



*Supplement of*

## **Molecular composition of aged secondary organic aerosol generated from a mixture of biogenic volatile compounds using ultrahigh resolution mass spectrometry**

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Table S1. Tentative assignments of the major LC/MS peaks in SOA from dark ozonolysis of the BVOC mixture containing  $\alpha$ -,  $\beta$ -pinene,  $\Delta_3$ -carene and isoprene.

Retention time, min	Measured [M-1]	Molecular formula	Tentative assignment <sup>ref</sup>	Source
<b>monomers</b>				
19.2	187.06097	C <sub>8</sub> H <sub>12</sub> O <sub>5</sub>	unknown terpenoic acid <sup>1,2</sup>	$\alpha$ -, $\beta$ -pinene
21.17	157.05040	C <sub>7</sub> H <sub>9</sub> O <sub>4</sub>	terebic acid <sup>1,2,3</sup>	$\alpha$ -, $\beta$ -pinene, $\Delta_3$ -carene
22.9	171.06609	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	terpenylic acid <sup>1,2,3</sup>	$\alpha$ -, $\beta$ -pinene, $\Delta_3$ -carene
24.14	203.05582	C <sub>8</sub> H <sub>12</sub> O <sub>6</sub>	MBTCA <sup>2,3,4,5</sup>	$\alpha$ -pinene
25.98	185.08191	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	homoterpenylic acid <sup>1,2,3</sup>	$\alpha$ -, $\beta$ -pinene, $\Delta_3$ -carene
26.7	215.09230	C <sub>10</sub> H <sub>16</sub> O <sub>5</sub>	Unknown <sup>2,6</sup>	$\alpha$ -pinene
29.43	231.08711	C <sub>10</sub> H <sub>16</sub> O <sub>6</sub>	diaterpenylic acid acetate (DTA) <sup>2,3</sup>	$\alpha$ -, $\beta$ -pinene
30.38	185.08167	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	<i>cis</i> -pinic acid <sup>2,3,7,8,9</sup>	$\alpha$ -, $\beta$ -pinene
32.58	185.08168	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	<i>cis</i> -caric acid <sup>2,3</sup>	$\alpha$ -, $\beta$ -pinene, $\Delta_3$ -carene
33.34	169.08710	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	3-norcaronic acid <sup>2,7</sup>	$\Delta_3$ -carene
34.05	183.10248	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	<i>cis</i> -pinonic acid <sup>1,2,3,10</sup>	$\alpha$ -, $\beta$ -pinene
36.46	187.09731	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	2-hydroxyterpenylic acid <sup>2,3</sup>	$\alpha$ -, $\beta$ -pinene
<b>Dimers</b>				
35.12	343.13983	C <sub>16</sub> H <sub>23</sub> O <sub>8</sub>	Pinyl-diaterebyl ester MW 344 <sup>11,12,13</sup>	$\alpha$ -, $\beta$ -pinene
37.42	357.15509	C <sub>17</sub> H <sub>26</sub> O <sub>8</sub>	Pinyl-diaterpenyl ester MW 358 <sup>11,12,13</sup>	$\alpha$ -, $\beta$ -pinene
38.36	357.15509	C <sub>17</sub> H <sub>26</sub> O <sub>8</sub>	Pinyl-diaterpenyl ester MW 358 <sup>11,12,13</sup>	$\alpha$ -, $\beta$ -pinene
40.15	367.17599	C <sub>19</sub> H <sub>28</sub> O <sub>7</sub>	Pinonyl-pinyl ester MW 368 <sup>11,12,13</sup>	$\alpha$ -, $\beta$ -pinene
40.68	367.17599	C <sub>19</sub> H <sub>28</sub> O <sub>7</sub>	Pinonyl-pinyl ester MW 368 <sup>11,12,13,14</sup>	$\alpha$ -, $\beta$ -pinene
41.58	387.20221	C <sub>19</sub> H <sub>31</sub> O <sub>8</sub>	MW 388 dimer ester <sup>11,12,13</sup>	$\alpha$ -, $\beta$ -pinene
45.53	337.20172	C <sub>19</sub> H <sub>30</sub> O <sub>5</sub>	MW 337 dimer ester	unknown
46.17	337.20172	C <sub>10</sub> H <sub>18</sub> O <sub>5</sub>	MW 337 dimer ester	unknown
42.76	369.19141	C <sub>19</sub> H <sub>29</sub> O <sub>7</sub>	MW 369 dimer ester	unknown

References: (1) Gómez-González et al. (2012); (2) Kourtchev et al. (2014); (3) Yasmeen et al. (2011); (4) Szmigielski et al. (2007); (5) Müller et al. (2012); (6) Putman et al. (2011); (7) Yu et al. (1999); (8) Glasius et al. (2000); (9) Carmedon et al. (2010); (10) Christoffersen et al. (1998); (11) Yasmeen et al. (2010); (12) Kristensen et al. (2013); (13) Kristensen et al. (2014); (14) Müller et al. (2008).

Table S2. P values derived from ANOVA test of variations in relative dimer to SOA concentrations at different ageing conditions.

Ageing condition	m/z 357	m/z 337	m/z 343	m/z 367	m/z 387	m/z 369
dark ageing	0.98	0.854	1	0.979	0.395	0.949
UV&OH ageing	0.829	0.333	0.533	0.533	0.8	0.933
UV-only ageing	0.933	0.933	0.933	0.933	0.533	0.933

p $\geq$ 0.05 indicates no significant difference between the treatments.

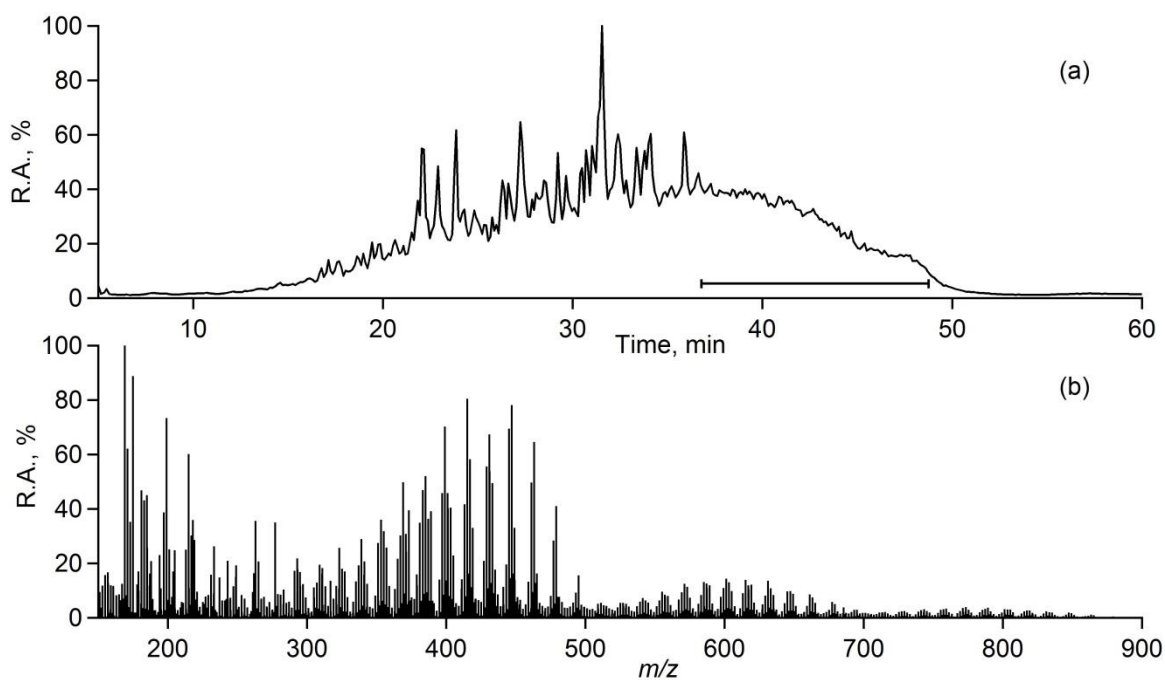


Fig. SI 1. (a) Total Ion Chromatogram of SOA from OH-initiated reaction with  $\alpha$ -pinene; (b) (-) ESI-UHR mass spectra showing high molecular weight compounds obtained by integration of chromatographic 'hump' between 36 and 48 min.

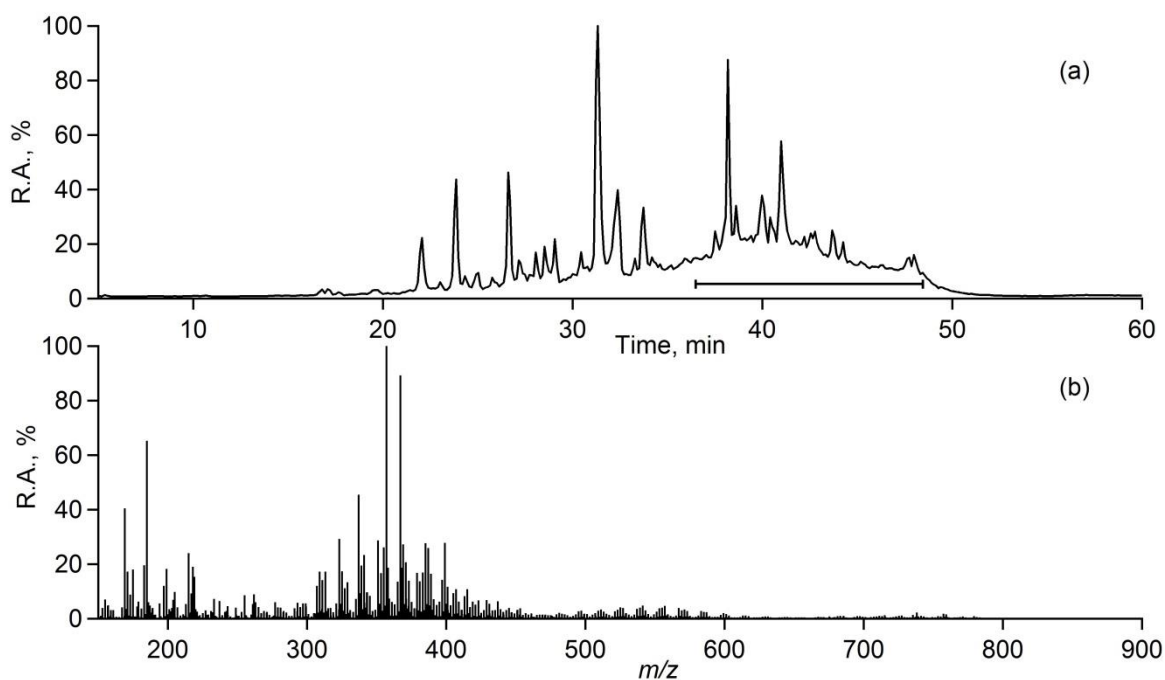


Fig. SI 2. (a) Total Ion Chromatogram of SOA from dark ozonolysis reaction with  $\alpha$ -pinene in the presence of OH scavenger; (b) (-) ESI-UHR mass spectra showing high molecular weight compounds obtained by integration of chromatographic 'hump' between 36 and 48 min. The resolved chromatographic peaks in (a) correspond to dimers with  $m/z$  357;  $m/z$  367 and  $m/z$  387.

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