

Supplement of

On the formation of highly oxidized pollutants by autoxidation of terpenes under low temperature combustion conditions: the case of limonene and α -pinene.

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Fig. S1: Comparison of the mass spectra of pure (standard) and oxidated limonene

Tab. S1: APCI source +/-, α -Pinene, limonene and APCI source α -Pinene/limonene

Tab. S2: HESI source +/-, α -Pinene, limonene and HESI source α -Pinene/limonene

Fig. S2: AP and LM mass Spectra acquired with a HESI source in negative mode

Fig. S3: molecular forms resulting from an autoxidation mechanism of limonene: (a) even number of oxygens (b) odd number of oxygens.

Fig. S4: 3-D representation of all limonene oxidation data where DBE is used as third dimension and OSc vs DBE graph

Fig. S5: Some proposed formation routes to $C_{10}H_{16}O_x$ species via autoxidation

Fig. S6: Superposition of chromatographs (UHPLC) of limonoaldehyde (left) and pinonic acid (right) standards and $C_{10}H_{16}O_2$ and $C_{10}H_{16}O_3$ isomers (positive ionization mode).

Fig. S7: D₂O exchanges for limonene and α -pinene (direct infusion, negative ionization mode) - top; and derivatization of carbonyls in limonene and α -pinene oxidation samples using 2,4-DNPH (UHPLC, positive mode) – bottom.

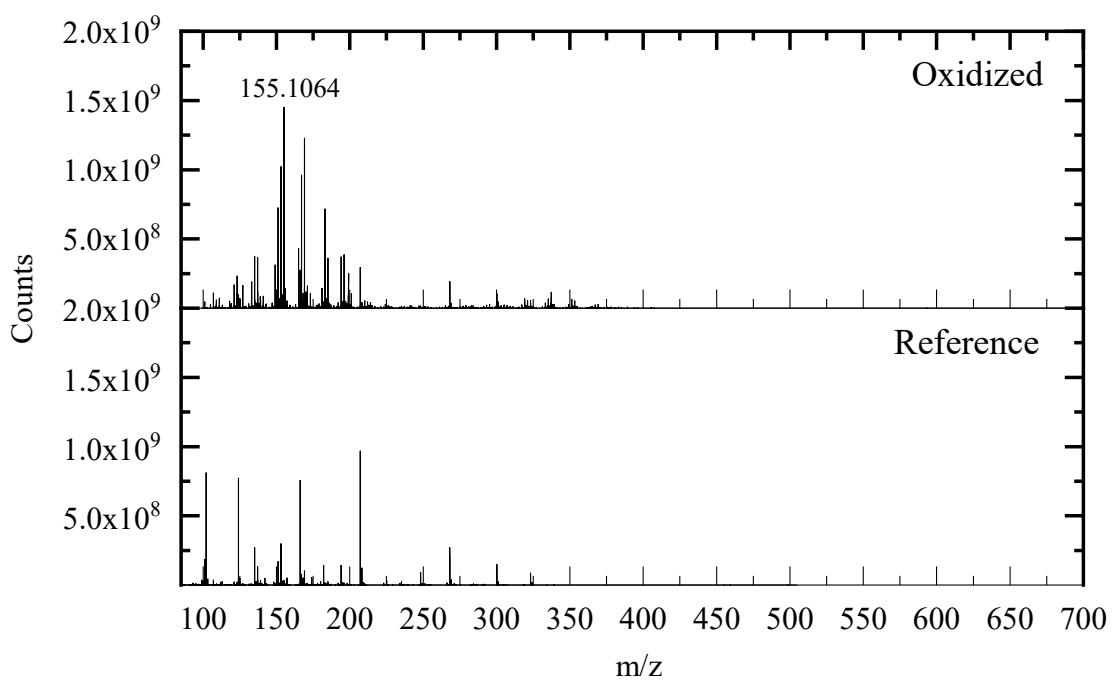


Fig. S1: Comparison of the mass spectra of pure (standard) and oxidated limonene

Table S1. Representation of the mass spectrometry data characterizing the oxidation of α -pinene and limonene (ionization source: APCI positive and negative mode, JSR experiments).

	α -Pinene			Limonene																						
Source and mode	APCI ⁺		APCI ⁻	APCI ⁺		APCI ⁻																				
Number of compounds	646		503	1321		1346																				
Distribution	specific to positive mode 327	common 319	specific to negative mode 174	specific to positive mode 516	common 805	specific to negative mode 542																				
Venn graph	<p>Alpha-Pinene Venn Diagram Data:</p> <table border="1"> <thead> <tr> <th>Region</th> <th>Count</th> </tr> </thead> <tbody> <tr> <td>APCI+ only</td> <td>327</td> </tr> <tr> <td>APCI- only</td> <td>174</td> </tr> <tr> <td>Common</td> <td>319</td> </tr> <tr> <td>Total</td> <td>820</td> </tr> </tbody> </table>			Region	Count	APCI+ only	327	APCI- only	174	Common	319	Total	820	<p>Limonene Venn Diagram Data:</p> <table border="1"> <thead> <tr> <th>Region</th> <th>Count</th> </tr> </thead> <tbody> <tr> <td>APCI+ only</td> <td>516</td> </tr> <tr> <td>APCI- only</td> <td>542</td> </tr> <tr> <td>Common</td> <td>805</td> </tr> <tr> <td>Total</td> <td>1863</td> </tr> </tbody> </table>			Region	Count	APCI+ only	516	APCI- only	542	Common	805	Total	1863
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VK vs DBE	<p>Alpha-Pinene VK vs DBE Plot Regions:</p> <ul style="list-style-type: none"> APCI+ O/C < 0.2 APCI- O/C > 0.4 APCI+/- 			<p>Limonene VK vs DBE Plot Regions:</p> <ul style="list-style-type: none"> APCI+ O/C < 0.2 APCI- O/C > 0.5 APCI+/- 																						
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Table S2. Representation of the mass spectrometry data characterizing the oxidation of α -pinene and limonene (ionization source: HESI positive and negative modes, JSR experiments).

	α -Pinene			Limonene		
Source and mode	HESI ⁺	HESI ⁻		HESI ⁺	HESI ⁻	
Number of compounds	594	693		1017	1864	
Distribution	specific to positive mode 282	common 312	specific to negative mode 381	specific to positive mode 353	common 482	specific to negative mode 1342
Venn Graph	<p>α-Pinene HESI + α-Pinene HESI - Common</p> <p>282 312 381</p> <p>Total : 975</p>	<p>Limonene HESI + Limonene HESI - Common</p> <p>535 482 1382</p> <p>Total : 2399</p>				
VK vs DBE	<p>\bullet α-Pinene HESI+ (only) \bullet α-Pinene HESI- (only) \bullet Common</p>	<p>\bullet Limonene HESI+ (only) \bullet Limonene HESI- (only) \bullet Common</p> <p>HESI+ O/C<0.2 HESI- O/C>0.5 DBE=12</p>				
	<p>α-Pinene (only) Limonene (only) Common</p> <p>83 892 1507</p> <p>Total : 2482</p>	<p>\bullet Alaphpine HESI (only) \bullet Limonene HESI (only) \bullet Common</p>				

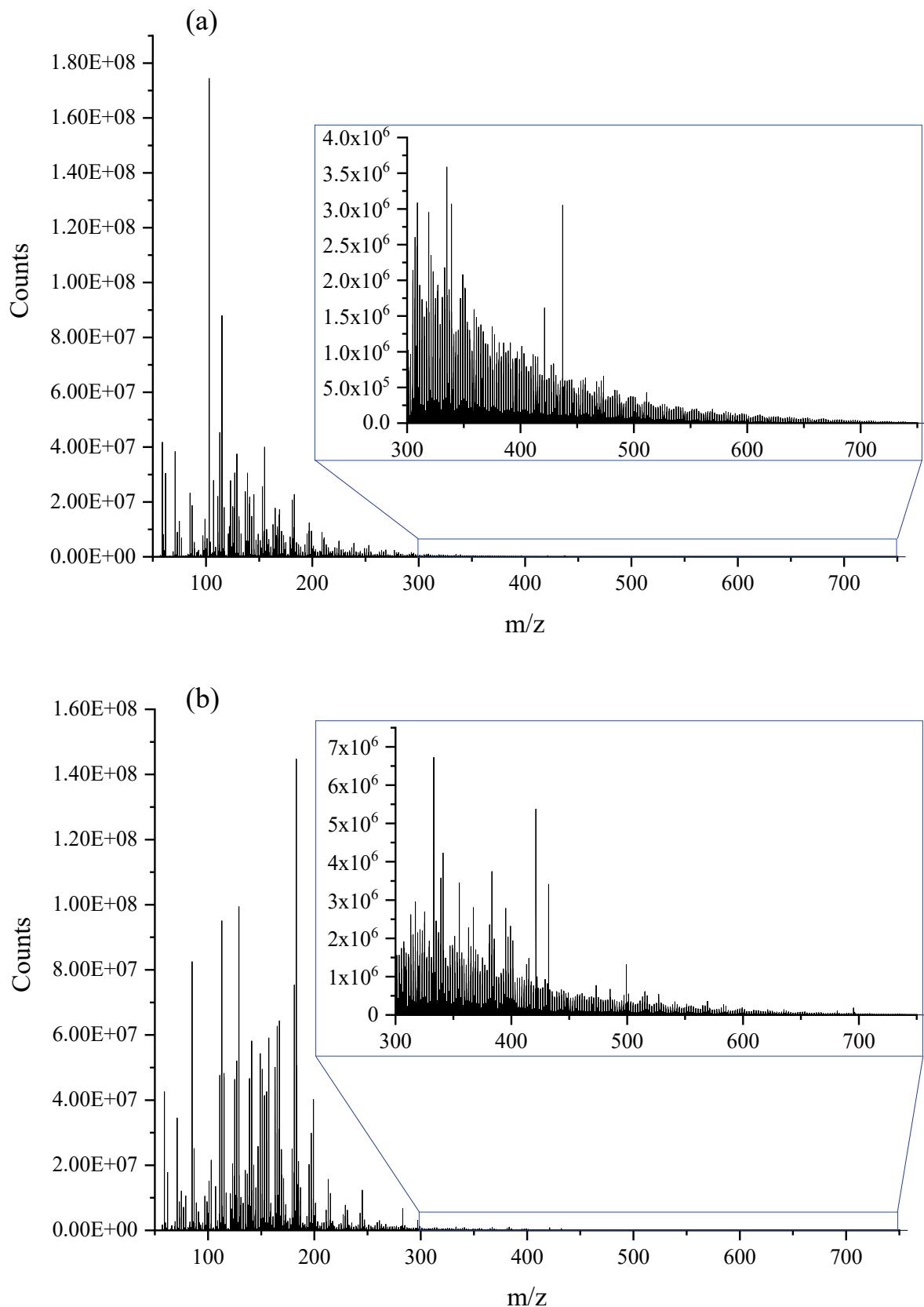
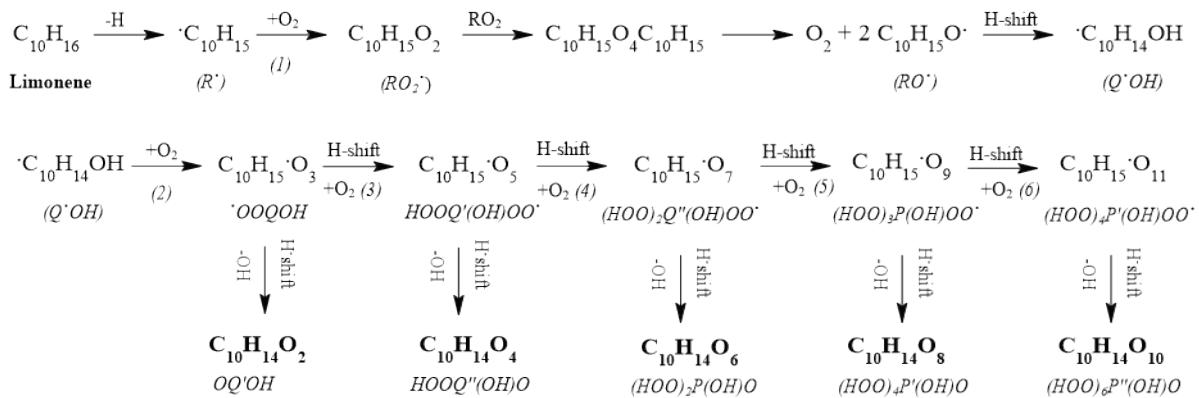


Fig. S2: α -pinene and limonene mass Spectra acquired with a HESI source in negative mode

(a)



(b)

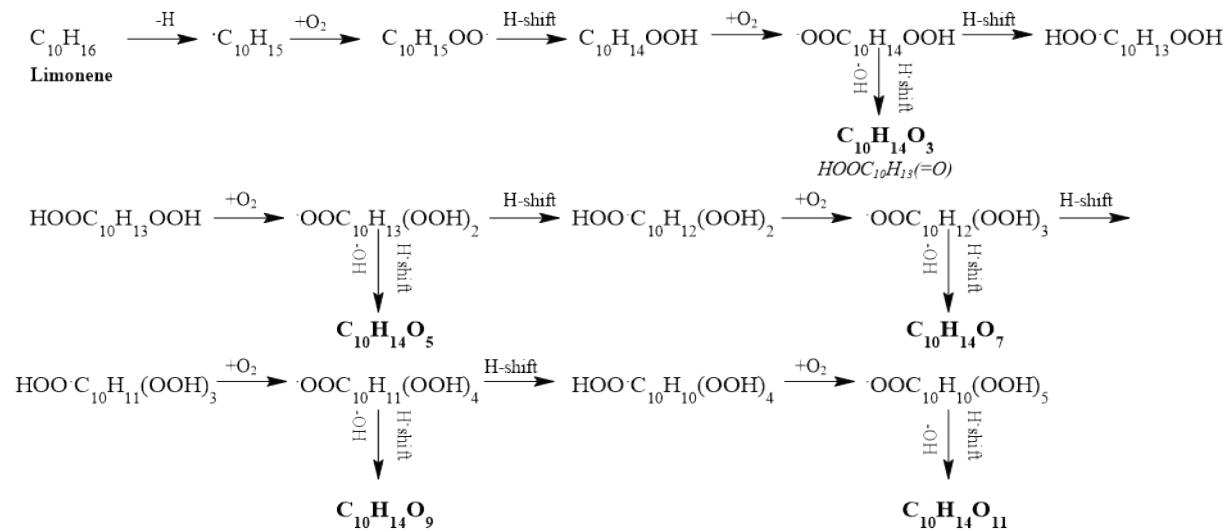


Fig. S3: Molecular forms resulting from an autoxidation mechanism of limonene: a) even number of oxygens b) odd number of oxygens.

- Only identified in combustion
- Only identified by ozonolysis
- Combustion chemical formulae present in some ozonolysis experiments
- Combustion chemical formulae present in all experiments

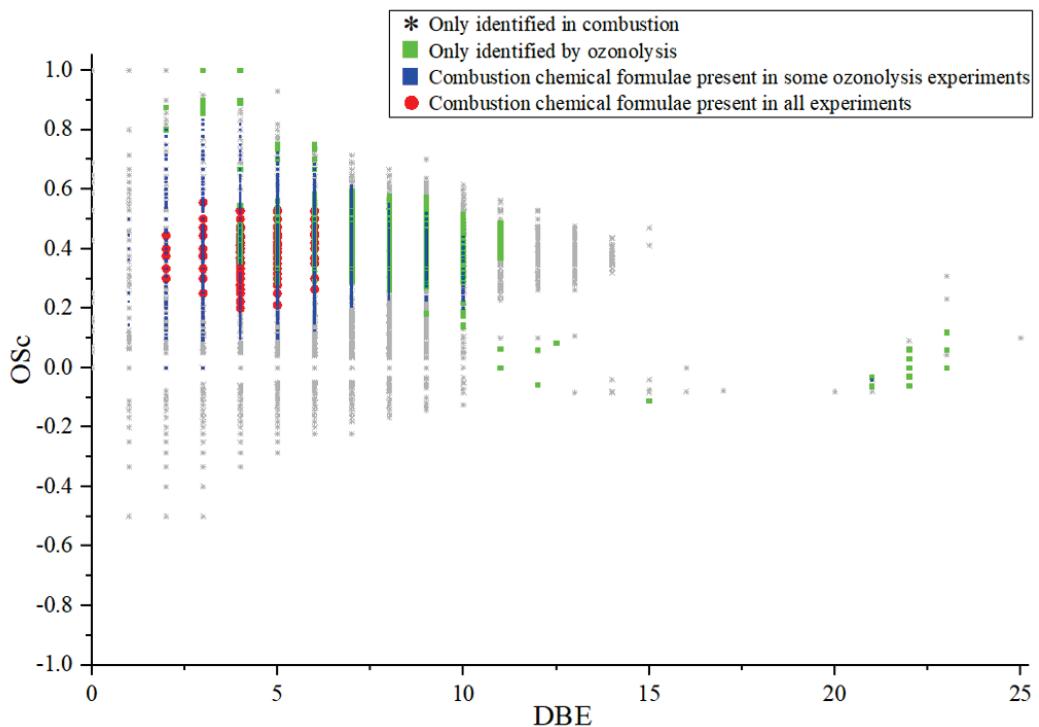
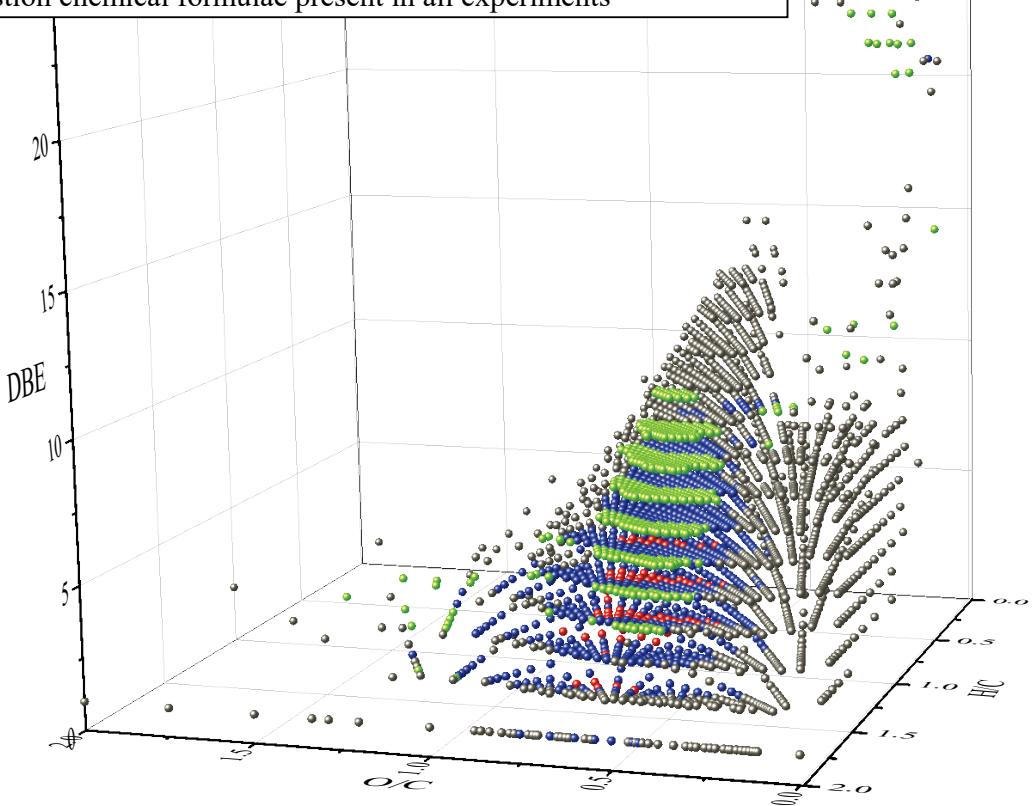


Fig. S4: a) 3-D representation of all limonene oxidation data where DBE is used as third dimension and b) OSc vs DBE graph

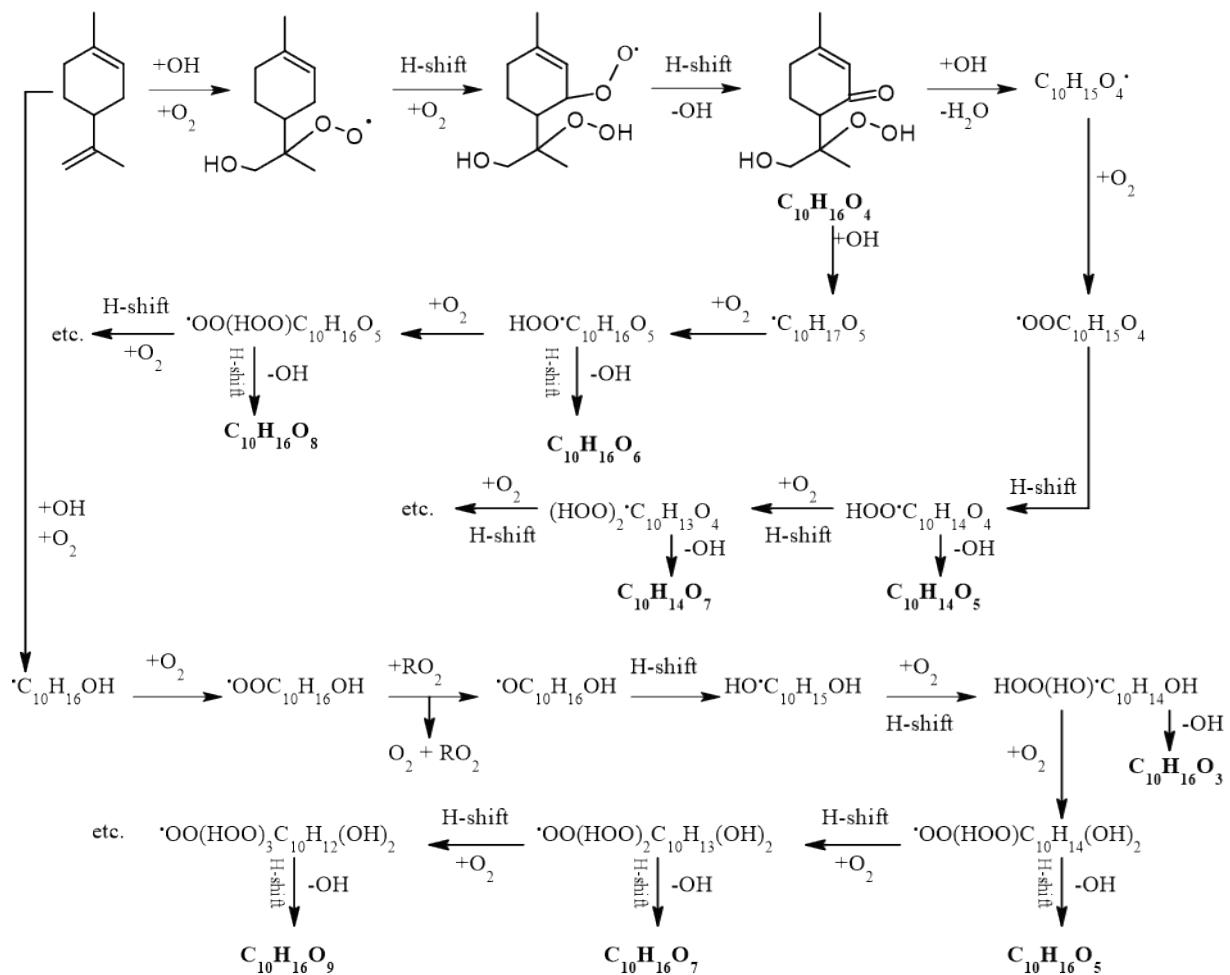


Fig. S5: Some proposed formation routes to $\text{C}_{10}\text{H}_{16}\text{O}_x$ species via autoxidation

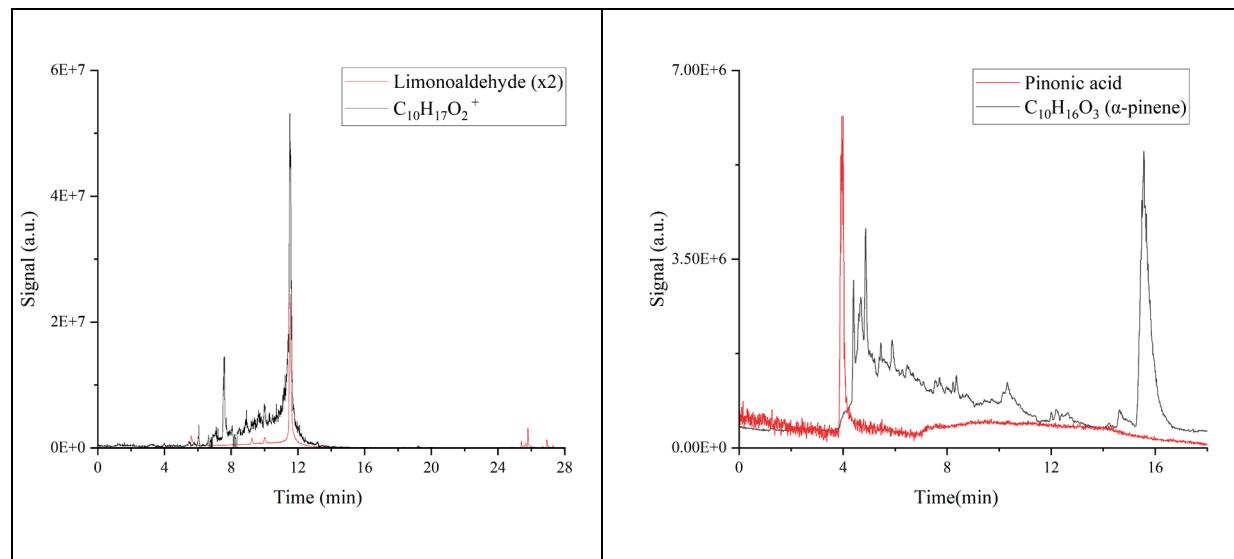


Fig. S6: Superposition of chromatographs (UHPLC) of limonoaldehyde (left) and pinonic acid (right) standards and $\text{C}_{10}\text{H}_{16}\text{O}_2$ and $\text{C}_{10}\text{H}_{16}\text{O}_3$ (α -pinene) (positive ionization mode).

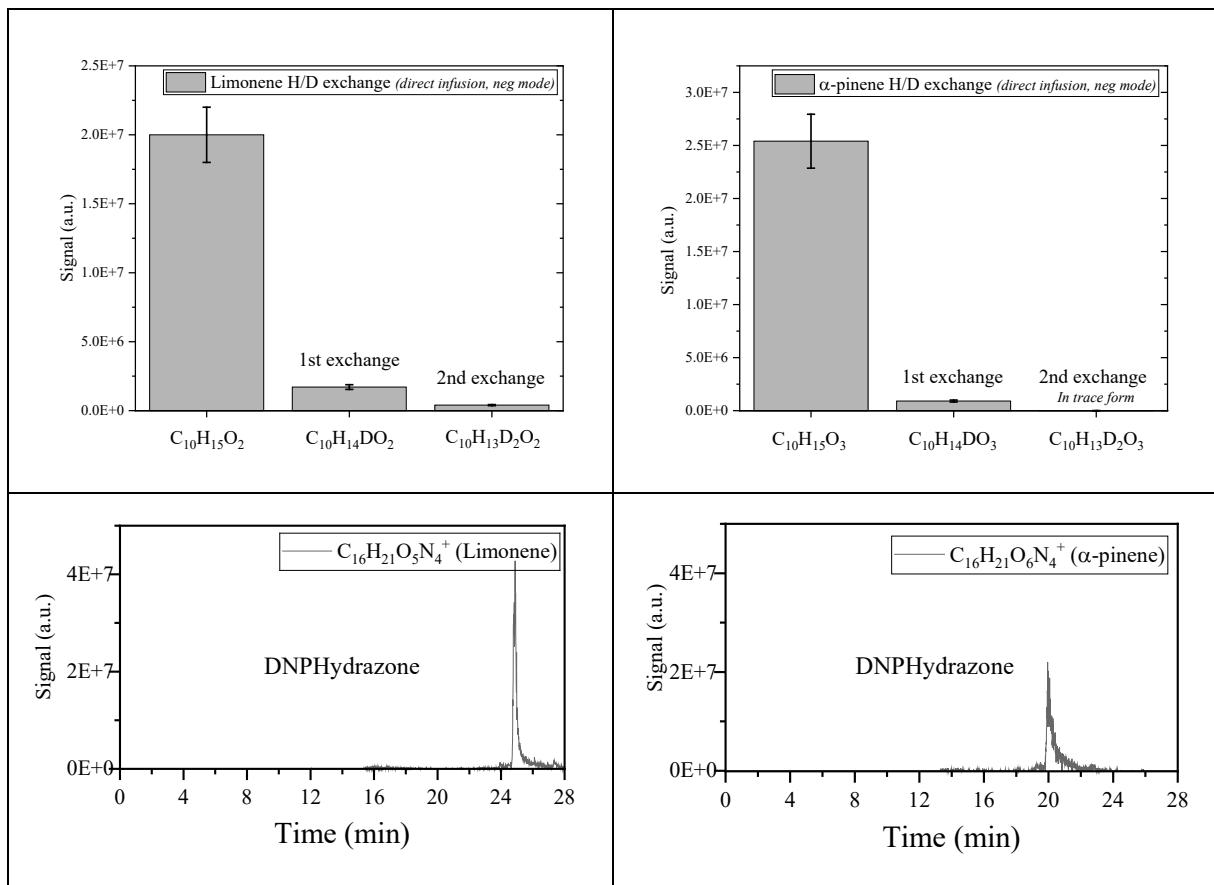


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