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Supplement of

Secondary organic aerosol formation and composition from the photo-oxidation of methyl chavicol (estragole)

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Supplementary Information.

Table S1 – The molecular formulae (MF) and associated errors of the identified SOA compounds in experiment MC_{high} using FTICR-MS and HPLC-QTOFMS in negative ionisation mode.

t_R	MW [g mol^{-1}]	FTICR-MS MF	Error [ppm]	Score [%]	HPLC-QTOFMS MF	Error [ppm]	Score [%]
14.3	138				$C_7H_6O_3$	-9.7	100
30.1	152	$C_8H_8O_3$†	0.3	100	$C_8H_8O_3$	-1.4	100
28.1	166	$C_9H_{10}O_3$	0.8	100	$C_9H_{10}O_3$	1.2	100
33	168	$C_8H_8O_4$	0.7	100	$C_8H_8O_4$	0.2	100
12.5	180	$C_9H_8O_4$	0.9	100	$C_9H_8O_4$	2.6	100
16.1	182	$C_9H_{10}O_4$	0.8	100	$C_9H_{10}O_4$	-0.3	100
17.6	191	$C_{10}H_9NO_3$	0.7	100	$C_{10}H_9NO_3$	-3.2	100
33.7	194	$C_{11}H_{14}O_3$	0	100	$C_{11}H_{14}O_3$	-0.9	0
25.2	196	$C_{10}H_{12}O_4$	1	100	$C_{10}H_{12}O_4$	2.5	100
20.2	198	$C_{10}H_{14}O_4$†	0.9	100	$C_{10}H_{14}O_4$	2.4	100
20.7	199	$C_8H_9NO_5$	0.2	100	$C_8H_9NO_5$	-0.2	100
39.6	209	$C_{10}H_{11}NO_4$†	0	100	$C_{10}H_{11}NO_4$	4.3	100
27.8	210	$C_{11}H_{14}O_4$	0.9	100	$C_{11}H_{14}O_4$	1.4	100
21.3	213	$C_9H_{11}NO_5$	0.7	100	$C_9H_{11}NO_5$	0.5	100
21	214	$C_{11}H_{18}O_4$	0.4	100	$C_{11}H_{18}O_4$	2	100
18.6	236	$C_8H_{12}O_8$†	0.5	100	$C_8H_{12}O_8$	36.6	0.13
31.8	238	$C_{12}H_{14}O_5$	0.9	100	$C_{12}H_{14}O_5$	9.9	100
22.2	243	$C_{10}H_{13}NO_6$	0.6	100	$C_{10}H_{13}NO_6$	-0.7	100
35.9	252	$C_{13}H_{16}O_5$	1.6	100	$C_{13}H_{16}O_5$	8.1	30.3
12.8	277	$C_9H_{11}NO_9$	0.2	100	$C_9H_{11}NO_9$	0.9	100
28.8	292	$C_{15}H_{16}O_6$	1.2	100			
23.3	296	$C_{18}H_{16}O_4$	-6.8	100	$C_{18}H_{16}O_4$	3.5	100
36.1	317	$C_{16}H_{15}NO_6$	-0.3	100	$C_{16}H_{15}NO_6$	1.8	100
36.2	428	$C_{18}H_{20}O_{12}$	-0.1	100	$C_{18}H_{20}O_{12}$	-0.8	100

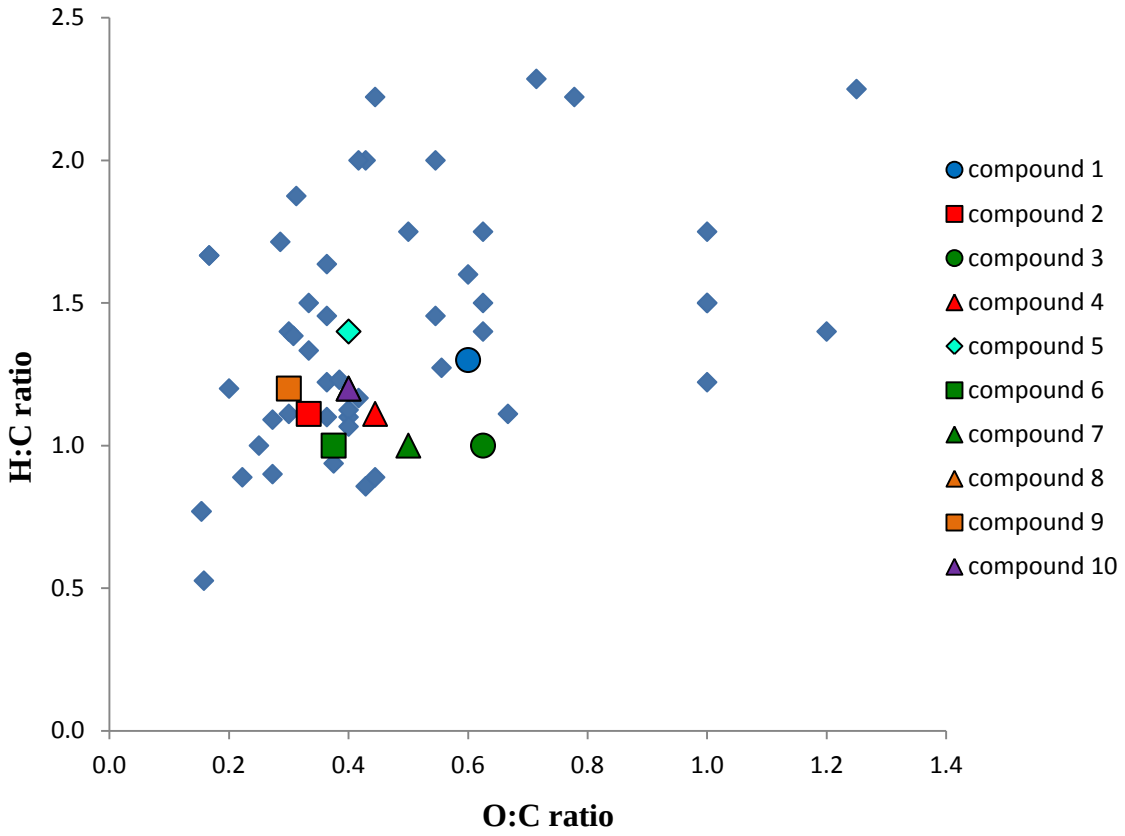
Error = displayed in ppm and calculated by taking the difference between the exact and measured mass for the assigned molecular formula; dividing the difference by the exact mass and multiplying by 10^6. MF score = the fit of the theoretical and measured isotopic distribution and abundance for the assigned molecular formula (displayed in percent). † Compound observed in both positive and negative ionisation mode.

Table S2 – The molecular formulae (MF) and associated errors of the identified SOA compounds in experiment MC_{high} using FTICR-MS and HPLC-QTOFMS in positive ionisation mode.

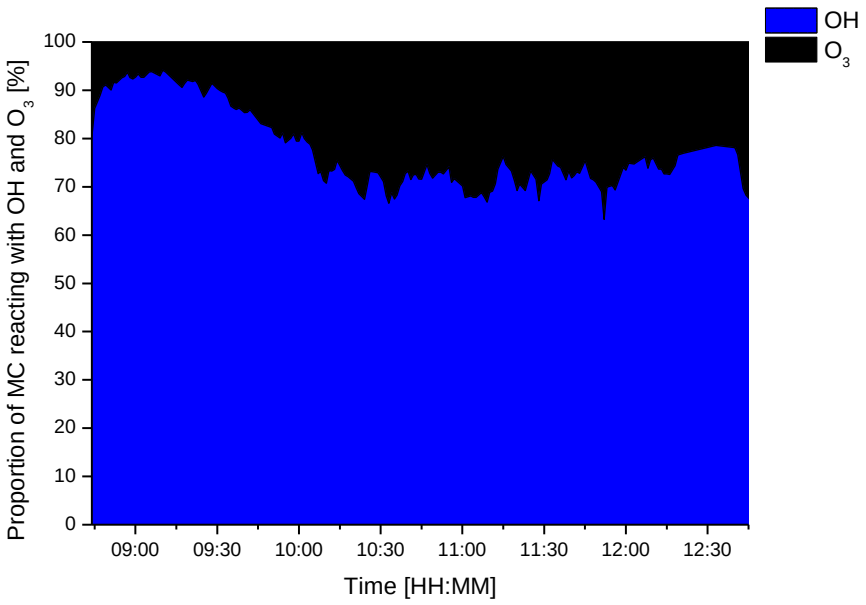
t_R	MW [g mol^{-1}]	FTICR-MS MF	Error [ppm]	Score [%]	HPLC-QTOFMS MF	Error [ppm]	Score [%]
34.3	98				$C_6H_{10}O$*	18	100
36.4	98				$C_6H_{10}O$*	14	100
33.7	120				$C_4H_7O_4$	31.3	100
28.2	146	$C_7H_{14}O_3$	-1.9	100	$C_8H_{12}O$*	30.1	100
18.5	151				$C_4H_9NO_5$	-21.2	100
30.2	152	$C_8H_8O_3$†	1.2	100	$C_8H_8O_3$	2.5	100
27.3	164				$C_{10}H_{12}O_2$	16.6	100
12.1	168	$C_9H_{12}O_3$*	4.7	100	$C_9H_{12}O_3$*	12.1	100
27.9	170	$C_8H_{10}O_4$*	4.4	100	$C_{11}H_{12}O_3$	-2.6	100
20.5	174				$C_8H_{14}O_4$*	-5.5	100
14.5	177				$C_5H_7NO_6$	-26.2	100
22.5	180	$C_{10}H_{12}O_3$*	4.3	100	$C_{10}H_{12}O_3$*	2	100
27.6	180				$C_{10}H_{12}O_3$	-7.8	100
36	180	$C_{10}H_{12}O_3$*	4.2	100	$C_7H_{16}O_5$*	2.9	100
33.5	182	$C_{10}H_{14}O_3$*	4.4	100	$C_{10}H_{14}O_3$*	-43.3	1.2
10.2	184				$C_8H_8O_5$	48	0
15.7	188	$C_8H_{12}O_5$*	4.6	100	$C_8H_{12}O_5$*	-3.8	100
19	190	$C_8H_{14}O_5$*	5.1	100	$C_8H_{14}O_5$*	-0.8	100
41.2	192	$C_9H_{20}O_4$*	3.9	100	$C_9H_{20}O_4$*	37.7	100

19.8	196	$C_{10}H_{12}O_4$*	5	100	$C_{10}H_{12}O_4$*	9.4	100
10.8	198	$C_{13}H_{10}O_2$*	4.2	100	$C_{13}H_{10}O_2$*	-27.8	0.3
14.1	198	$C_{13}H_{10}O_2$*	3.9	100	$C_{13}H_{10}O_2$*	22.9	3.1
16.3	198	$C_{10}H_{14}O_4$*	4.2	100	$C_{10}H_{14}O_4$*	24	100
20.2	198	$C_{10}H_{14}O_4$*†	4.2	90.1	$C_{10}H_{14}O_4$*	1.3	100
14.8	204	$C_{12}H_{12}O_3$*	16	100			
39.7	209	$C_{10}H_{11}NO_4$†	0.9	100	$C_{10}H_{11}NO_4$	6.9	100
33	212	$C_{11}H_{16}O_4$*	5.1	100	$C_{10}H_{18}O_6$	23.4	0.5
21.4	214	$C_{11}H_{18}O_4$*	5	100			
20.9	226	$C_{12}H_{18}O_4$*	5.4	100	$C_{12}H_{18}O_4$*	48	0
30.4	232	$C_{10}H_{16}O_6$	5.3	100	$C_{10}H_{16}O_6$	-10.7	100
18.8	237	$C_8H_{12}O_8$†	-2.9	100	$C_8H_{12}O_8$	5.5	100
33.8	238	$C_{13}H_{18}O_4$*	5.4	100	$C_{13}H_{18}O_4$*	33.1	0
41.5	240	$C_9H_{14}O_6$*	5	100	$C_9H_{20}O_7$	-1.9	0
17.1	244	$C_{11}H_{16}O_6$*	5.6	100			
47.4	248	$C_{12}H_{24}O_5$*	4.7	100	$C_{12}H_{24}O_5$*	43.2	0
37.7	250	$C_{11}H_{22}O_6$*	6.2	100	$C_{11}H_{22}O_6$*	-17.4	4.1
43.2	256	$C_{14}H_{24}O_4$*	-3.3	100	$C_{14}H_{24}O_4$*	6.6	100
8.9	286	$C_{19}H_{10}O_3$	5.2	100	$C_{19}H_{10}O_3$	43.7	0
44	302	$C_{16}H_{30}O_5$*	6.2	100	$C_{16}H_{30}O_5$*	8	92

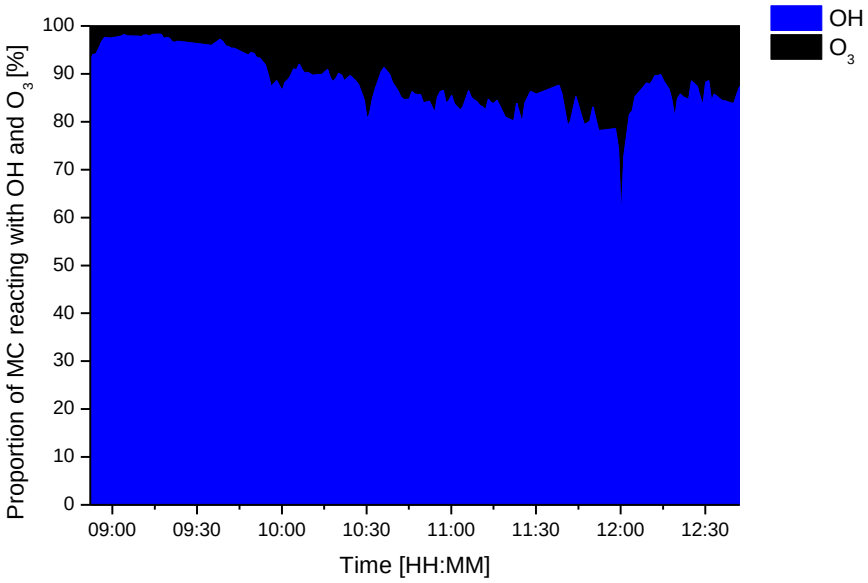
* Identified as $[M+Na]^+$, the Na adduct has been removed from molecular formula and the molecular weight corrected. Error = displayed in ppm and calculated by taking the difference between the exact and measured mass for the assigned molecular formula; dividing the difference by the exact mass and multiplying by 10^6. MF score = the fit of the theoretical and measured isotopic distribution and abundance for the assigned molecular formula (displayed in percent). † Compound observed in both positive and negative ionisation mode.



SI Figure 1 – Van Krevelen plot of the 59 SOA compounds observed in MC_{high}. Blue diamond's represent structurally unidentified compounds. Legend shows the structurally identified compounds 1 to 10, refer to Table 2 for compound identification. For the structurally identified compounds only; related generations of compounds are shown in the same colour. The change of shape but use of the same colour indicates a change in the SOA compound structure through the reaction with $^{\bullet}OH$ radicals or NO_2. Compounds 8 and 10 are structural isomers; compound 8 is hidden by compound 10.



SI Figure 2 – Proportion of methyl chavicol (MC) reacting with $^{\bullet}OH$ and O_3 at each measured time point during $MC_{high.}$ The proportion of methyl chavicol reacting with $^{\bullet}OH$ and O_3 was calculated using Eq.1 and Eq.2, respectively.



SI Figure 3 – Proportion of methyl chavicol (MC) reacting with $^{\bullet}OH$ and O_3 at each measured time point during $MC_{low.}$ The proportion of methyl chavicol reacting with $^{\bullet}OH$ and O_3 was calculated using Eq.1 and Eq.2, respectively.

Eq.1 $$\% OH = \left(\frac{k_{MC+OH}[OH]}{(k_{MC+OH}[OH] + k_{MC+O_3}[O_3])}\right) x\ 100$$

Eq.2 $$\% O_3 = \left(\frac{k_{MC+O3}[O_3]}{(k_{MC+O3}[O_3] + k_{MC+OH}[OH])}\right) x\ 100$$

$k_{MC + OH}$ = rate constant of the reaction of methyl chavicol with OH (cm^3 $molecule^{-1}$ s^{-1})

$k_{MC + O3}$ = rate constant of the reaction of methyl chavicol with O_3 (cm^3 $molecule^{-1}$ s^{-1})

[OH] = concentration of OH (ppbv)

[O_3] = concentration of O_3 (ppbv)