Understanding Terpene Hydroperoxide Chemistry: Peroxyhemiacetals

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Background/Overview

› Previous "Round Robin Testing" by IDEA committee members have shown that low terpene hydroperoxide recoveries were frequently seen analytically.

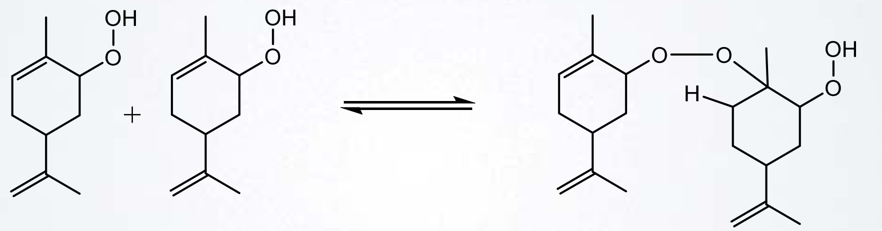
› In an HPLC-Chemiluminescence method, late eluting unknowns were observed that had a reversible chemical relationship with the target analytes

› These late eluting compounds have been identified

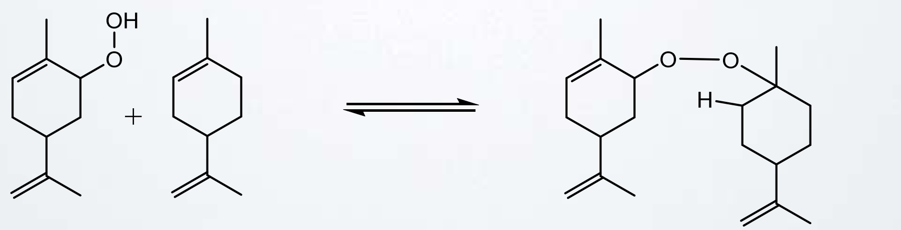
› They offer an explanation for the low observed analytical recoveries

What are these unknowns?

- Our initial hypothesis : Dimers? Plausible structures were proposed
- **<u>No conditions</u>** were found to drive these putative reactants to the unknowns



2X Limonene Hydroperoxide　　Limonene Hydroperoxide "Dimer"

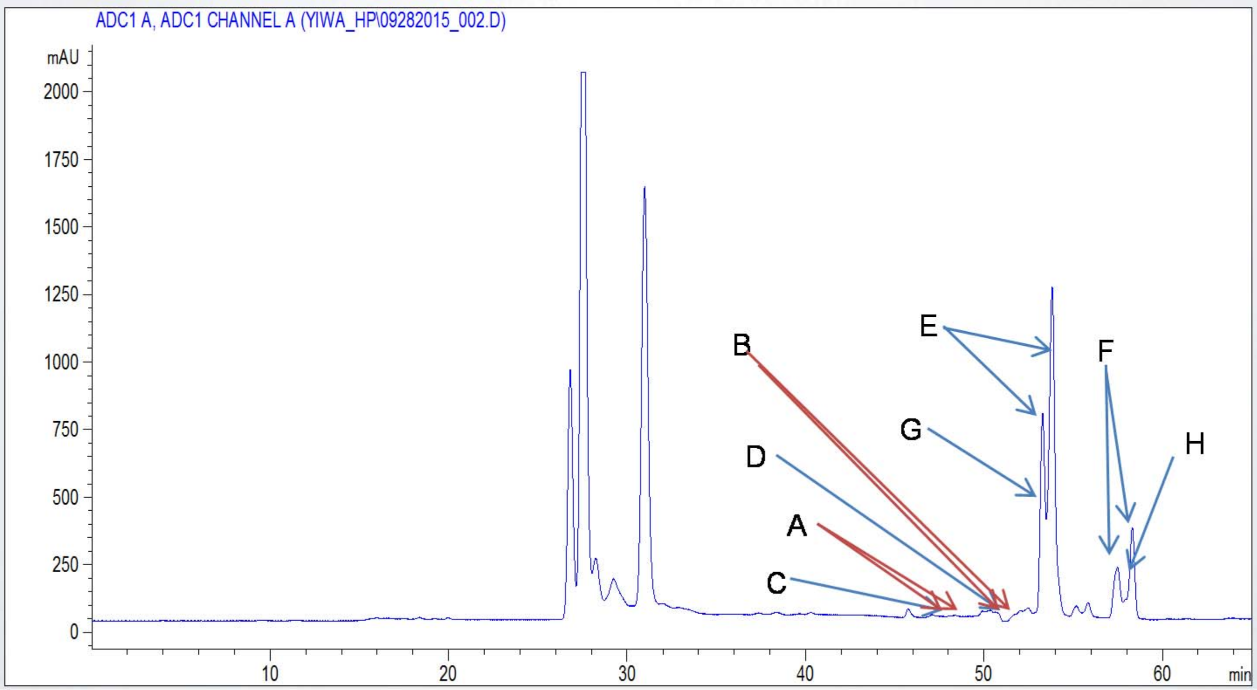


Limonene-HP + Limonene　　Limonene Dihydrolimonene Peroxide

- NMR: no spectrum modification, whatever the polarity of the solvent

What else could the “dimers” be?

- **Aldehydes** are highly reactive molecules present in citrus oil.
- A 1948 patent described peroxyhemiacetals from hydroperoxides & aldehydes
- We reacted octanal and decanal with limonene & linalool hydroperoxides
- The unknowns all formed rapidly at room temperature in heptane



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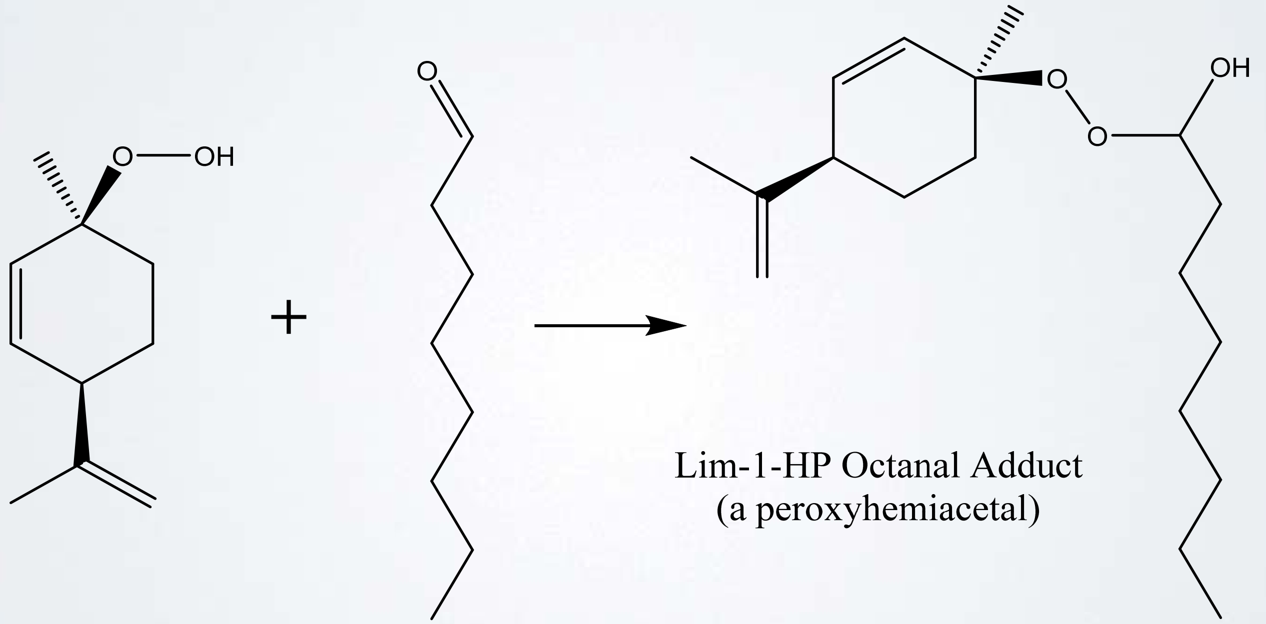
Reaction of Lim-1-Hydroperoxide with Octanal

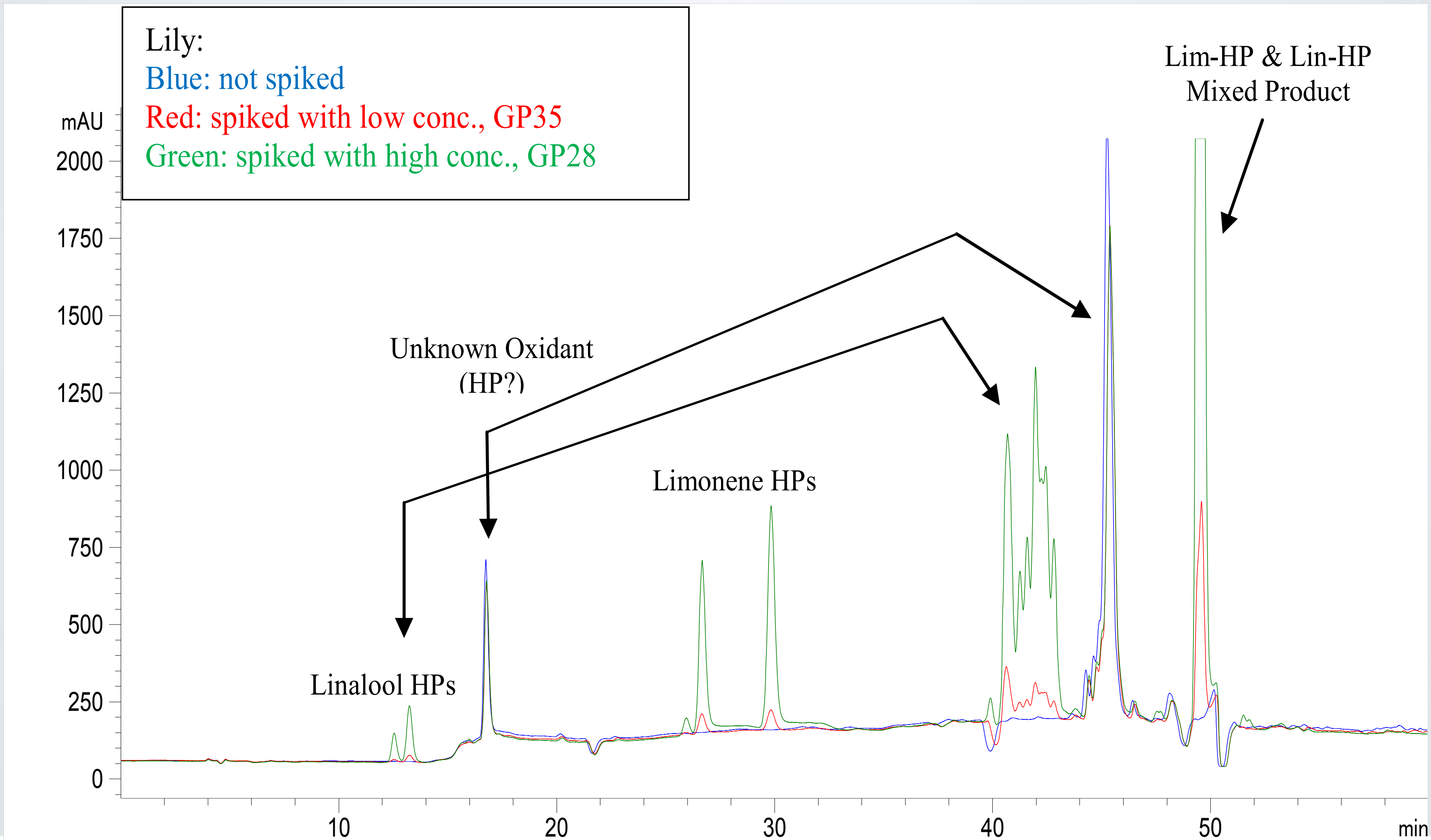


Lim-1-HP Octanal Adduct
(a peroxyhemiacetal)

Evidence	Source	Comment
Known reaction	Literature	Very clean
NMR	Firmenich	See slide 7
Reversible rxn./equilibrium	HPLC-CL	No rearrangements

Unspiked vs. Spiked Lily Sample;

Freshly Prepared Solutions



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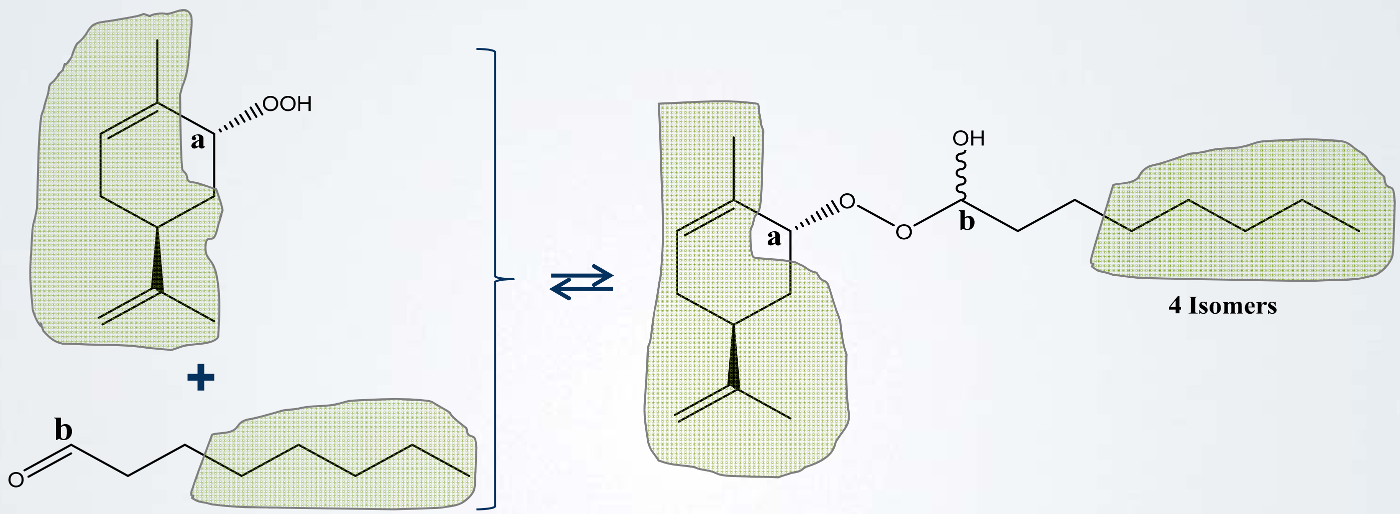
Adduct's structure



- ^{13}C-NMR → carbon a shifted from 198.5 (aldehyde) to 100 ppm (-O-C-O-)
- NMR diffusion experiment
  - Proton *a* & *b* in the adduct → same diffusivity coefficient → belong to the same compound
  - Molecular mass in agreement at 4% with that of the adduct (296g/mole)
- Green area → no change of ^{13}C-NMR shifts → not involved in the reaction

➡ **Unambiguous structure confirmation**

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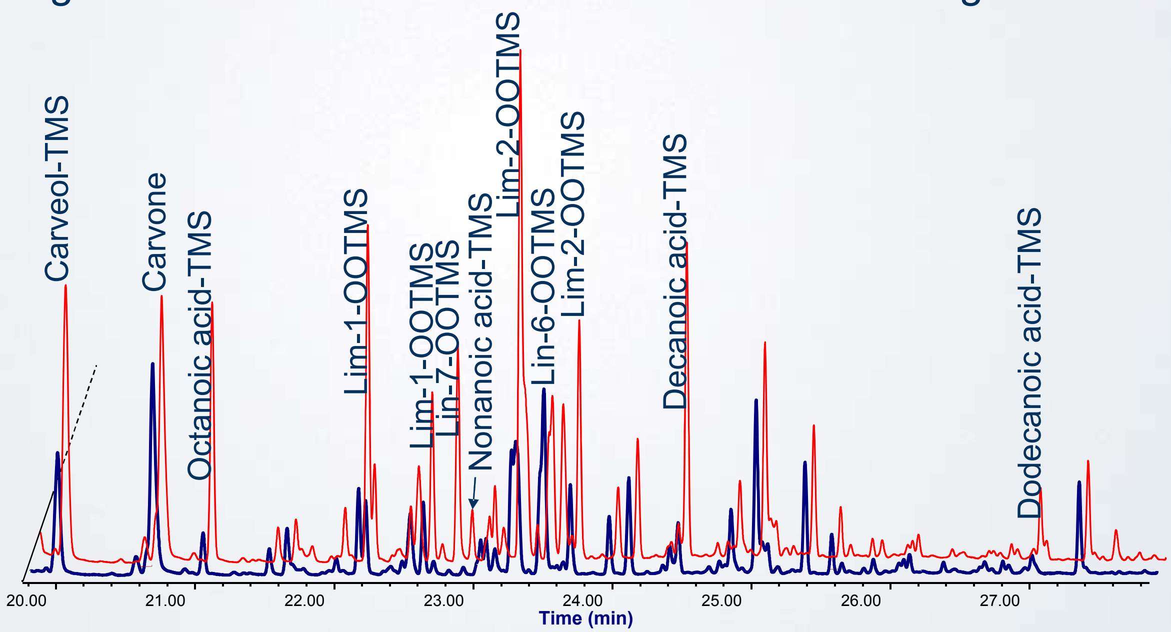
Possible adduct degradation

- Orange oil analysis after silylation:
  - Untreated (blue),
  - After spiking with Lim-OOH and Lin-OOH + 2 months storage



→ Formation of carboxylic acids

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Conclusion

- The late eluting unknowns are peroxyhemiacetals
- They are formed from terpene hydroperoxides and endogenous aldehydes in citrus oils
  - Octanal, decanal, etc.
- The reaction occurs easily at room temperature
- The reaction also occurs with many other fragrance aldehydes
  - As seen in Lily during the Round Robin tests
- Formation of peroxyhemiacetals can lead to low analytical recovery because the target analyte is CONSUMED by aldehydes
- Manuscript submitted for publication; currently in review