



Hops (*Humulus lupulus*) provide important sources of thiol precursors. A key ingredient to obtain fruity beers

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ELEVATE
BEER

Introduction

AIM OF THE STUDY

- Understand the link between hop usage and thiols in beer
- Bring information to better manage thiols during brewing

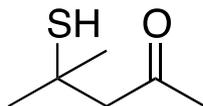
SUMMARY

- Thiols: Origins and odors
- Thiols and their precursors in commercial beers and in hops
- Hypotheses about thiol origin in beer
- Thiol precursor evolution during boiling and dry hopping

GENESIS OF THIOLS IN WINE AND IN BEER

4MMP

4-mercapto-4-methylpentan-2-one



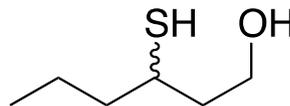
0,8 ng/L in wine
1,5 ng/L in beer



Box tree, Blackcurrant bud

3MH

3-mercaptohexan-1-ol



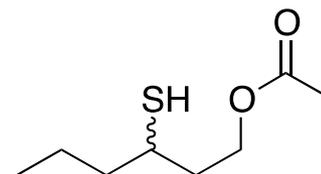
60 ng/L in wine
55 ng/L in beer



'Exotic, Rhubarb' like, citrus

3MHA

3-mercaptohexyl acetate



4 ng/L in wine
4 ng/L in beer



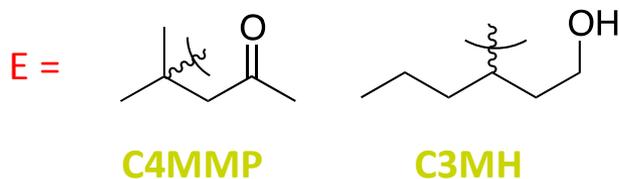
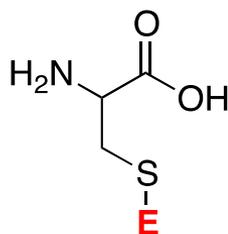
Goyava, Passion fruit

Du plessis et al., 1981; Darriet et al., 1991; Cosser et al., 1980

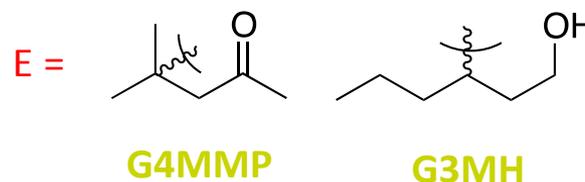
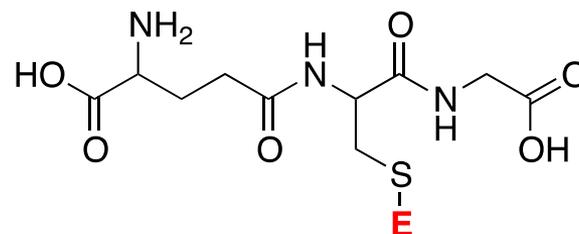
Tominaga et al., 1998; Kishimoto et al., 2006, Vermeulen et al., 2006

THIOL PRECURSORS

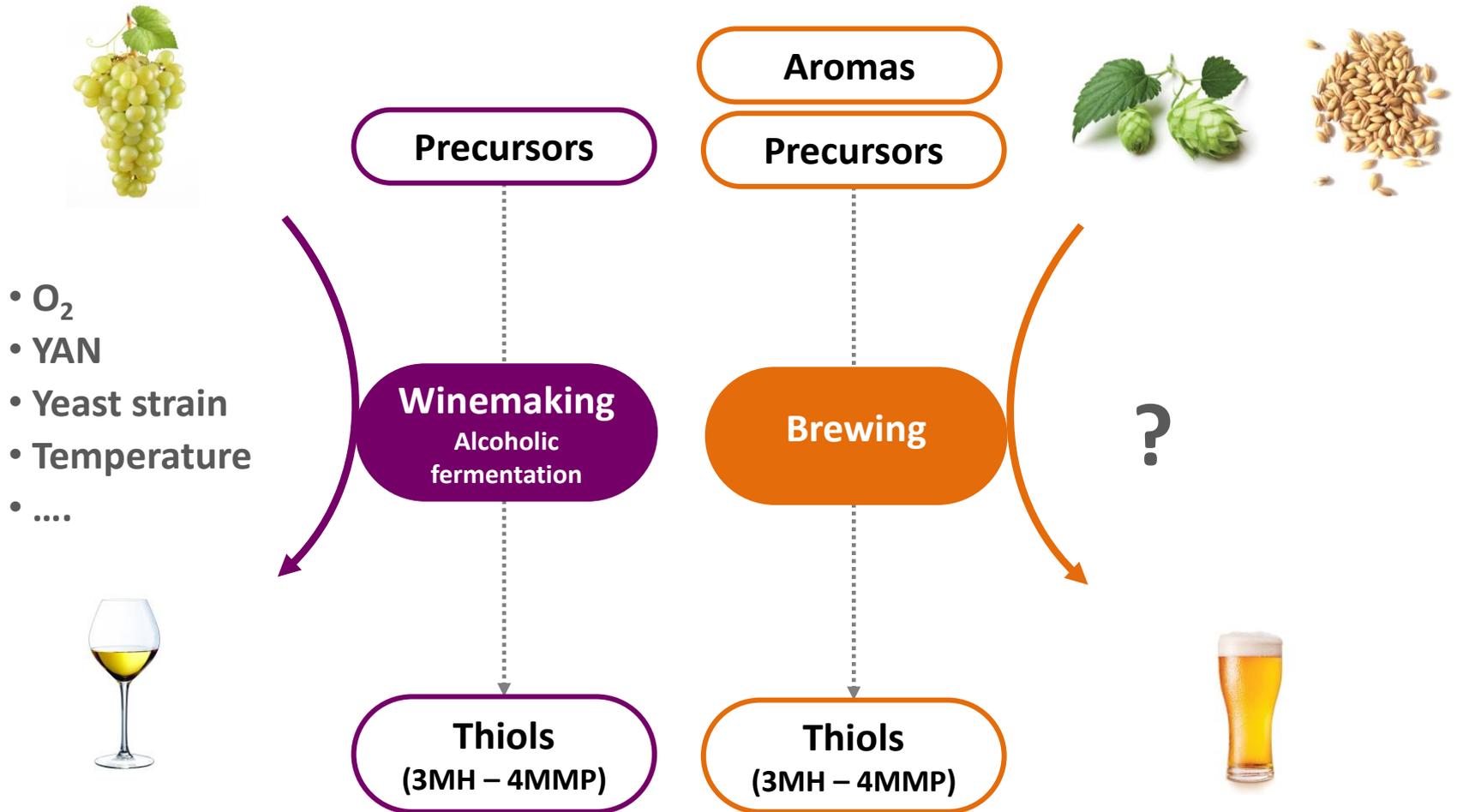
Cysteinylated precursors
of 3MH and 4MMP



Glutathionylated precursors
of 3MH and 4MMP



THIOLS IN WINE AND IN BEER



MATERIAL AND METHODS

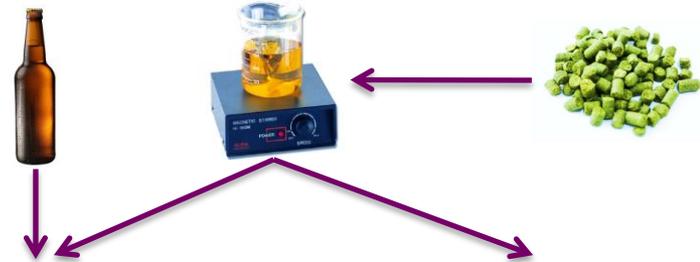


17 Commercial Beers
2015
Craft and industrial
Ale, Belgian, Pils, IPA



12 Pellets Type 90
2014 - 2015 (Hop producers)
Herkules (Hallertau)
Cascade (Hallertau – US – Other)
Citra (US)
Perle (US)
H. Tradition (Hallertau)
Nugget (Hallertau - Spain)
Saaz (Tchez R. 3 samples)

Experimental wort and beers
2015
Pilot scale



THIOLS

(Roland *et al.*, Anal Chem., 2016, under review)

THIOL PRECURSORS

(Roland *et al.*, FFJ, 2016)

Derivatization
1 mL of sample,

SPE

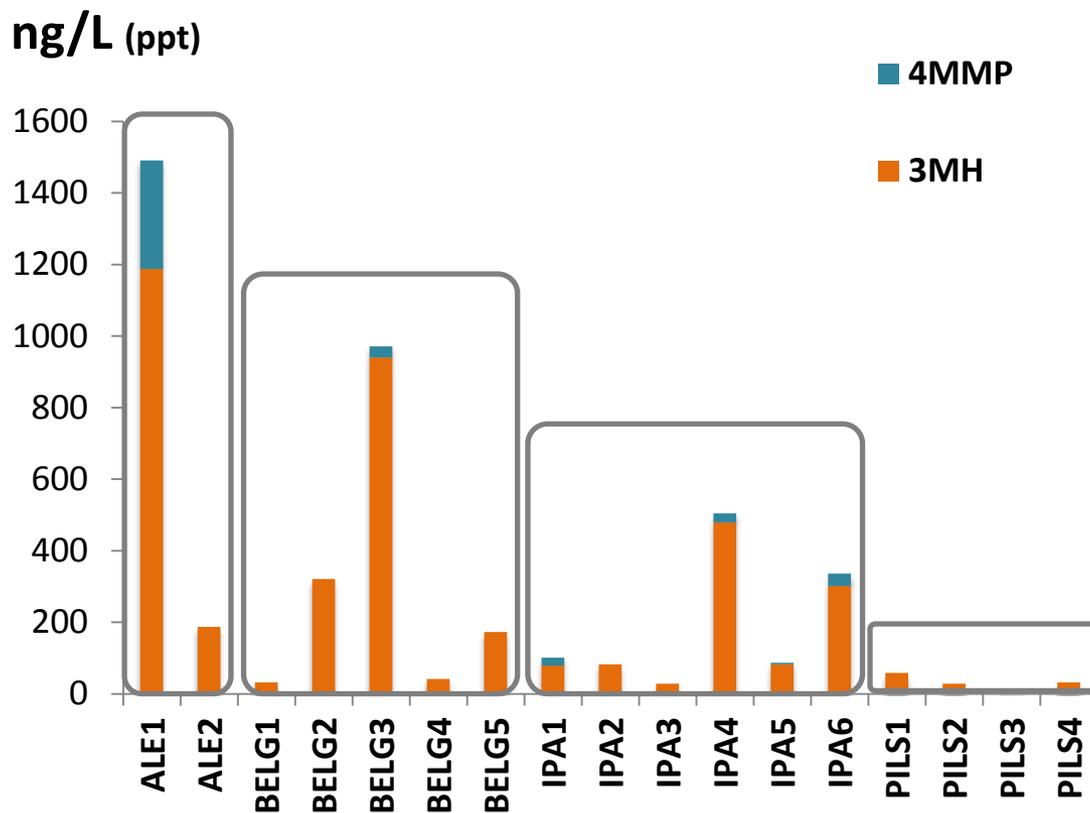


SPE DOWEX

SPE C18
Salt extract

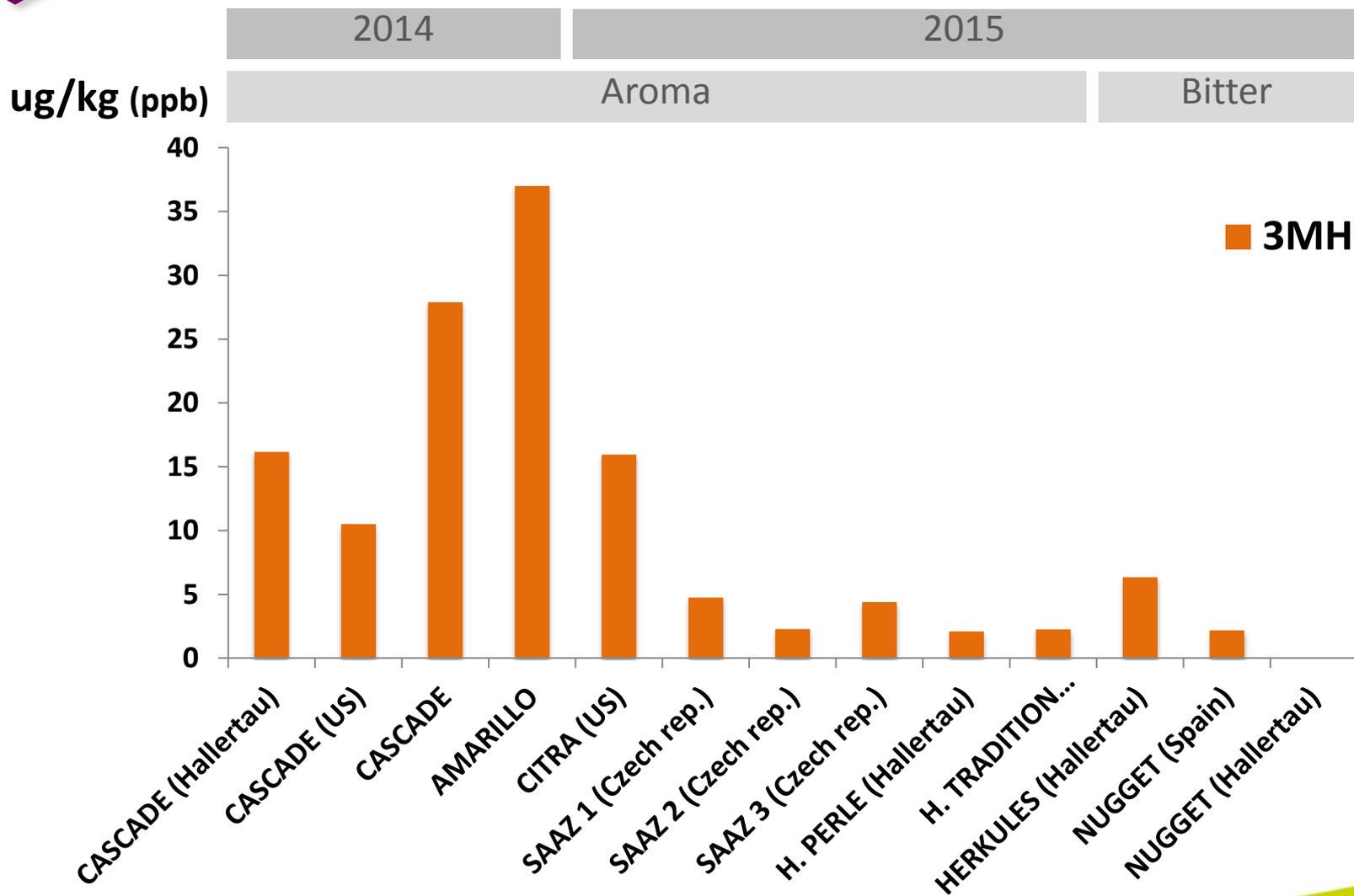
SIDA
nanoLC-MS/MS

Thiols in 17 commercial beers

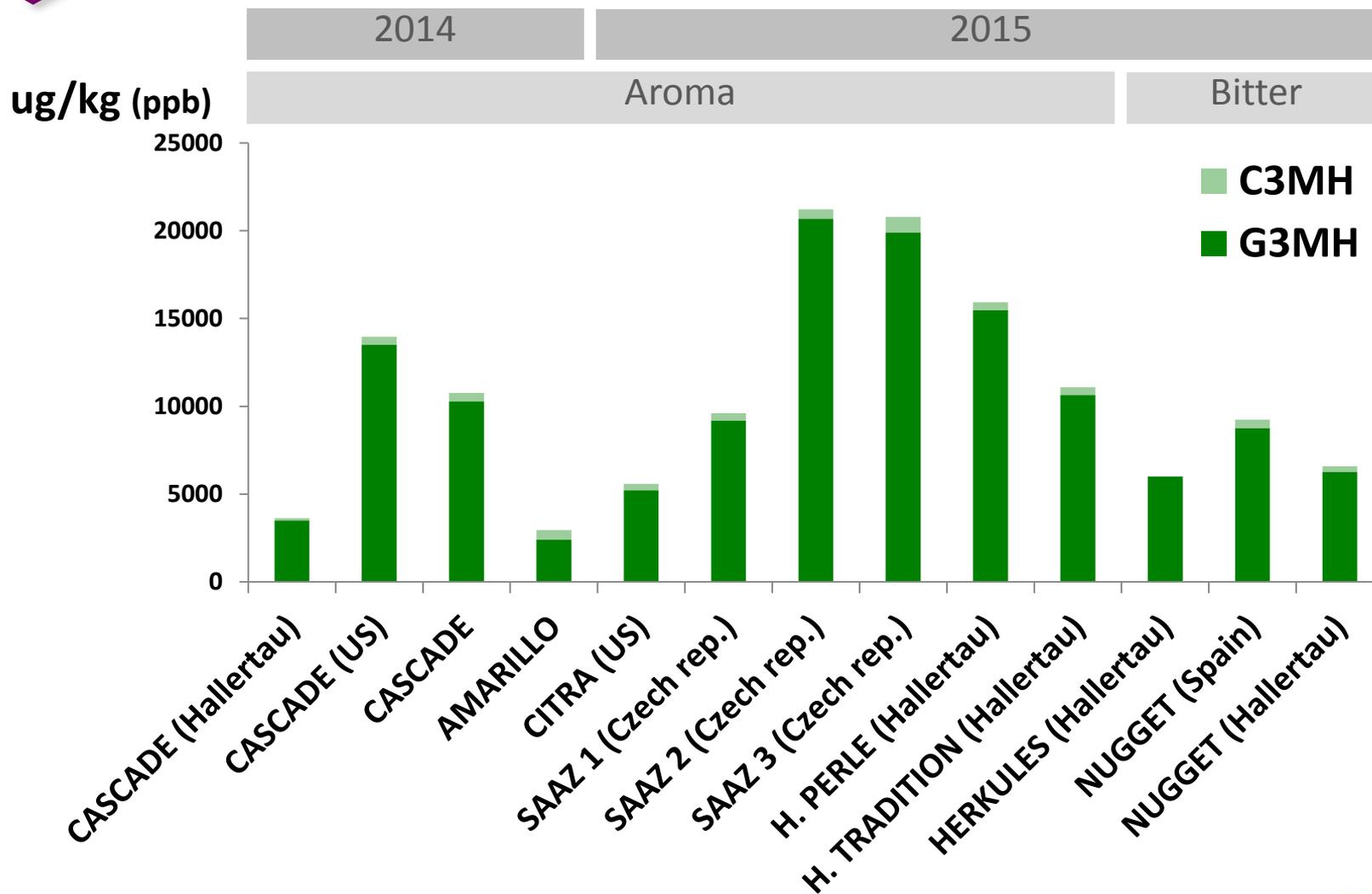


- Thiol levels above their perception thresholds
- From 10 to 1200 ng/L for 3MH
- 4MMP can be present
- No correlation with beer style

Thiols in hops: 3MH

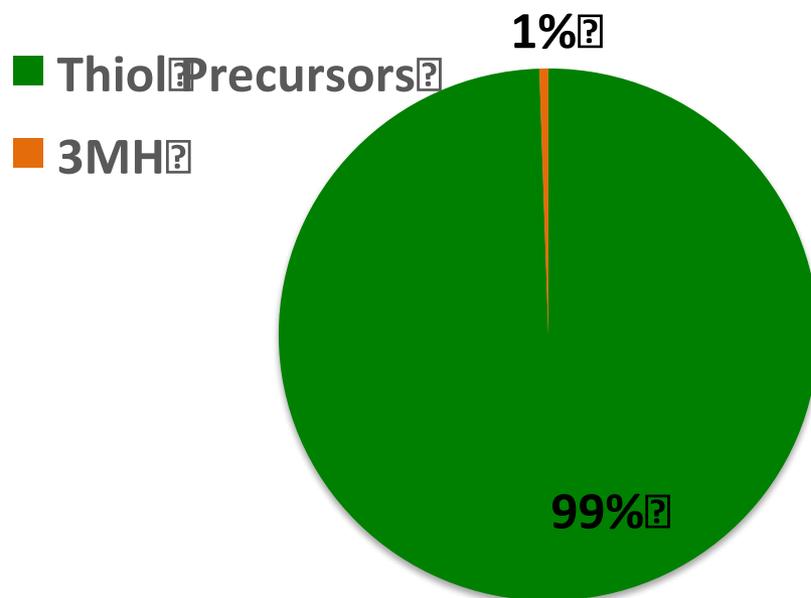


Thiol precursors in hops



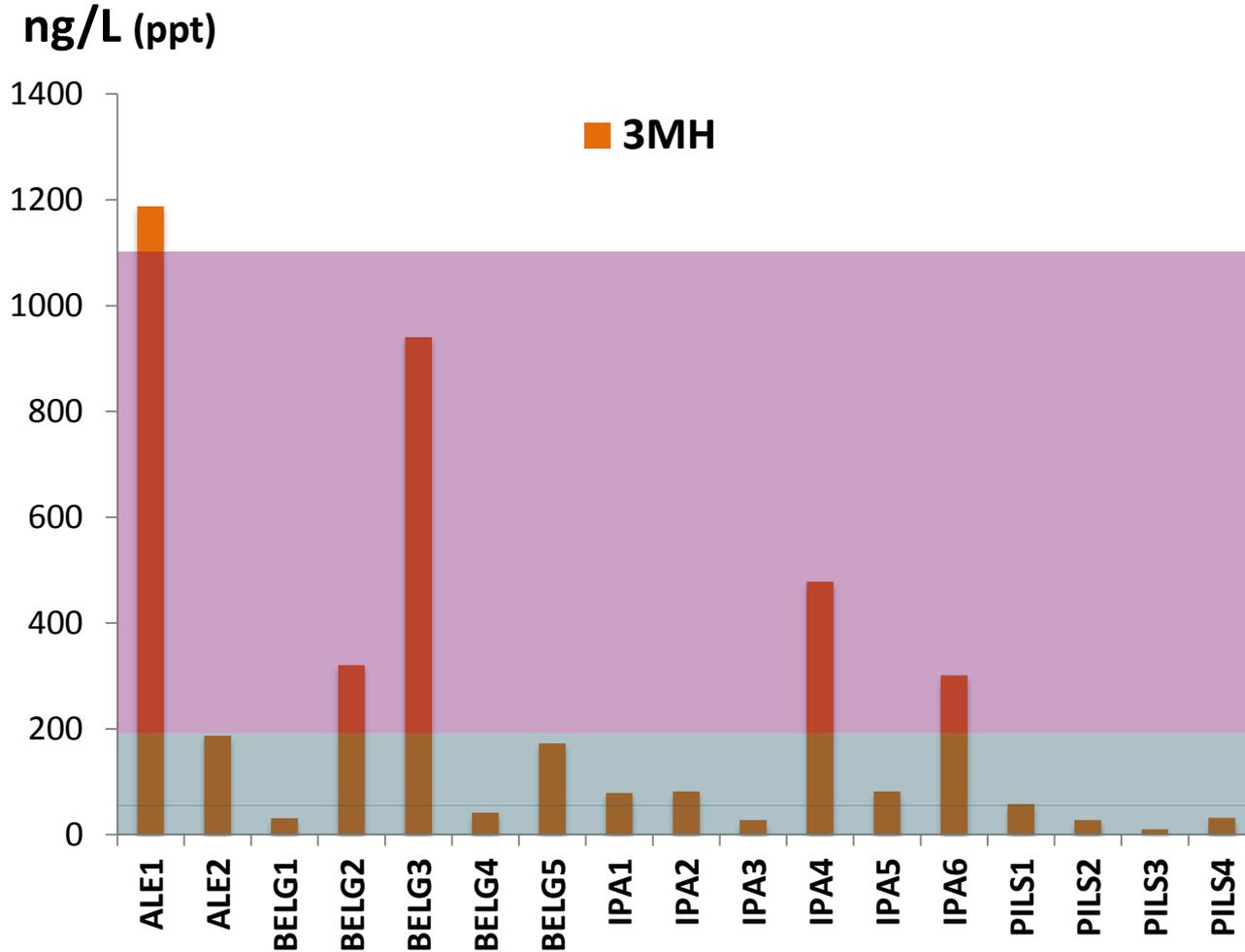
Thiols and thiol precursors in hops

% average of 3MH and corresponding precursors in hops



Thiol precursors represent the biggest part of thiols in hops

Hypothesis regarding thiol origins in beers



Kettle hopping 4g/L
Thiol precursor
(3% fermentation yield)

Kettle hopping 1g/L
Thiol precursor
(1% fermentation yield)

Dry hopping 5g/L
Thiols
(100% extraction yield)

Dry hopping 1g/L
Thiols
(100% extraction yield)

Preliminary experiment during brewing

1) WORT TREATMENTS



Red Ale
Cascade hops
22 IBU est.
5,6% est.

120L
67°C – 60min
76°C – 5min
Malt Pale Ale

Analysis of:

- Thiol precursors in wort

2) DRY HOPPING EXPERIMENT



200g/HL – 5 days

Wort DH0

No dry hopping

Wort DH1



T0 Before fermentation

Wort DH2



T0+27 days

Wort DH3

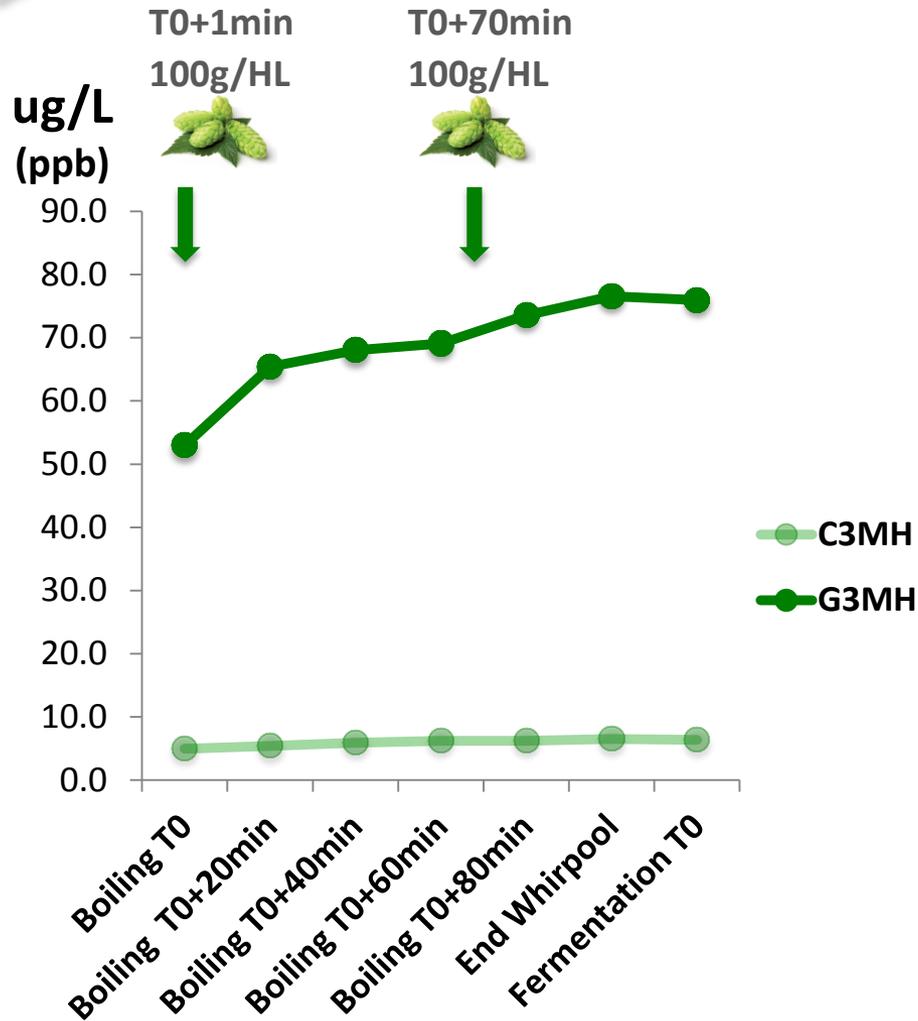


T0+36 days

Analysis of:

- Thiol precursors during fermentation
- Thiols and oxidized thiols in beers

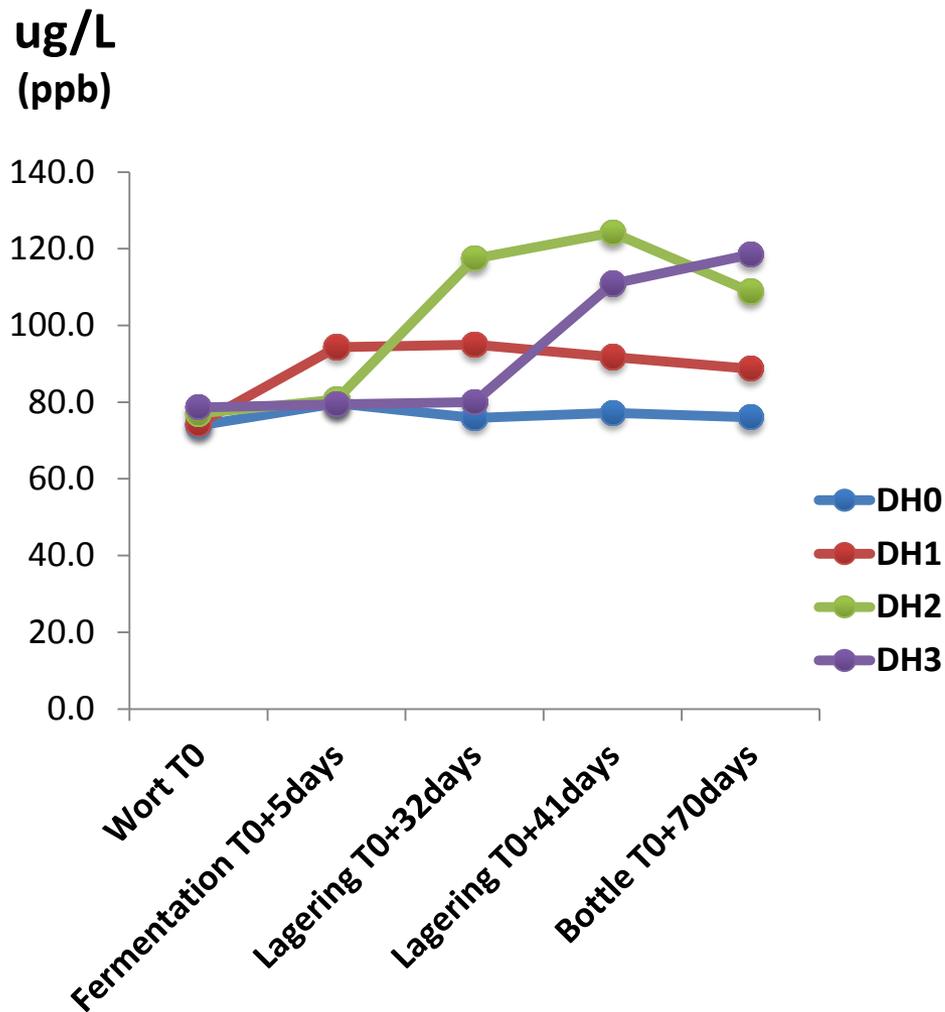
Thiol precursors during wort preparation: G3MH and C3MH



DURING BOILING:

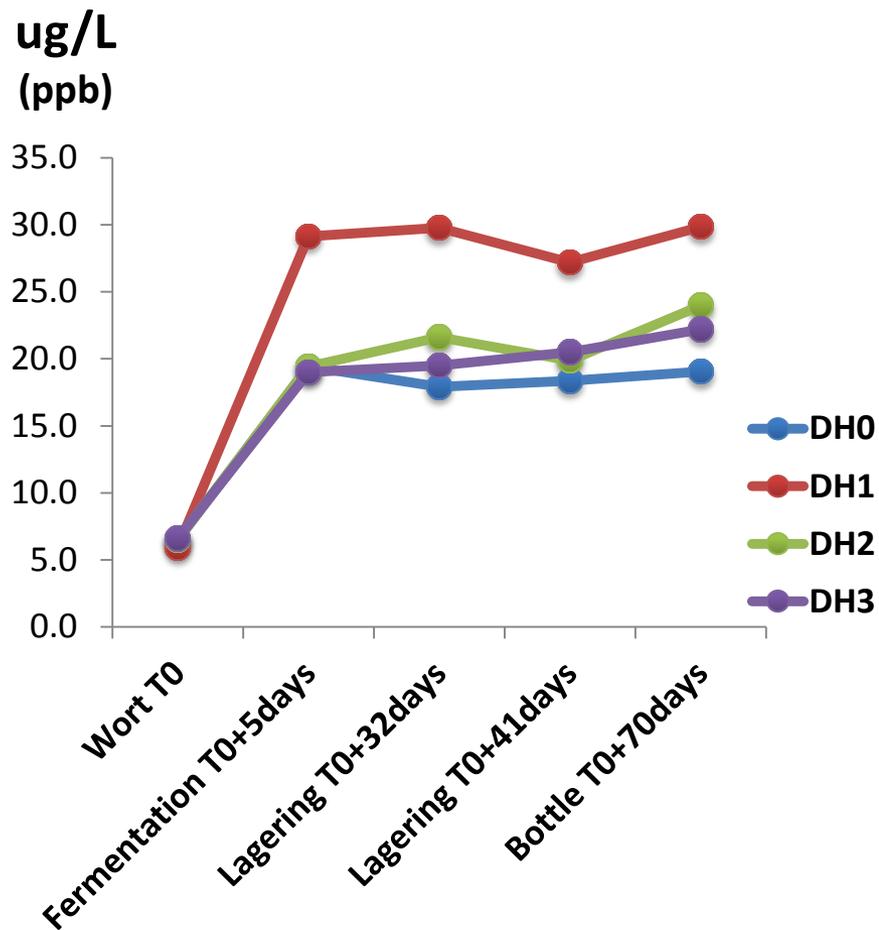
- Thiol precursors are present
- G3MH increases
- Hop addition seems to be responsible for this increase
- 62% of precursors are present before hop addition

Thiol precursors during dry hopping: G3MH



- G3MH is present during fermentation and lagering
- Hop addition increases G3MH levels:
 - 20% more during fermentation (**DH1**)
 - 50% more during lagering (**DH2 - DH3**)
- Fermentation impact G3MH

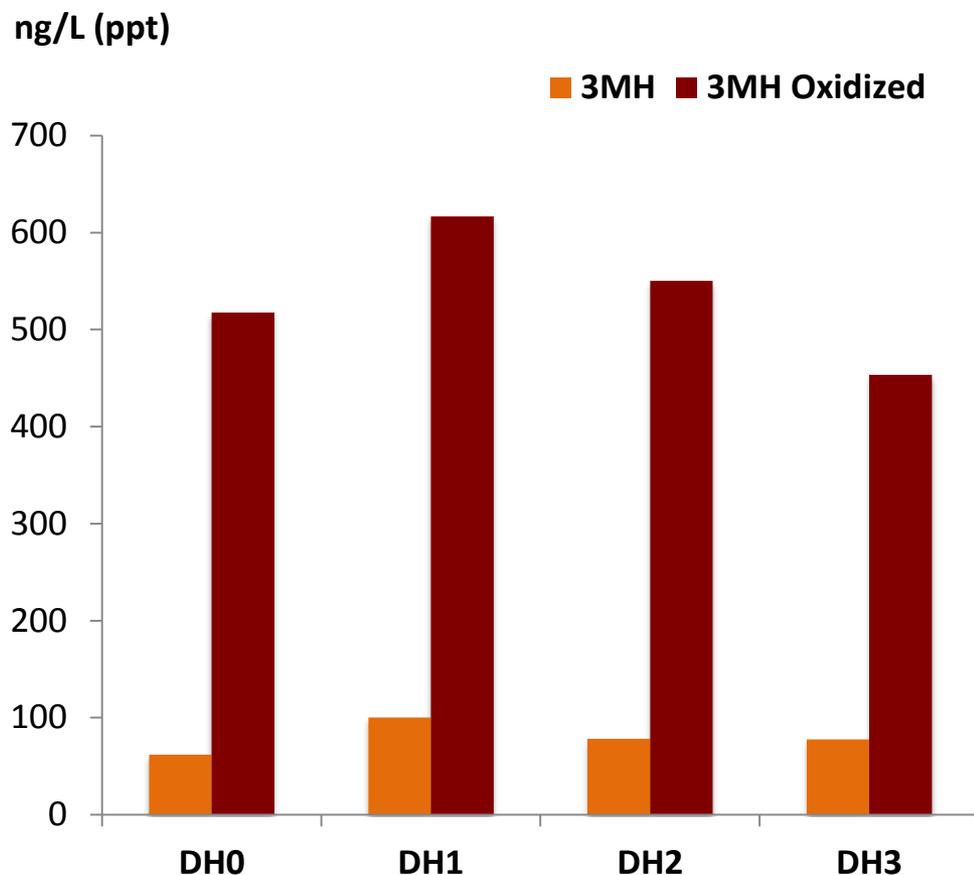
Thiol precursors during brewing: C3MH



DURING FERMENTATION AND LAGERING

- C3MH increases in all conditions, even DH0
- For DH1, C3MH increases twice more than each of the others
- Fermentation changes thiol precursor levels

Thiols and oxidized thiols in beers



3 weeks after bottling

- Hop usage impact 3MH levels
- Before fermentation → more efficient
- Low levels of 3MH
- High levels of 3MH oxidized

CONCLUSION



- Hops are a source of thiols in beer
- Precursors have to be considered to produce beer with high thiol levels
- Hop usages impact thiol levels in beer
- Other process parameters have to be controlled (O2...)
- Malt contains thiol precursors -> **POSTER 143**

PROSPECTS



- 4MMP, Terpenols, PDMS studied in the same approach
- Brewer knowhow is a basis to continue these researchs and identify the most important parameters to control thiols in brewing.
- Hop characterization: other thiol precursors ?
- Better understanding of sensorial contribution of thiols in different beer styles

Thank you for your attention !

