

Hydroperoxide taskforce Meeting: Recent results Givaudan

3.12.2015

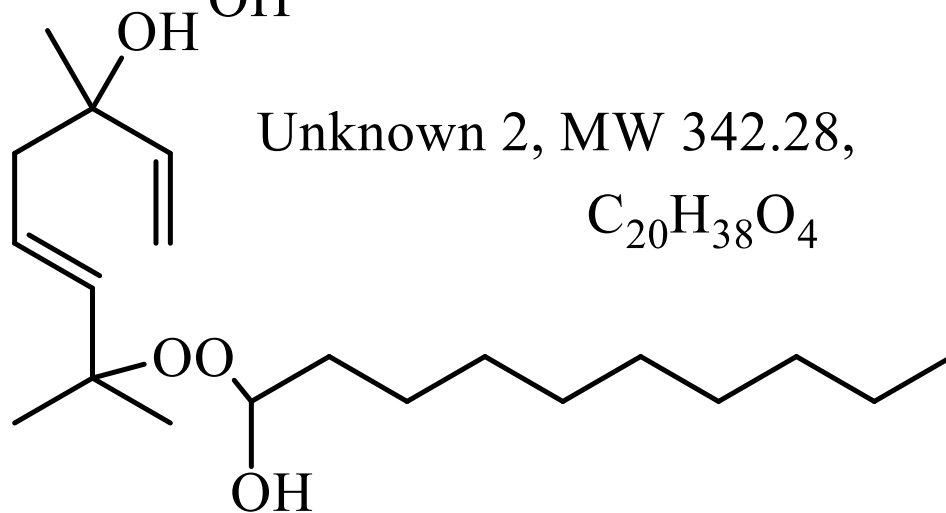


Givaudan

engage your senses

Adducts identified in Orange oil spiked with Linalool-HP

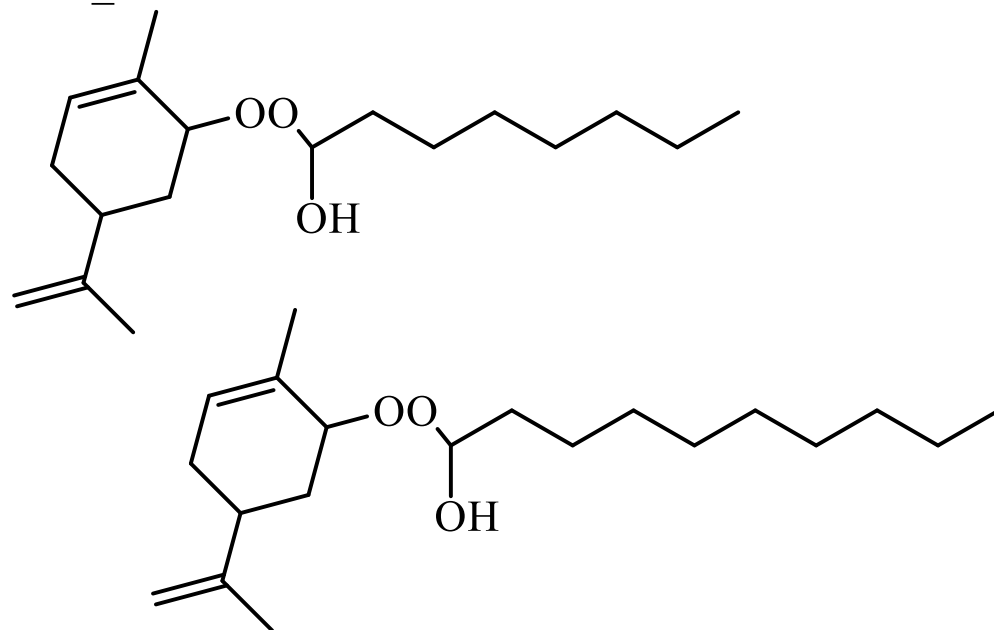
- Adduct with decanal and octanal contained as trace impurities in orange oil



Adducts identified in Orange oil spiked with Limonene-HP

- Adduct with decanal and octanal contained as trace impurities in orange oil
- These adducts are already present at low levels from endogenous limonene-HP present in orange oil

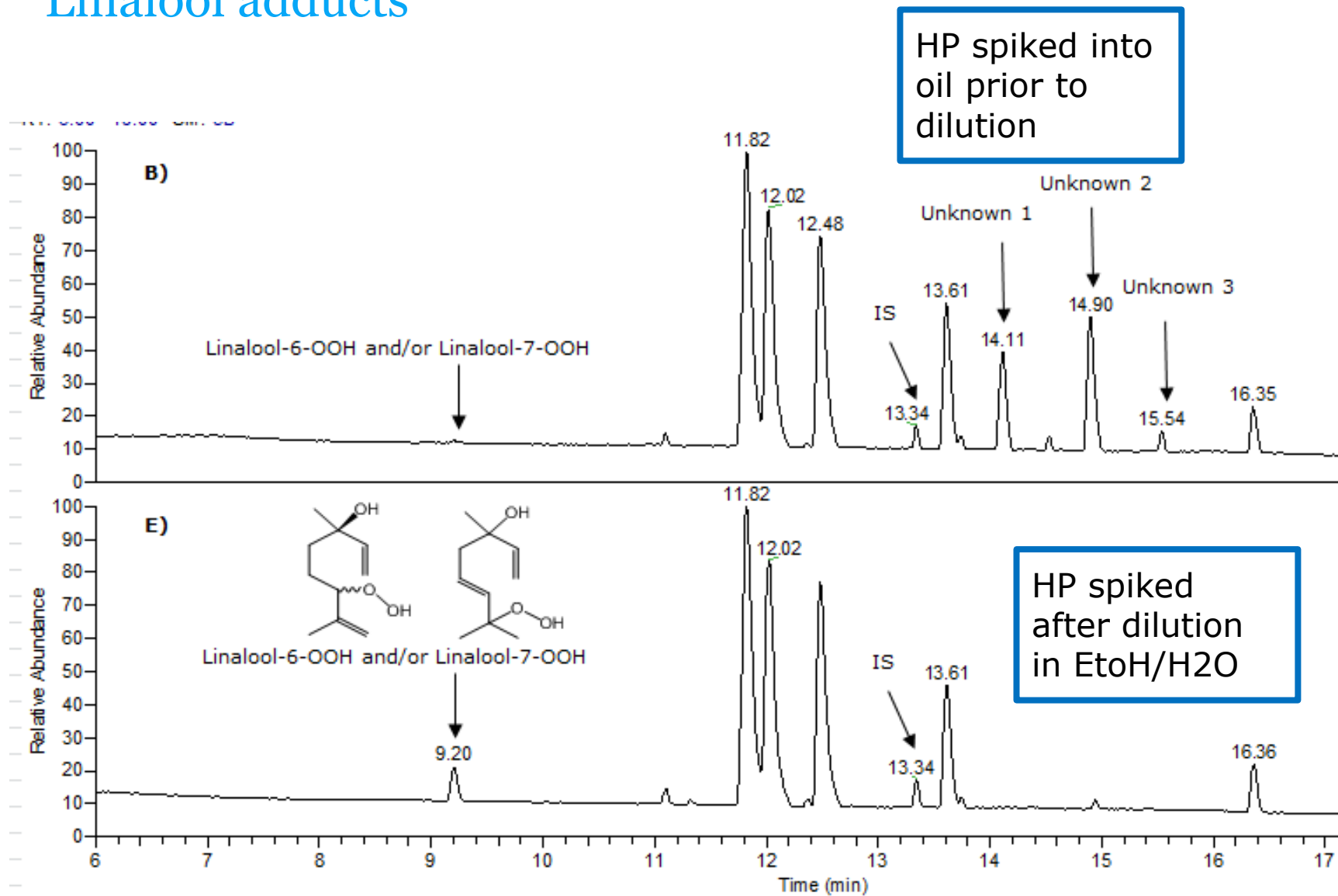
Limonene-OOH_Unkown 1 C₁₈H₃₂O₃ na+ adduct =319.2244
Limonene-OOH_Unkown 2 C₂₀H₃₆O₃ na+ adduct =347.2557



Effect of adduct formation on recovery

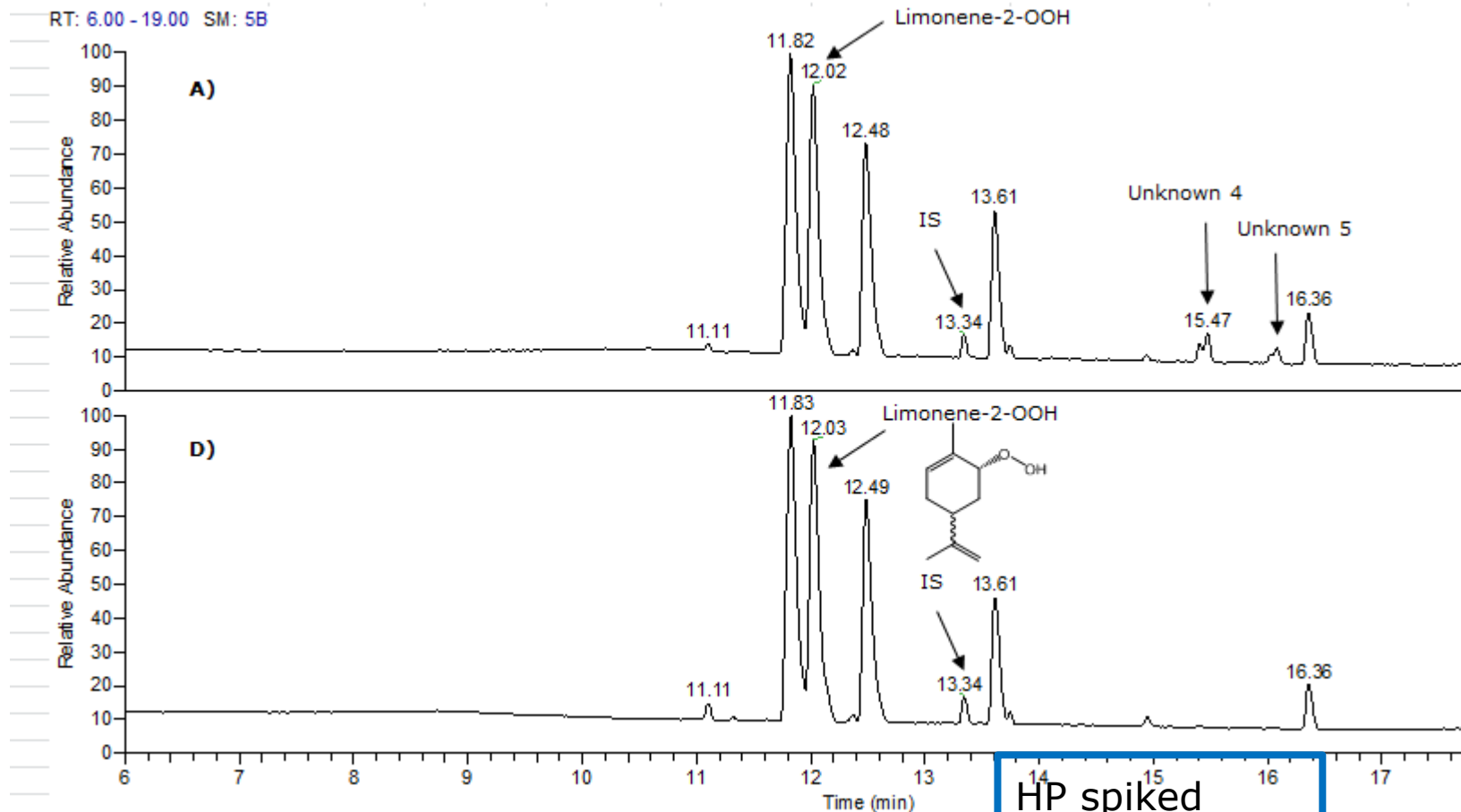
- If hydroperoxide is added to orange oil, and orange oil is then diluted in EtOH / H₂O 80/20, we find around 50% quenching of the hydroperoxide content
- This is particularly evident for Linalool-HP (60% quenching) and less for limonene (40%) – however this is not based on replicate measurements
- This is in agreement with the ring trial
- If the orange oil is added first to EtOH / H₂O 80/20, and then spiked with the hydroperoxide (i.e. as if HP would be formed in an EdT) – then we see no quenching, and no of the new adducts
- This indicates, that adduct formation mainly occurs in neat oils

Linalool adducts



Limonene adducts

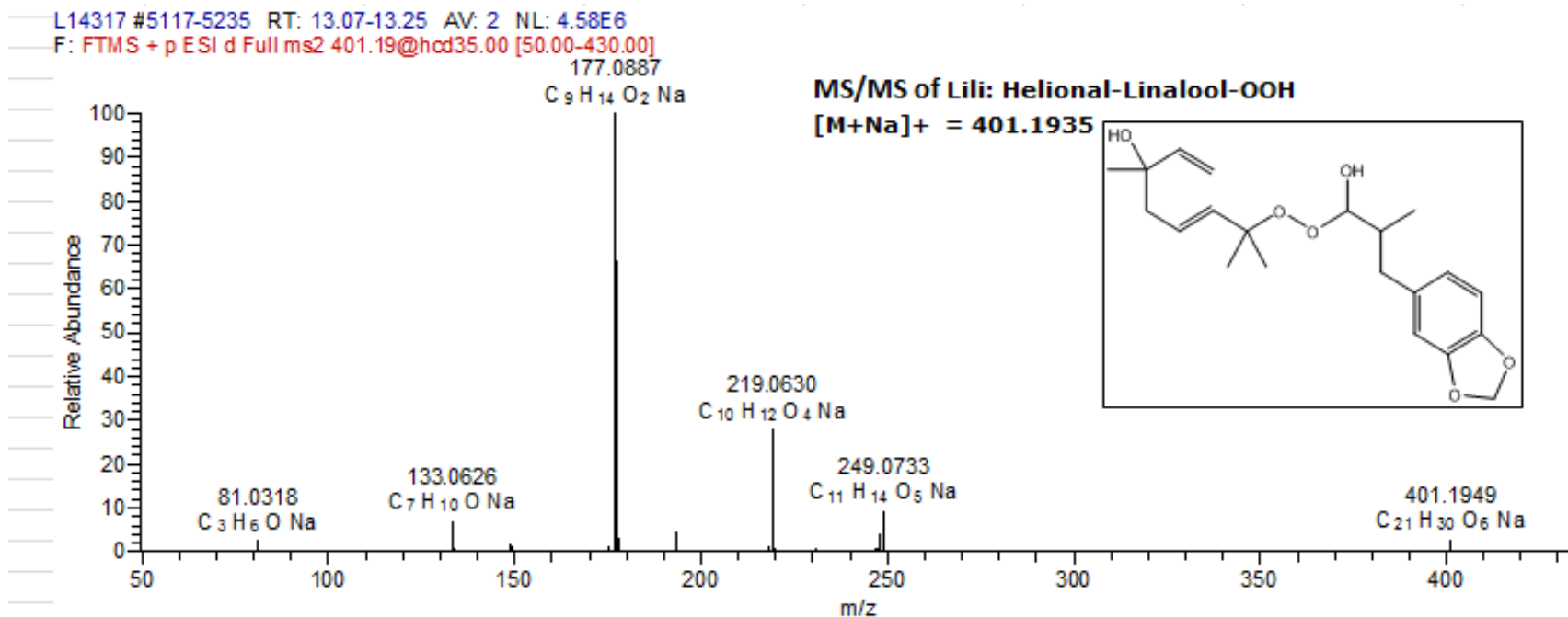
HP spiked into
oil prior to
dilution



HP spiked
after dilution
in EtoH/H2O

Adducts in Lili

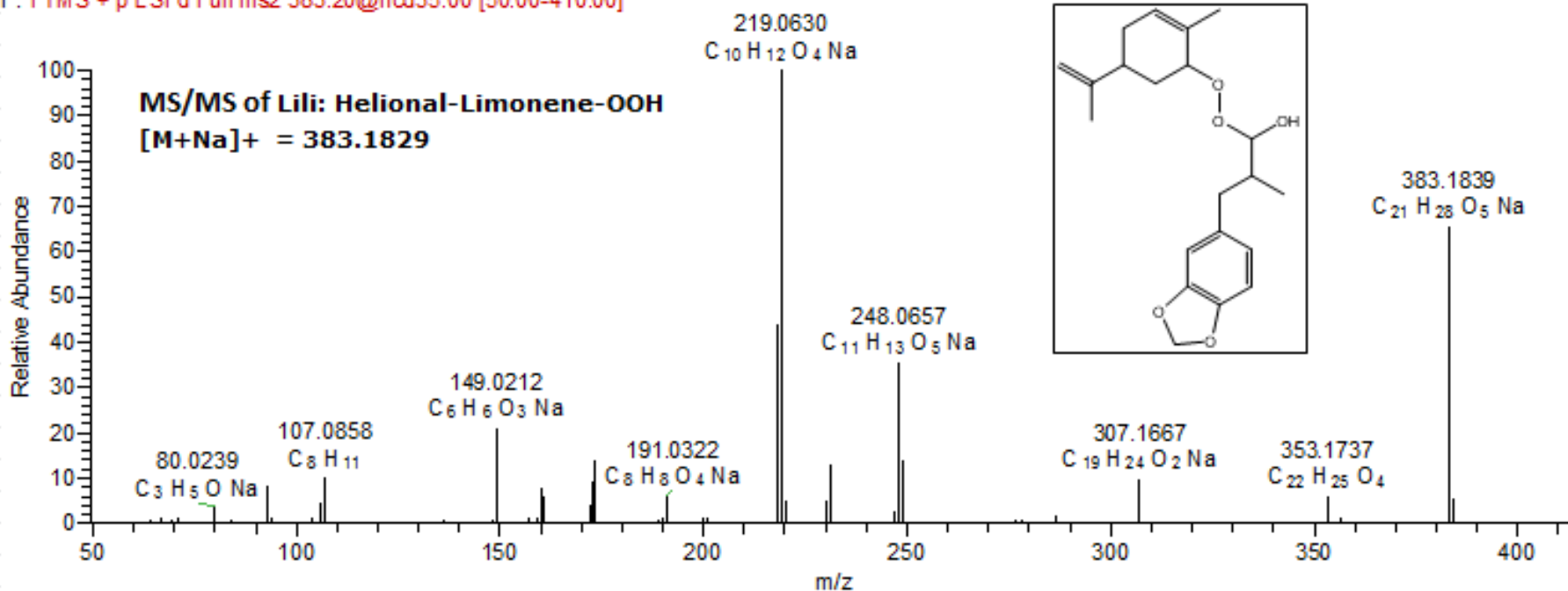
- Key aldehyde is Tropional / Heliopropional (10% of Fragrance)
- Forms similar adduct
- We found even 80% quenching by Lili (higher than in ring trial) – no significant quenching if HP spiked to diluted oil
- This adduct also found, if oil was first diluted in alcohol prior to spiking – however 7-fold lower levels as compared to dilution first in EtOH
 - Levels of available aldehyde for reaction are far higher!



Adducts in Lili - limonene

- Forms similar adduct – lower levels as compared to linalool
- Less quenching of added HP in Lili
- This adduct also found, if oil was first diluted in alcohol prior to spiking – however 7-fold lower levels as compared to dilution first in EtOH
 - Levels of available aldehyde for reaction are far higher!

L14316 #5726-5849 RT: 14.63-14.81 AV: 2 NL: 6.58E5
F: FTMS + p ESI d Full ms2 383.20@hcd35.00 [50.00-410.00]



Results ring trial 2 – TPP method – ext. calibration

	Limonen-1- OOH	Limonen-2- OOH	Linalool- 6-OOH	Linalool- 7-OOH
Me Pivalate (blank)	not detected	not detected	not detected	not detected
Me Pivalate (low)	293.6	171.8	151.2	159.6
low	297	217	206	229
Recovery	98.8	79.2	73.4	69.7
Me Pivalate (high)	1977.4	1246.0	1680.2	2076.1
high	1600	1257	1943	2286
Recovery	123.6	99.1	86.5	90.8
Lili (blank)	not detected	not detected	not detected	not detected
Lili (low)	214.1	113.0	109.6	70.9
low	284	200	255	225
Recovery	75.4	56.5	43.0	31.5
Lili (high)	1086.2	870.4	1082.4	786.2
high	1322	1469	2253	1959
Recovery	82.2	59.3	48.0	40.1
Orange oil (blank)	432.0	284.9	not detected	not detected
Orange oil (low)	995.9	704.4	129.1	136.3
low	270	285	256	242
Recovery	208.8	147.2	50.4	56.3
Orange oil (high)	2679.6	1970.3	649.4	1534.3
high	1957	1661	1305	2491
Recovery	126.3	109.8	49.8	61.6

Open question

- Can adduct be isolated by column chromatography?
- Does adduct revert to free hydroperoxide?
 - In oils ?
 - In products ?
- What happens to adduct upon TPP reduction?
- Is adduct measured by iodometric titration?
 - If yes, no issue for QC
 - If no, is level of adduct in commercial oils relevant for risk assessment?
- Can adduct be reverted to hydroperoxide upon mild treatment with base?
- Is there a rapid equilibrium anyway?
 - If it is far on the left side in products?
- Do we have to care for adduct when measuring HP in consumer products?

Thank you

Contact