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Supplement of

Highly oxygenated molecules (HOMs) and secondary organic aerosol (SOA) formation from the oxidation of α- and β-phellandrenes by NO_3 radicals

Sergio Harb et al.

Correspondence to: Sergio Harb (sergio.harb@ineris.fr) and Bénédicte Picquet-Varrault (benedicte.picquet-varrault@lisa.ipsl.fr)

Supporting Information

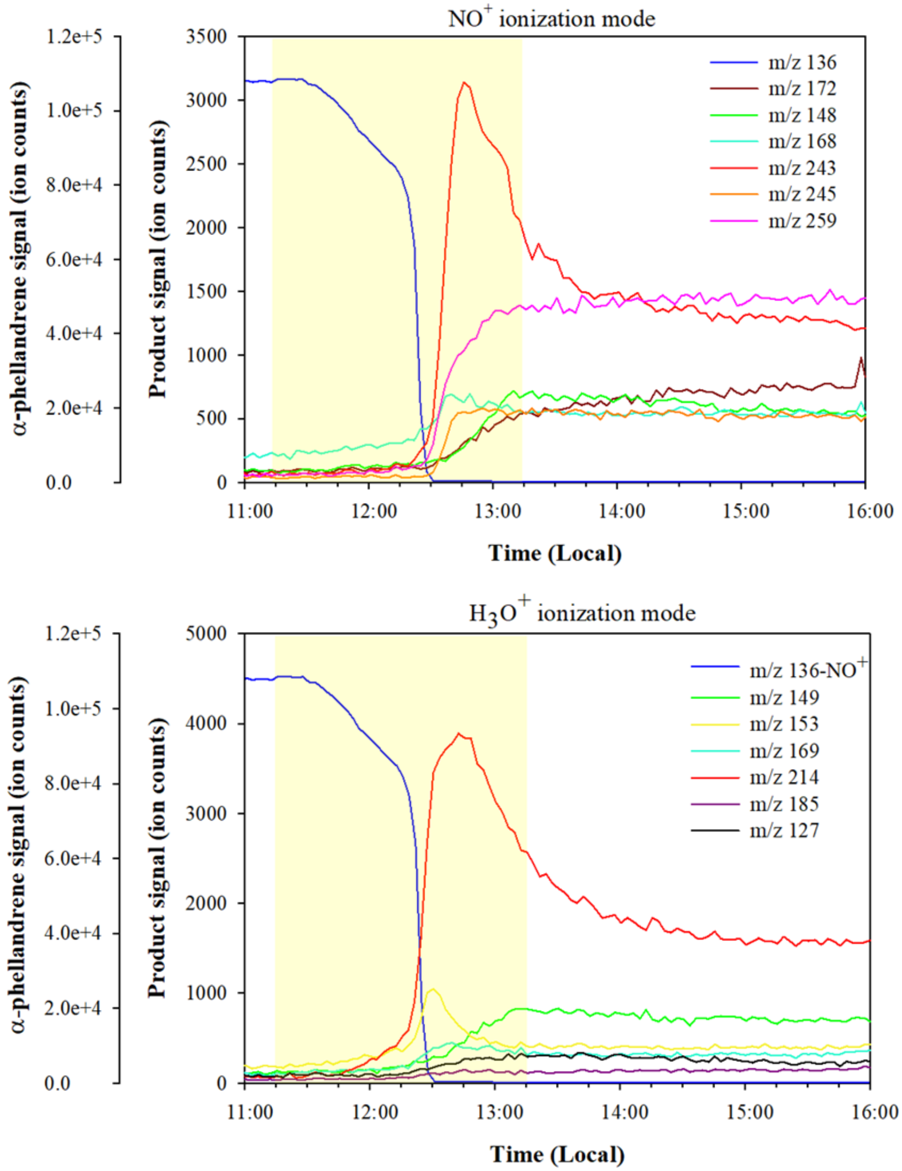

Figure S1: Example of typical time profiles of α-phellandrene and products detected with PTR-ToF-MS (NO^+ and H_3O^+ ionization modes) for Experiment 7. The N_2O_5 injection period is shown by the yellow area.

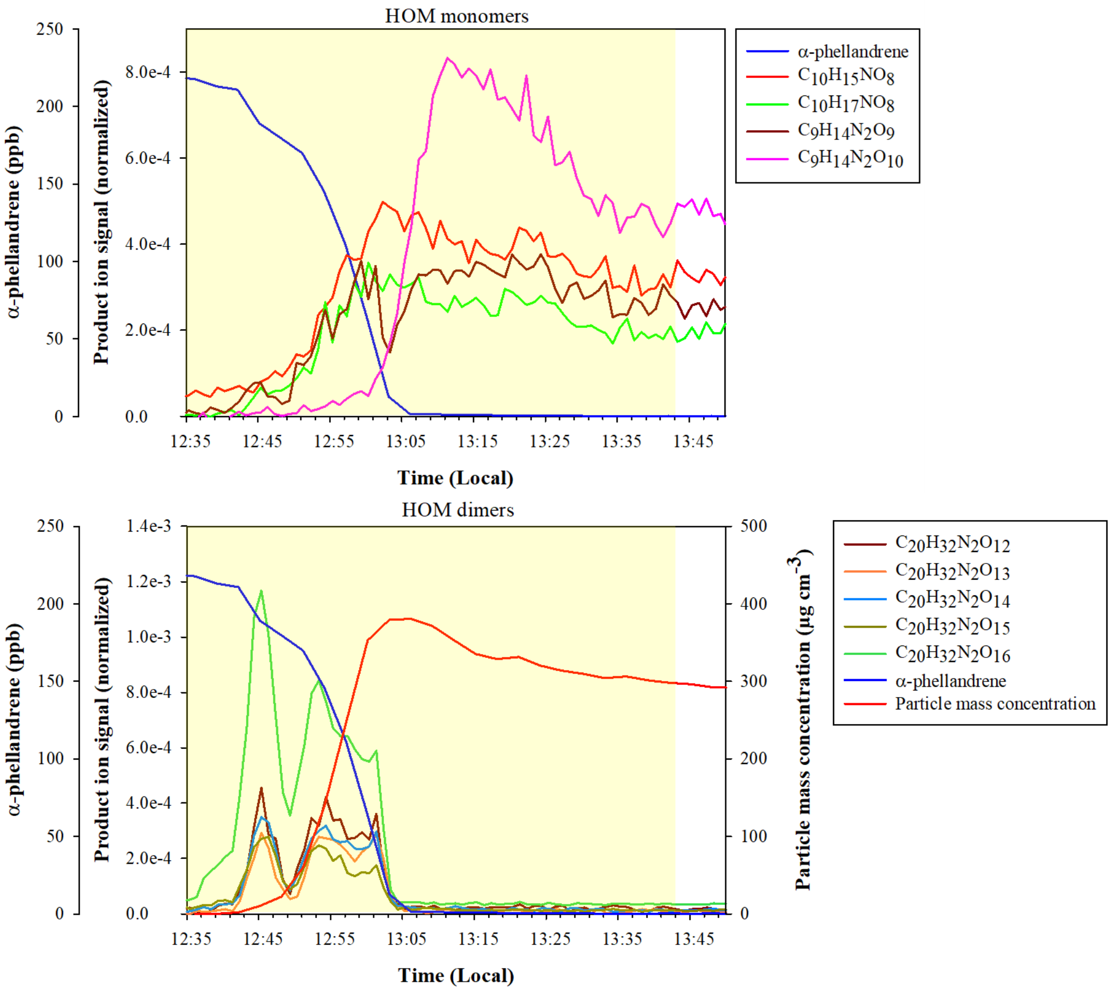

Figure S2: Time profiles of a selection of gas-phase HOM monomers and dimers produced by the oxidation of α-phellandrene by NO_3 radical (Experiment 6). The N_2O_5 injection period is shown by the yellow area. Further oxidation of some formed products could occur after complete BVOC consumption, which may explain the observed downward slope in some traces of HOM monomers.

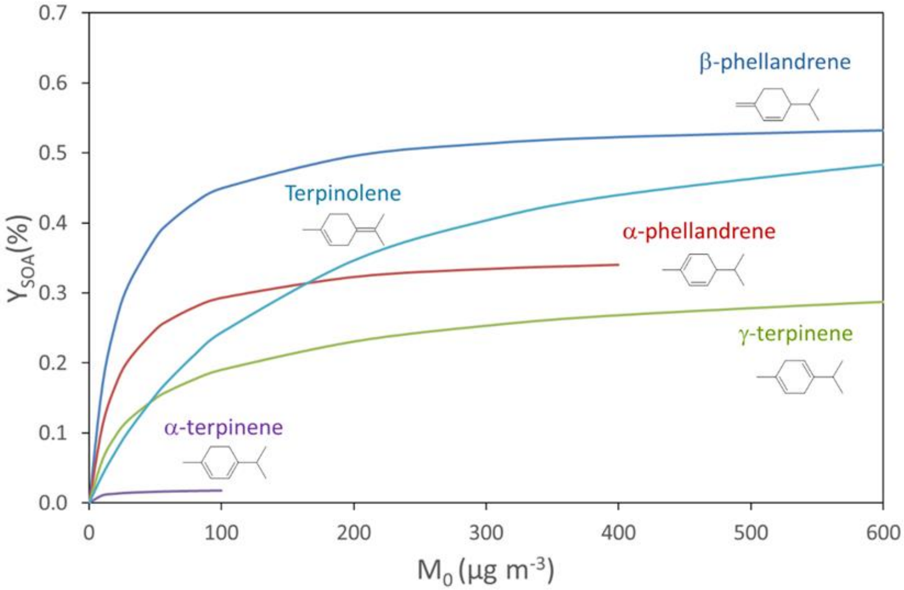

Figure S3: Odum parametrization describing the dependence of the SOA yields with the aerosol content (in µg/m³) for α- and β-phellandrenes (this study), α- and γ-terpinenes (Fouqueau et al., 2020) and terpinolene (Fouqueau et al., 2022).

Table S1: Products detected by PTR-ToF-MS in H_3O^+ and NO^+ ionization modes for the oxidation by NO_3 radical of α- and β-phellandrenes: raw formula, molecular weight, detected mass, ionization process (H^+ as proton adduct; NO^+ as NO^+ adduct; CT as charge transfer), and behavior.

Molecule		**H_3O^+ ionization mode**			**NO^+ ionization mode**		
Raw formula	**M (g mol^{-1})**	**m/z**	**Process**	**Behavior**	**m/z**	**Process**	**Behavior**
α-phellandrene							
C_3H_6O	58	59.0383	H^+	Primary-Secondary	88.0268	NO^+	Primary-Secondary
$C_3H_4O_2$	72	73.0133	H^+	Secondary	102.0035	NO^+	Secondary
$C_7H_{10}O_2$	126	127.0457	H^+	Secondary	/	/	/
$C_7H_{12}O_2$	128	129.0452	H^+	Secondary	/	/	/
$C_5H_{10}O_4$	134	/	/	/	164.0281	NO^+	Secondary
$C_7H_{10}O_3$	142	/	/	/	172.0275	CT	Secondary
$C_6H_{12}O_4$	148	149.0441	H^+	Secondary	148.0484	CT	Secondary
$C_{10}H_{16}O$	152	153.0848	H^+	Primary	/	/	/
$C_{10}H_{16}O_2$	168	169.0742	H^+	Primary	168.0816	CT	Primary
$C_{10}H_{16}O_3$	184	185.0637	H^+	Secondary	/	/	/
$C_{10}H_{15}NO_4$	213	214.0419	H^+	Primary	243.0469	NO^+	Primary

$C_{10}H_{15}NO_5$	229	230.0278	H^+	Primary	259.0345	NO^+	Primary
$C_{10}H_{15}NO_6$	245	/	/	/	245.0431	CT	Secondary
β-phellandrene							
C_3H_6O	58	59.0365	H^+	Primary	88.0198	NO^+	Primary
$C_7H_{12}O_2$	128	129.0438	H^+	Secondary	128.0340	CT	Secondary
$C_5H_{10}O_4$	134	/	/	/	164.0050	NO^+	Secondary
$C_3H_3NO_5$	133	/	/	/	163.9707	NO^+	Secondary
$C_9H_{14}O$	138	139.0622	H^+	Primary	/	/	/
$C_6H_{12}O_4$	148	149.0394	H^+	Primary	/	/	/
$C_{10}H_{16}O$	152	153.0670	H^+	Primary	/	/	/
$C_{10}H_{16}O_2$	168	169.0610	H^+	Primary	168.0551	CT	Primary
$C_9H_{13}O_3$	170	171.0396	H^+	Secondary	/	/	/
$C_{10}H_{15}NO_4$	213	214.0263	H^+	Primary	/	/	/
$C_{10}H_{15}NO_5$	229	230.0278	H^+	Detected	/	/	/

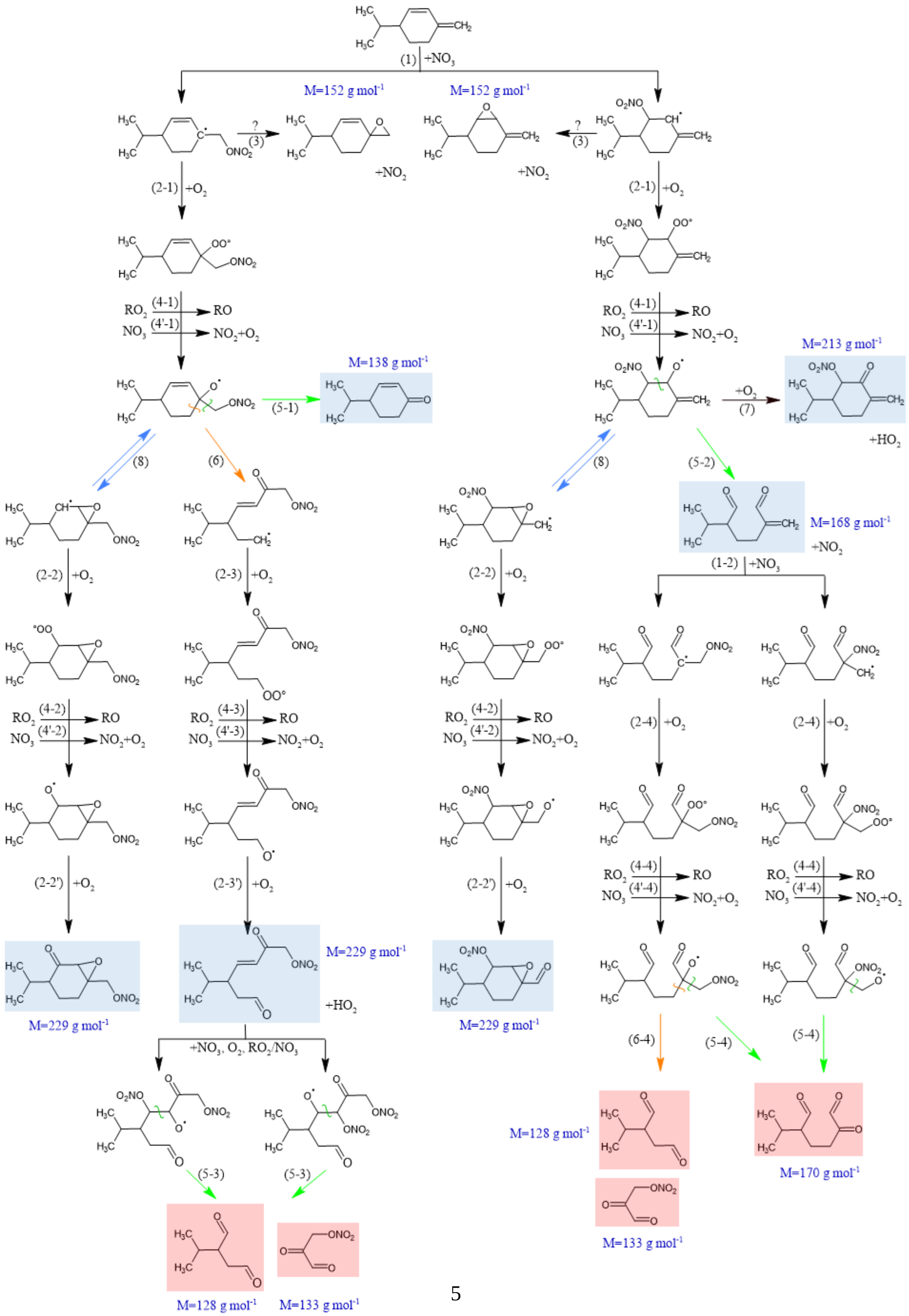
(1) +NO3
M=152 g mol-1
M=152 g mol-1
? (3)
+NO2
(2-1) +O2
RO2 (4-1) RO
NO3 (4'-1) NO2+O2
M=138 g mol-1
(5-1)
+O2 (7)
M=213 g mol-1
+HO2
(8)
(6)
(5-2)
M=168 g mol-1
+NO2
(1-2) +NO3
(2-2) +O2
(2-3) +O2
(2-4) +O2
RO2 (4-2) RO
NO3 (4'-2) NO2+O2
RO2 (4-3) RO
NO3 (4'-3) NO2+O2
RO2 (4-4) RO
NO3 (4'-4) NO2+O2
(2-2') +O2
(2-3') +O2
M=229 g mol-1
M=229 g mol-1
M=229 g mol-1
+HO2
+NO3, O2, RO2/NO3
(5-3)
(6-4)
(5-4)
M=128 g mol-1
M=133 g mol-1
M=128 g mol-1
M=133 g mol-1
M=170 g mol-1

Figure S4: Mechanism proposed to explain the formation of first-generation products (colored in blue) and second-generation products (colored in red) detected by PTR-ToF-MS for the reaction of β-phellandrene+NO_3.

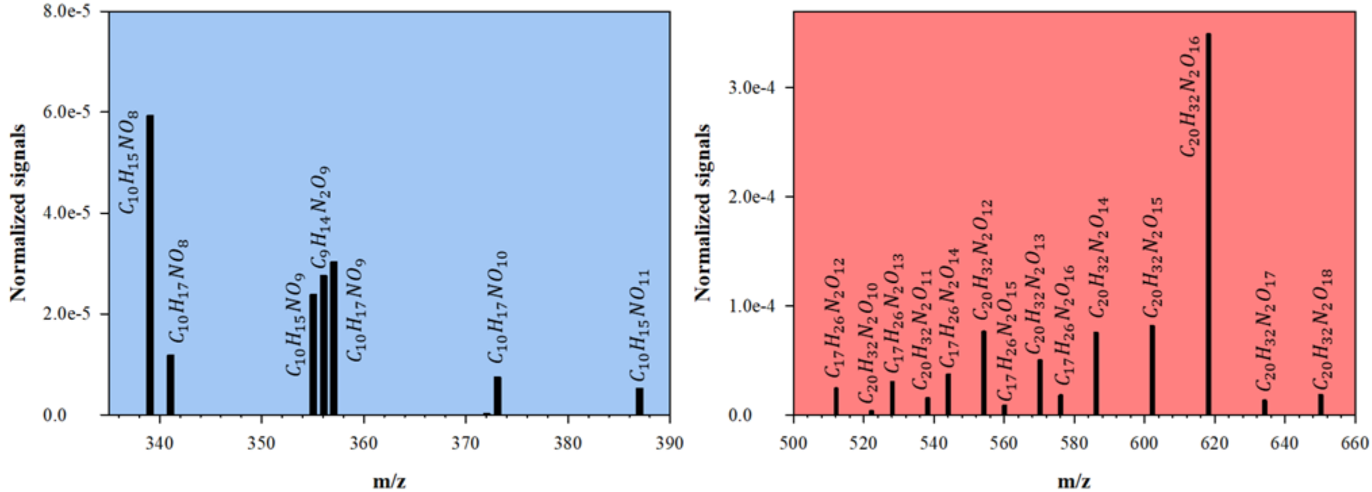

Figure S5: Average mass spectra of gas-phase HOMs for the NO_3-oxidation of α-phellandrene (average performed over 10 min following the start of the oxidation - Experiment 6). Labels display raw formulas of detected species, excluding the nitrate reagent ion cluster, but the *m/z* values (x-axis) include the nitrate mass (61.9883 *m/z*). Product signals are normalized to the reagent ion signals.

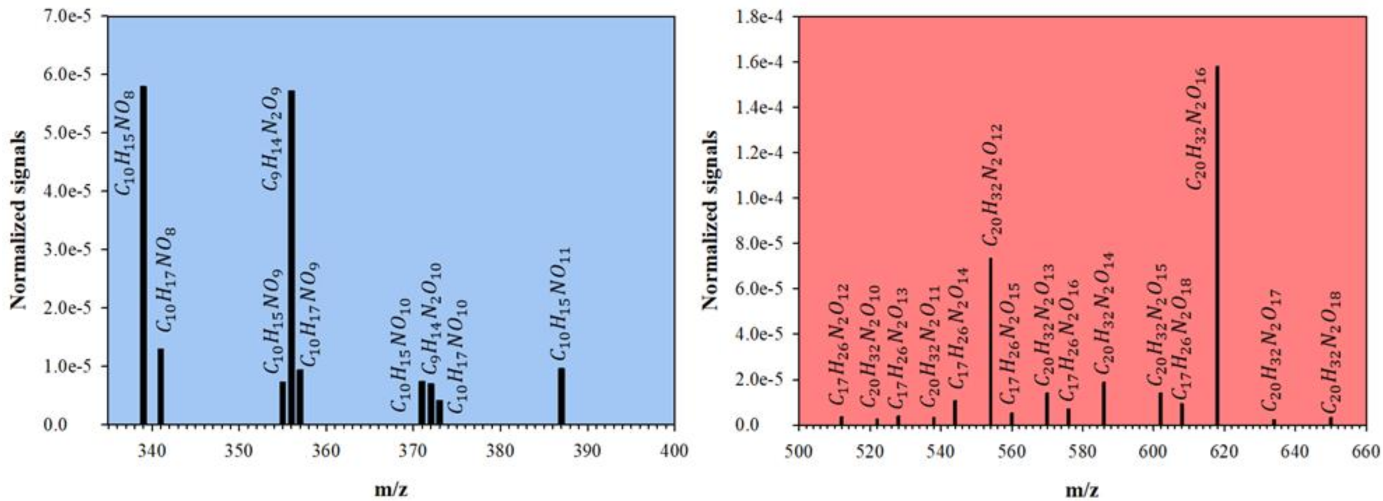

Figure S6: Average mass spectra measured of gas-phase HOMs for the NO_3-oxidation of β-phellandrene (average performed over 10 min following the start of the oxidation – Experiment 11). Labels display raw formulas of detected species, excluding the nitrate reagent ion cluster, but the *m/z* values (x-axis) include the nitrate mass (61.9883 *m/z*). Product signals are normalized to the reagent ion signals.

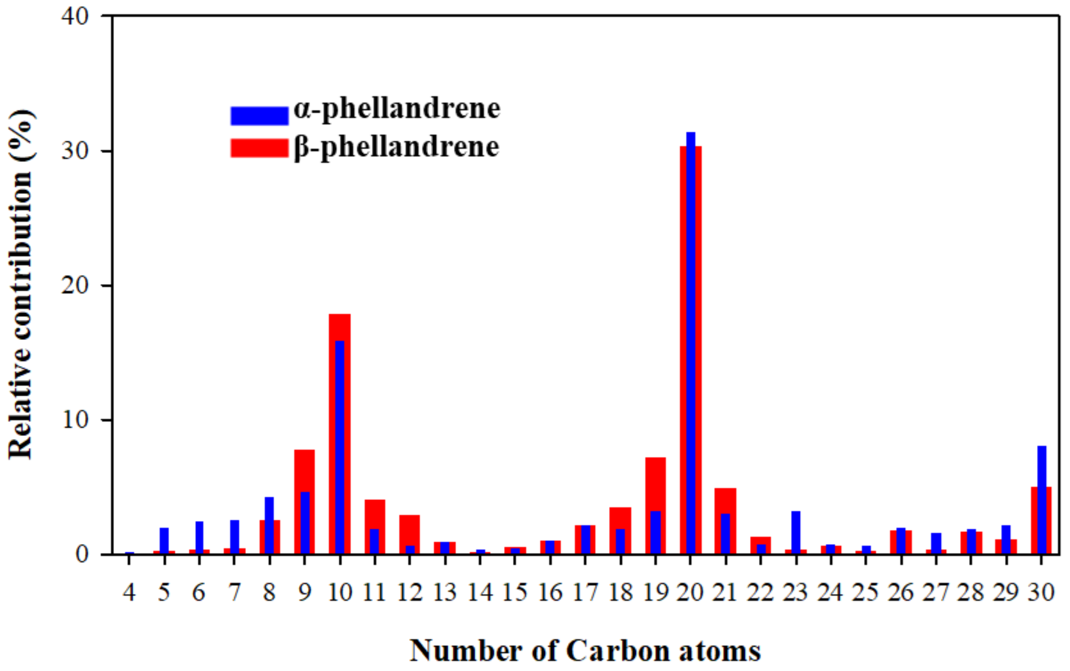

Figure S7. Distribution of the products detected in the aerosol phase as a function of the number of carbon atoms, for α- and β-phellandrenes.