Understanding Terpene Hydroperoxide Chemistry: Peroxyhemiacetals

Michael J. Calandra, Alain Chaintreau

Firmenich R & D

December 3, 2015

IDEA Meeting
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

• **No conditions** were found to drive these putative reactants to the unknowns

• 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.
Reaction of Lim-1-Hydroperoxide with Octanal

![Reagent structures](image)

**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

Lily:
Blue: not spiked
Red: spiked with low conc., GP35
Green: spiked with high conc., GP28

[Graph showing peaks labeled Lim-HP & Lin-HP, Mixed Product, Unknown Oxidant (HP?), Limonene HPs, Linalool HPs]
Adduct’s structure

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

Unambiguous structure confirmation
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
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