (%) of the compounds and, in parentheses, their abundance ranks counted in the sorted relative abundance list of all the compounds identified in the nano-DESI mass spectrum of the specified time period.
Figure S1. Evolution of concentrations of 3,4-DMB as a function of reaction time during individual experiments. Different reaction conditions are represented by corresponding colors.
Figure S2. The signal-weighted distributions of (a-b) SYR, (c-d) GUA, and (e-f) PhOH aqSOA formed during three different stages of the $^3$C*- and •OH-mediated reactions, respectively, based on the degree of oligomerization. The data are from the (–) nano-DESI MS spectra.
Figure S3. OSC and nC of SYR aqSOA formed during different stages of •OH-mediated reactions determined based on (-) nano-DESI MS spectra. Signals are colored by the relative abundance of the molecules. The black star at nC = 8 represents SYR. The shaded ovals indicate locations of different ambient organic aerosol classes reported in Kroll et al. (2011).
Figure S4. OSC and nC of GUA aqSOA formed during different stages of ^3^C*-mediated reactions determined based on (-) nano-DESI MS spectra. Signals are colored by the relative abundance of the molecules. The black star at nC = 7 represents GUA. The shaded ovals indicate locations of different ambient organic aerosol classes reported in Kroll et al. (2011).
**Figure S5.** OS$_C$ and $n_C$ of GUA aqSOA formed during different stages of •OH-mediated reactions determined based on (-) nano-DESI MS spectra. Signals are colored by the relative abundance of the molecules. The black star at $n_C = 7$ represents GUA. The shaded ovals indicate locations of different ambient organic aerosol classes reported in Kroll et al. (2011).
Figure S6. $O_{SC}$ and $n_C$ of PhOH aqSOA formed during different stages of $^{3}$C*-mediated reactions determined based on (-) nano-DESI MS spectra. Signals are colored by the relative abundance of the molecules. The black star at $n_C = 6$ represents PhOH. The shaded ovals indicate locations of different ambient organic aerosol classes reported in Kroll et al. (2011).
Figure S7. OSc and nC of PhOH aqSOA formed during different stages of •OH-mediated reactions determined based on (-) nano-DESI MS spectra. Signals are colored by the relative abundance of the molecules. The black star at nC = 6 represents PhOH. The shaded ovals indicate locations of different ambient organic aerosol classes reported in Kroll et al. (2011).
References


