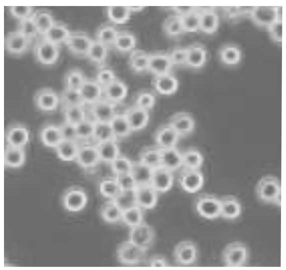

Versuchs- und Lehranstalt für Brauerei in Berlin (VLB) e.V.

Flavor changes in strongly hopped beers

Agenda

- current market situation - Why is the flavor stability of hop forward ales of interest?
- defining stability - What are typical indicators used to monitor beer ageing?
- Lager vs. Ales - What is (chemically) special about hop forward ales?
- project design - How do we try to understand flavor stability in hop forward ales?
- results - What do we know so far and what to do next?

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Current market state

+ increasing number of breweries

Germany		USA	
2016	**2017**	**2016**	**2017**
1 410	1 492	5 491	6 372

+ increasing number of German breweries that produce hoppy ales

  - Brewery Beck und Co. (Beck's Pale Ale)
  - Radeberger Brewery (Braufactum Beers)

source: EST.33 on Instagram

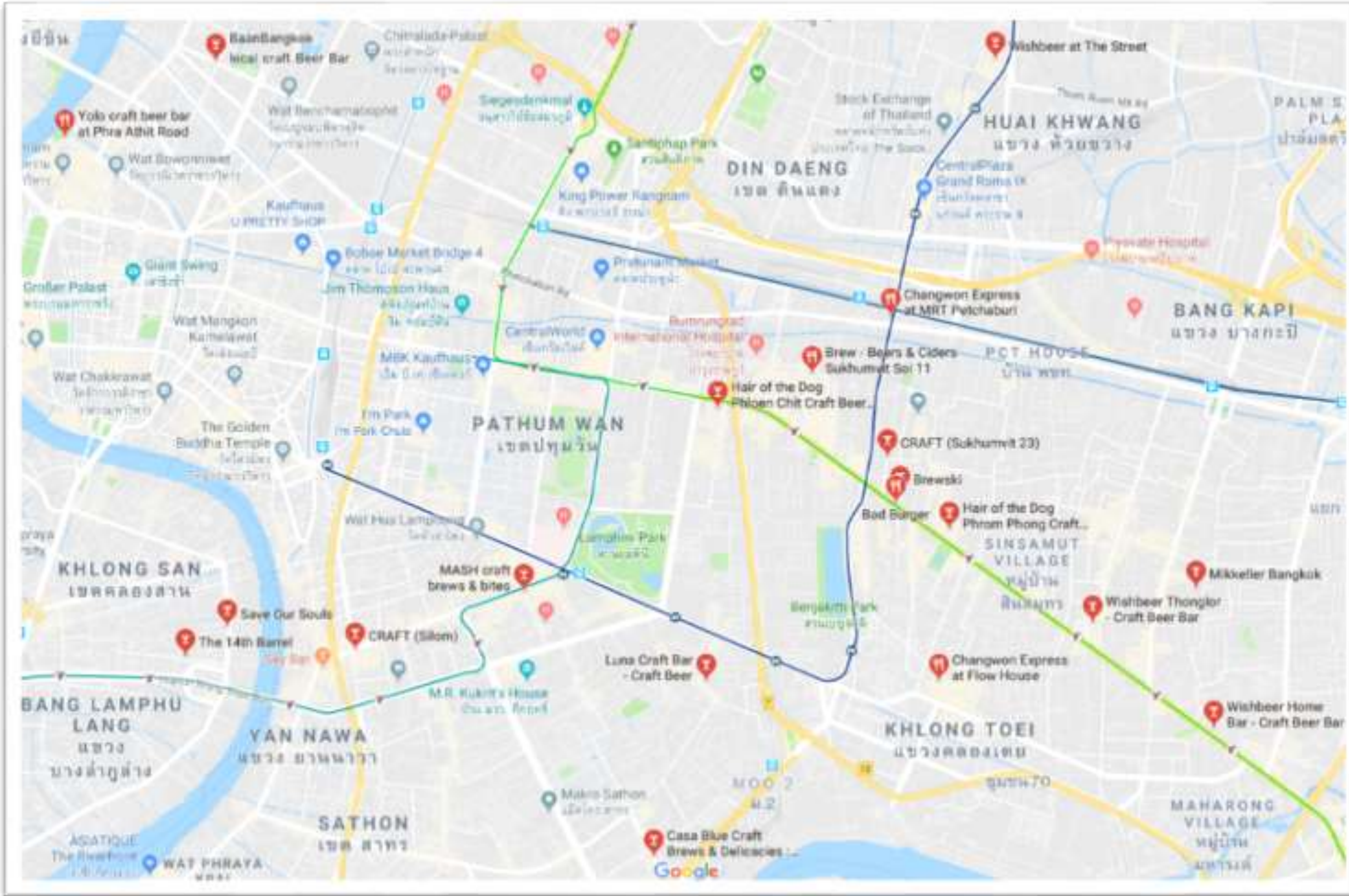
+ Singha Corparation Co., LTD. (EST. 33 Copper and Snowy Weizen)

+ hop forward beer styles are interesting for every brewery

source: Deutscher Brauer-Bund / Brewers Association / Statistisches Bundesamt

Current market state

searching: “Bangkok, craft beer” at Google Maps results in 20 hits, that sell special beer types



source: Google Maps

Agenda

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What is „ageing stability“?

- no fixed definition exists
- basically 3 categories of “stability”
- physical and flavor stability are partly connected

flavor stability

microbiological stability
physical stability

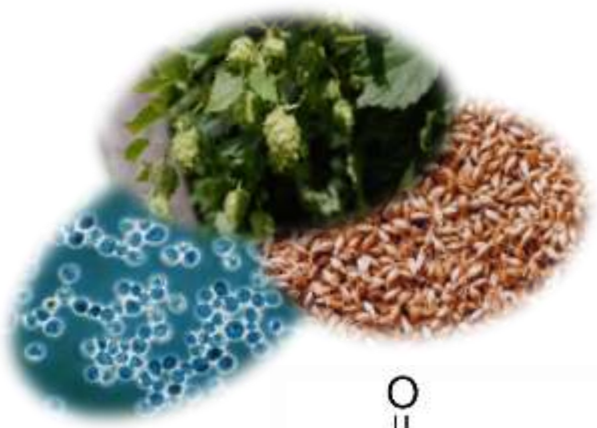
transportation, distribution, service

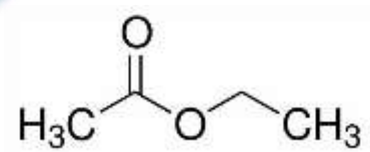
brewery site

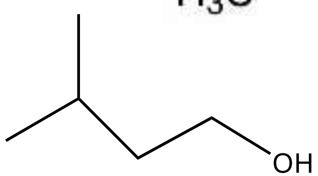
source: https://www.mein-buntes-leben.de/artikel/craftbeer-massvoller-biergenuss-bei-diabetes

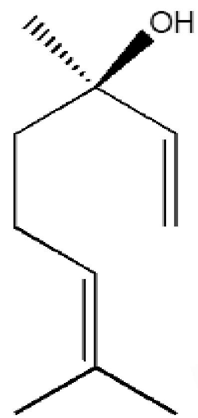
What is „ageing stability"?

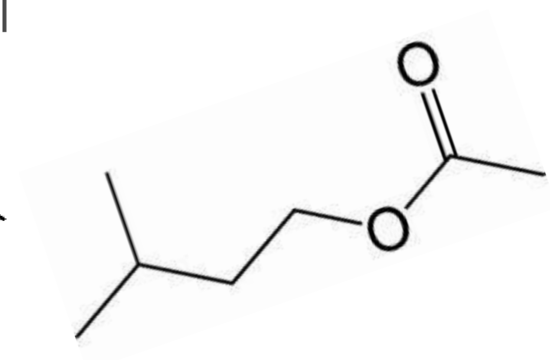
- aroma and taste are complex
  - they are an interaction of thousands of compounds from raw materials and technological aspects











- molecule formation → new aroma impressions can arise
- degradation / modification of existing substances → loss of flavor

source: Deutscher Brauer-Bund

Current state of research

flavor stability

- raw materials (pale / dark malt, adjuncts…)
- optimized filling conditions (O_2-uptake < 20ppb, pasteurization)
- brewing technology (LOX-activity, boiling, hopping regime…)
- storage conditions (temperature, light)
- brewing technique (mashing, boiling / stripping…)
- bottles, caps, cans

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Taste influences - Lager vs. Ales

- Maillard products can be positive in dark (bottom fermented) beers
  → malt aroma might cover carbonyl off-flavors

- precursors of carbonyl compounds:
  - Maillard reaction / Strecker degradation products (e.g. can result in 2-Methylbutanal, 3-Methylbutanal, Methional, Phenylacetaldehyd…)
  - thermal wort stress (results in increase of 2-Furfural, 5-Hydroxymethyl-2-furfural)
  - fatty acid degradation / oxidation of lipids (*trans*-2-Nonenal → cardboard flavor)

- increase of sweet, sherry like notes with ageing
  (sometimes wanted for special beers → barrel-aged or vintage beer)

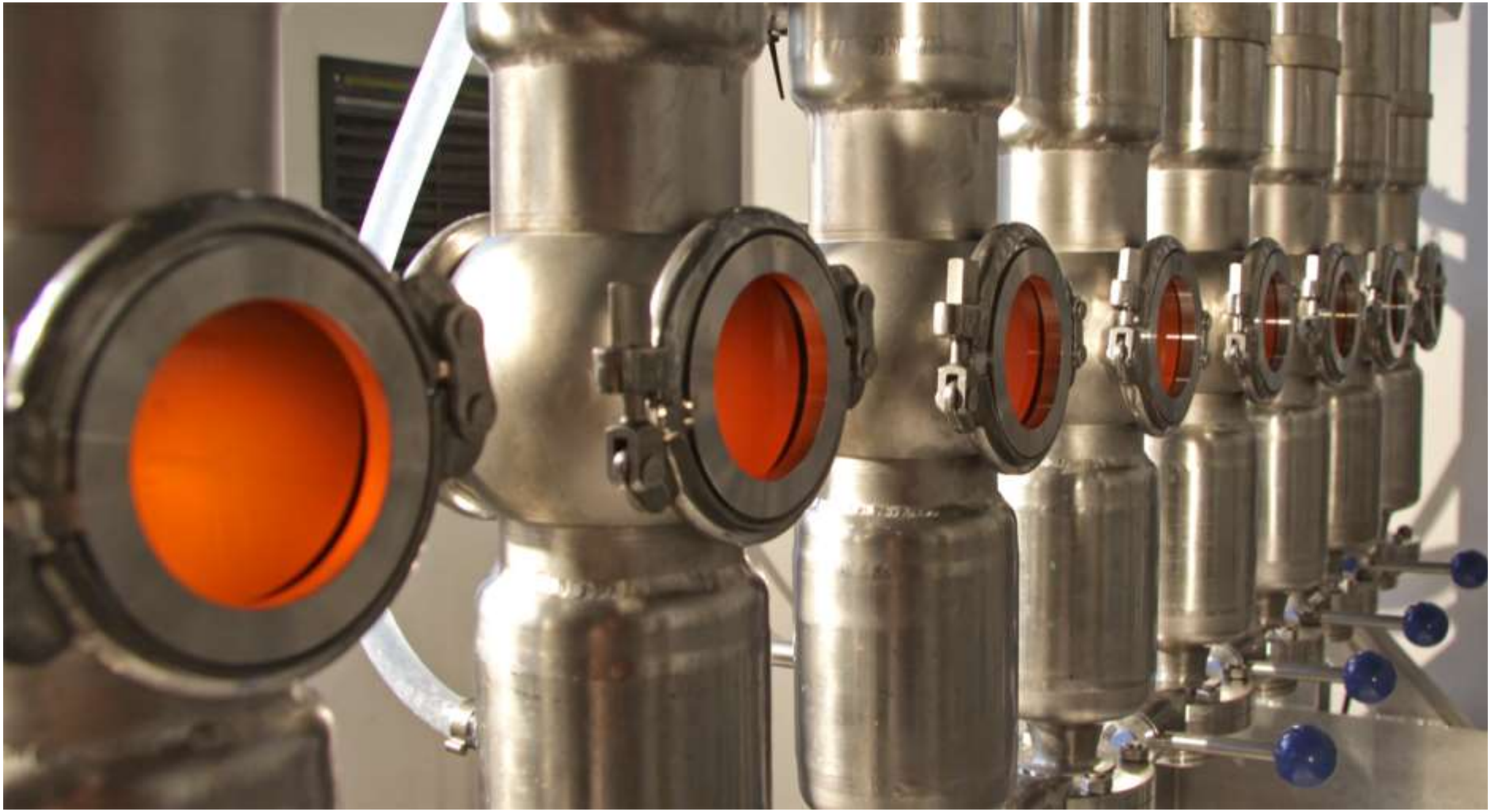
Taste influences - Lager vs. Ales

- fermenting by-products
  - top fermented beers (Ales) are normally fermented at higher temperature → more higher alcohols and esters → fruity, ester like notes are wanted
- amounts of pro- und antioxidant compounds vary in Ales and bottom fermented beers
  - pale / dark malt, rise of polyphenols from hops e.g. by dry hopping, O_2-amount in craft beer, SO_2-amounts in Ales are lower by using top fermenting yeast
- often high IBU‘s in Ales are wanted
- hop dosage in varying stages of Ale production

bitterness and hop aroma are crucial for flavor impressions in hoppy Ales

Hop characteristics in Ales

- hop compounds in high concentrations (compared with lager style)
- hop substances are present, that are absent in lager beers
- positive influence of (oxidative) stability by antioxidative constituents like polyphenols or bitter substances



Project

Flavor stability of hoppy, top fermented beers

VLB BERLIN

Agenda

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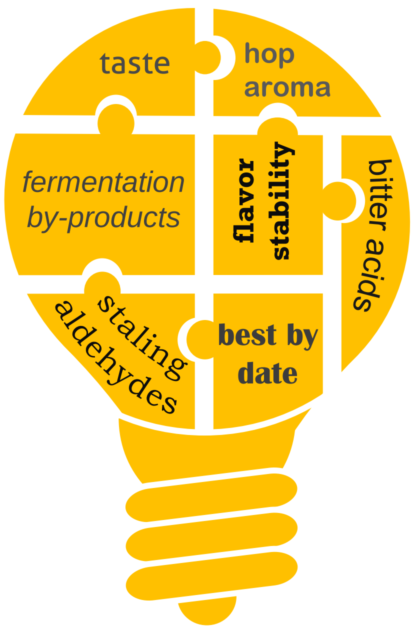
Pre-project procedure



brewery questionnaire on flavor stability and best by date

“Much shorter would be logistically impractical. Much longer would be unfair to consumers”

„We´d like it to be shorter than 6 months….“

„Consumers are very aware“

„Slight oxidative qualities can appear as early as after 1 month.“

Project outline

Stage 3: Verify data in brewing trials targeting hopped beers with improved shelf life.

Stage 2: Specify data from stage one by further screening trials for unknown substances.

Stage 1: Check the behavior of known ageing parameters in highly hopped beers.

Project outline

Stage 3: Verify data in brewing trials targeting hopped beers with improved shelf life.

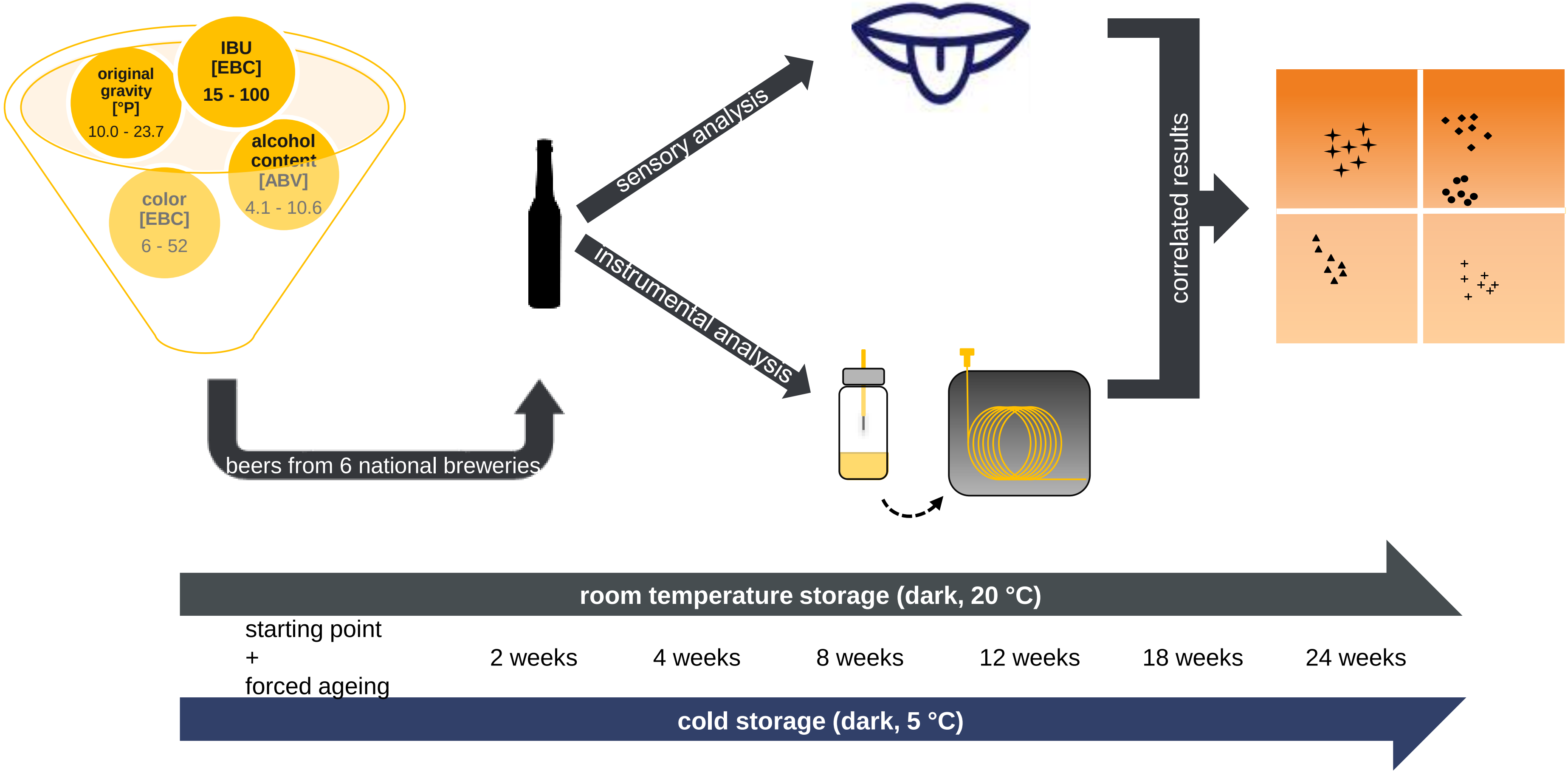
Stage 2: Specify data from stage one by further screening trials for unknown substances.

Stage 1: Check the behavior of known ageing parameters in highly hopped beers.

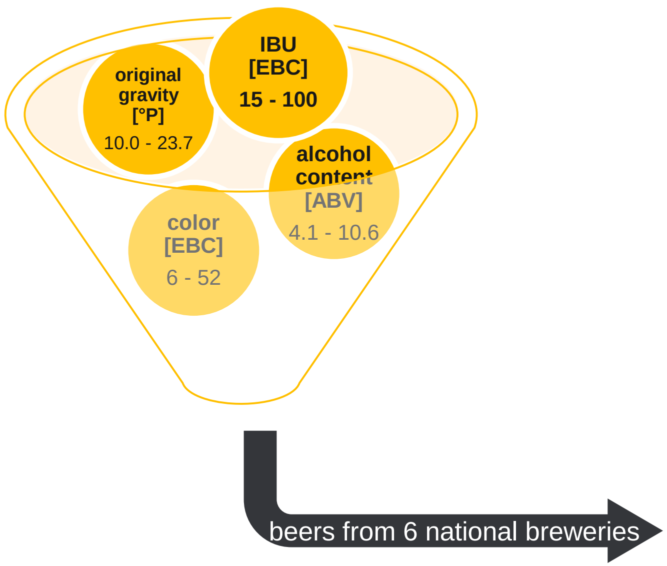
Experimental design - Stage one

Design of Experiment (DoE) based on Brewers Association „Beer Style Guidelines“ for Styles:

→ Blonde Ale / Pale Ale / Red Ale / India Pale Ale / Brown Ale / Double India Pale Ale



Experimental design - Stage one



beerstyle	bitterness [EBC]	color [EBC]	original gravity [% mas]	ABV
brown Ale	47	57	12.70	5.44
IPA #1	65	17	14.97	6.30
IPA #2	60	26	16.15	6.98
dark Rye IPA	72	170	17.72	7.16
non-alcoholic IPA	34	18	8.16	0.40
IPA #3	58	22	17.15	7.75
IPA #4	70	42	17.75	6.80
Pale Ale	35	17	13.57	5.40
IPA #5	47	29	17.26	8.20
IPA #6	59	18	16.67	7.70
imperial IPA	65	27	21.63	9.94

Analysis in stage one

Parameter	Method
sulfur dioxide	EBC 9.25.1
metal content (Fe, Cu, Mn)	ICP-MS (DIN EN ISO 17294-2:2005-02, mod.)
density, original gravity, alcohol content, apparent (and real extract)	EBC 9.43.2 und EBC 9.4
beer bitter acids (ratio of trans-cis iso-α-acid used for PCA)	UPLC-ToF-MS
pH-Value, color	EBC 9.35, EBC 9.6
bitterness of beer (IBU)	EBC 9.8
DMS	HS-GC-PFPD (EBC 9.39, mod.)
fermentation by products (higher aliphatic alcohols and esters)	HS-GC-FID (EBC 9.39, mod.)
hop aroma compounds	HS-SPME-GC-MS/MS
carbonyl compounds	HS-SPME-GC-MS/MS
short chain fatty acids (C4 – C12)	HS-SPME-GC-FID
sensory analysis	descriptive sensory trials with default attributes

point of measurement used for PCA:

fresh,
forced aged,
room temperature *12* und *24 weeks*,
cold storage *12* und *24 weeks*

Sensory trials stage one

- 9 trained VLB testers on average
- 14 descriptors
  - intensity of odor
  - quality of bitterness
  - malt character
  - duration of aftertaste
  - taste
  - intensity of hop aroma
  - sweetness
  - palatefulness
  - harmony
  - general quality
  - intensity of bitterness
  - acidity
  - oxidation
  - odor
- additional free text option for comments

Experimental results stage one

- in phase one we analyzed:

  11 beers resulting in
  88 samples, by using
  14 methods (measured in duplets), leading to
  1 056 chromatograms and
  60 192 peaks …

  → correspondingly large dataset

- we will focus on three major aspects here:

  - primary hop aroma compounds (terpenes)
  - staling aldehydes
  - bitter acids

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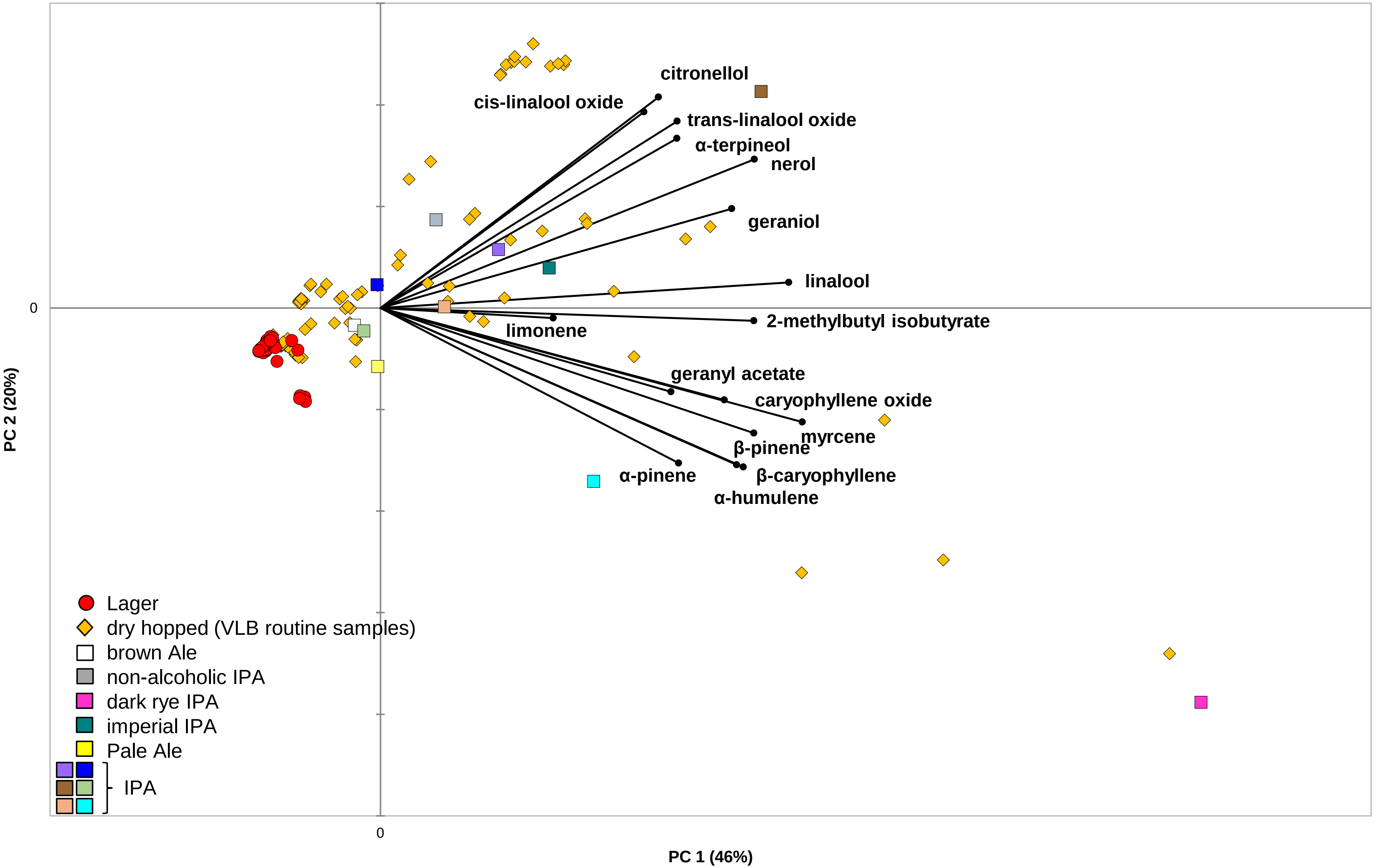
Hop aroma compounds (Biplot)



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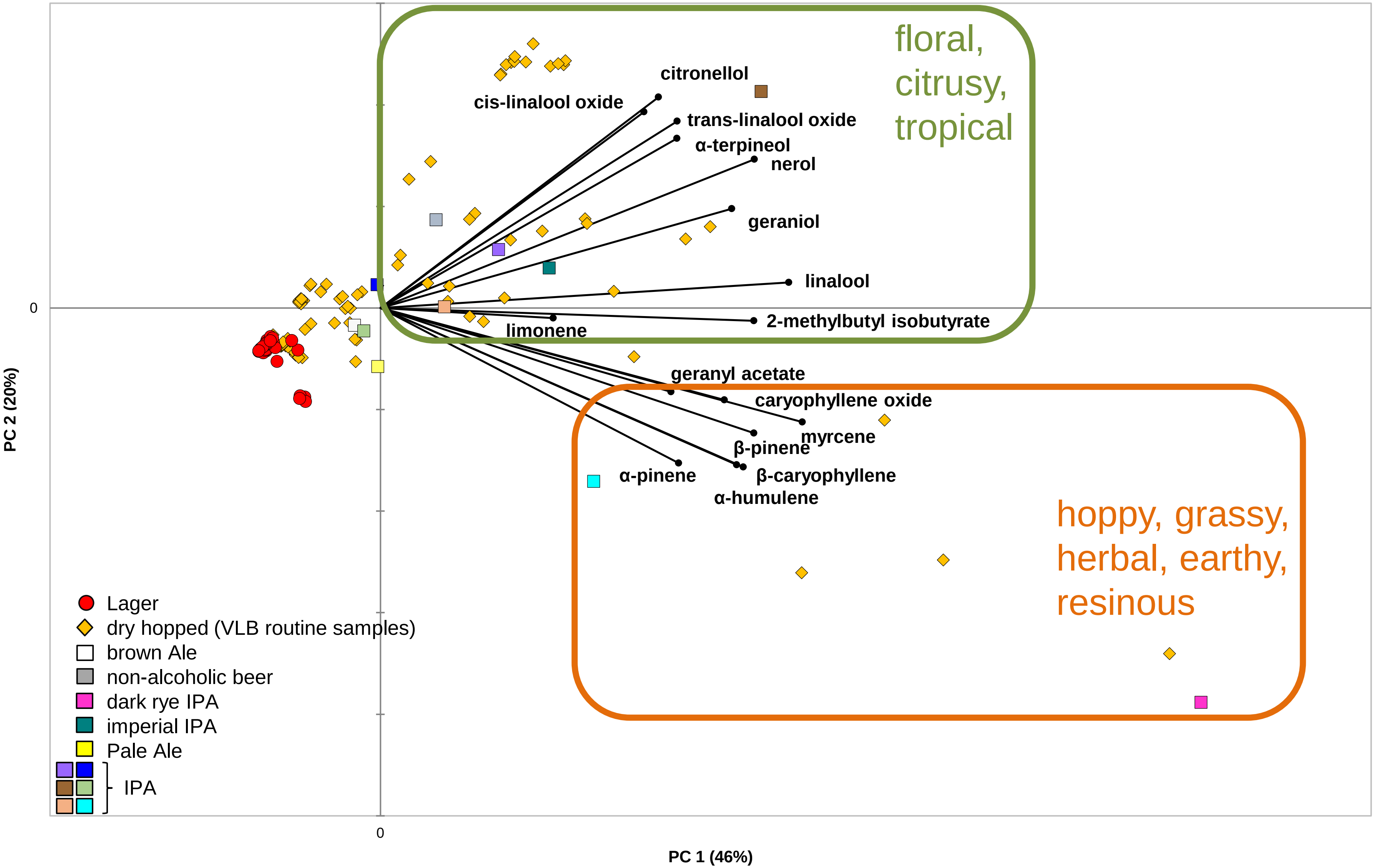


Summary hop aroma compounds

+ regarding hop aroma, beers split into two big groups

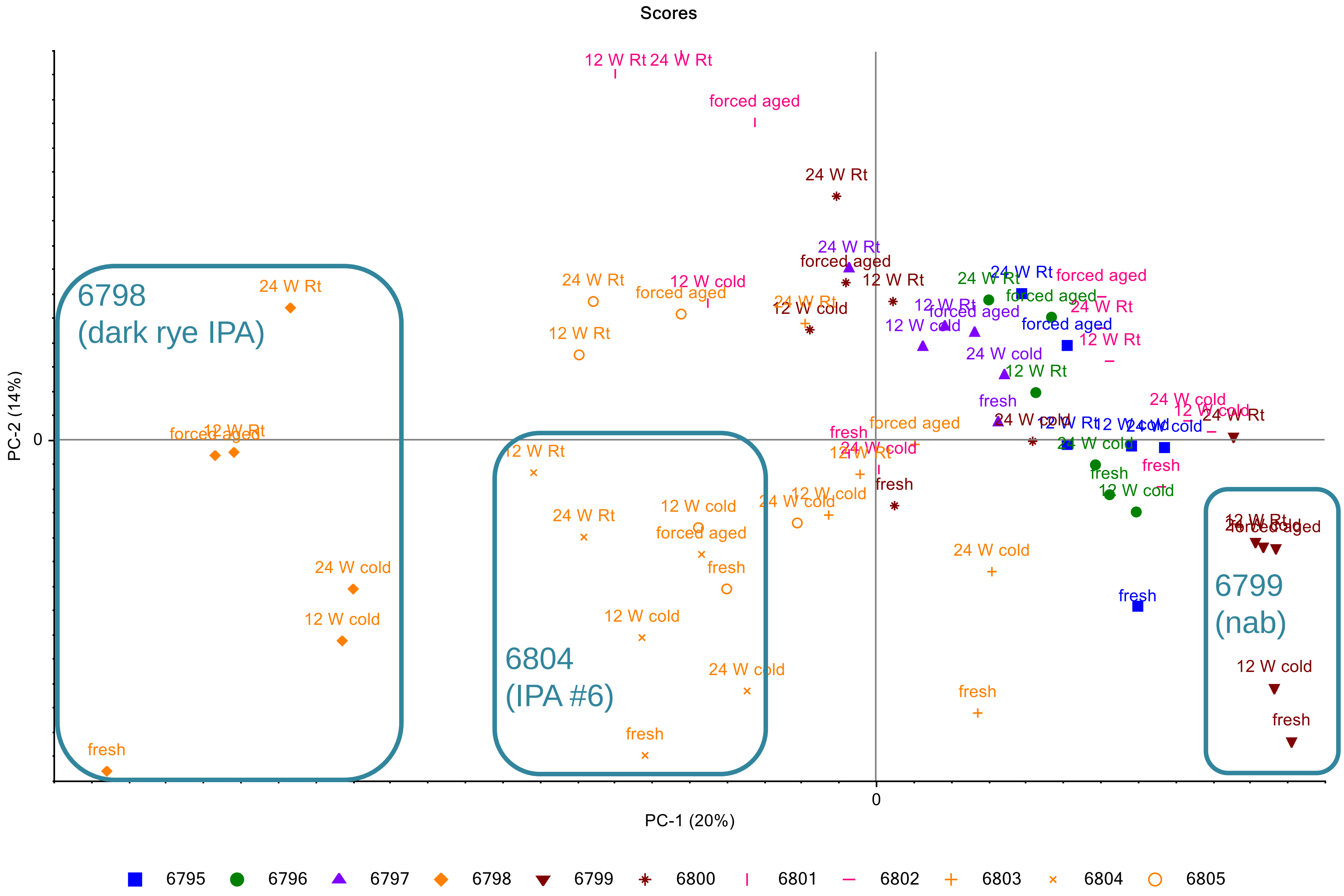
    1. earthy, resinous styles
    2. fruity, citrus styles

        - Lager style isn't any of them
(but they are extremely similar in a cluster)

        - in strong hopped beers, differences in beer styles are noticeable (IPA's can be highly different in hop aroma)

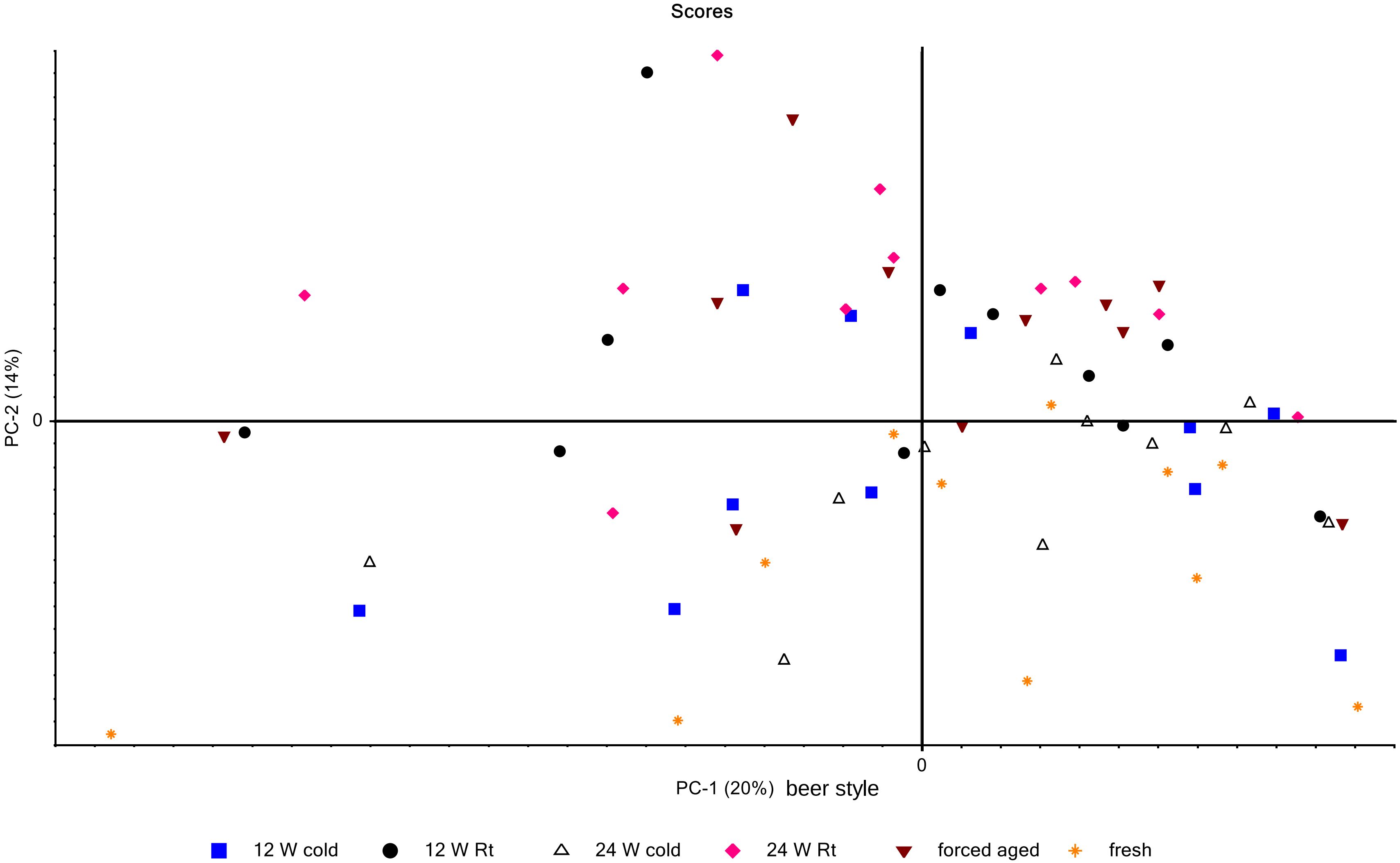
Hoppy, top fermented samples (grouping)

Hoppy, top fermented samples (grouping)



PC 1 shows the beer style

Hoppy, top fermented samples (storage conditions trend)



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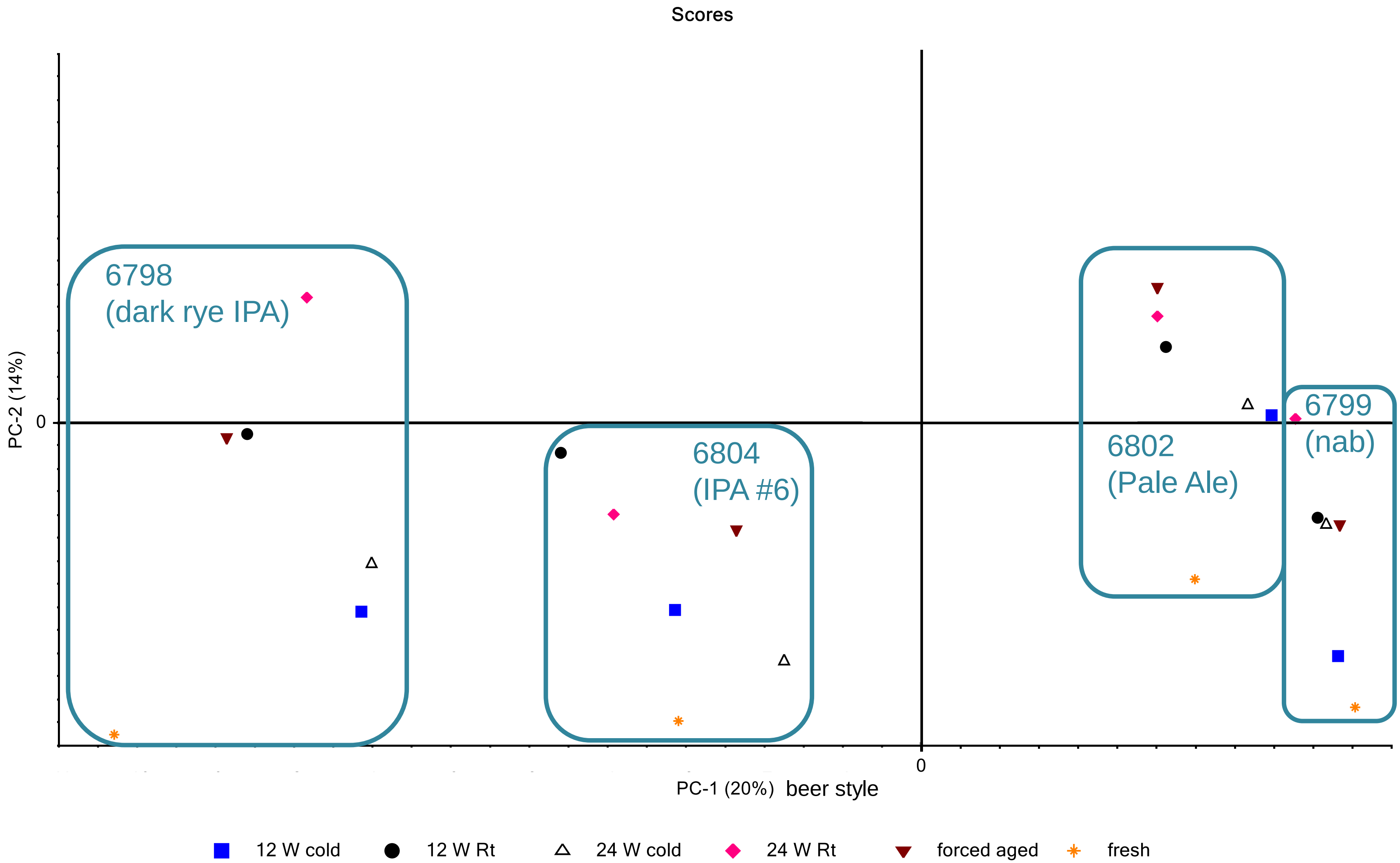
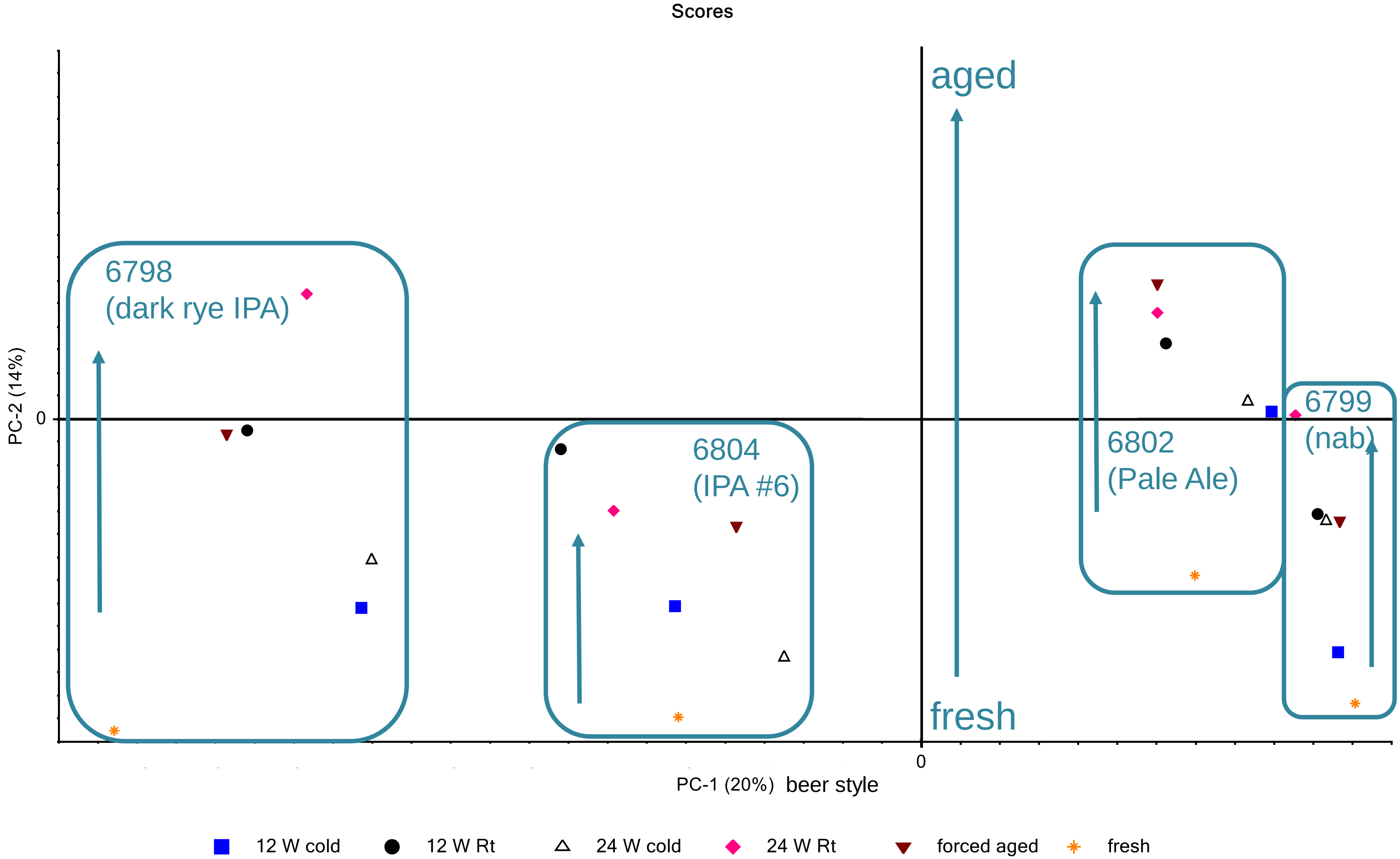
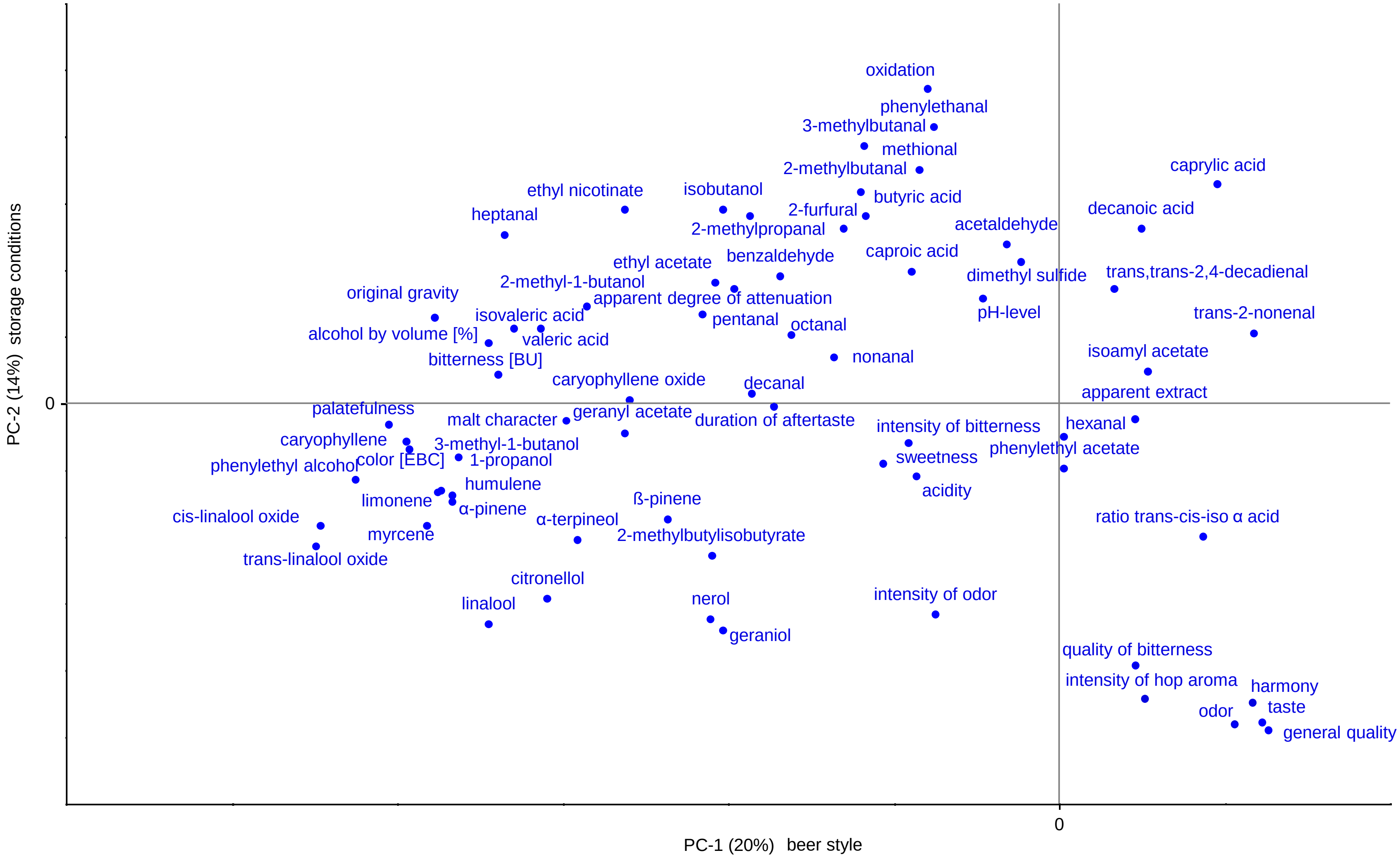


Hoppy, top fermented samples (storage conditions trend)

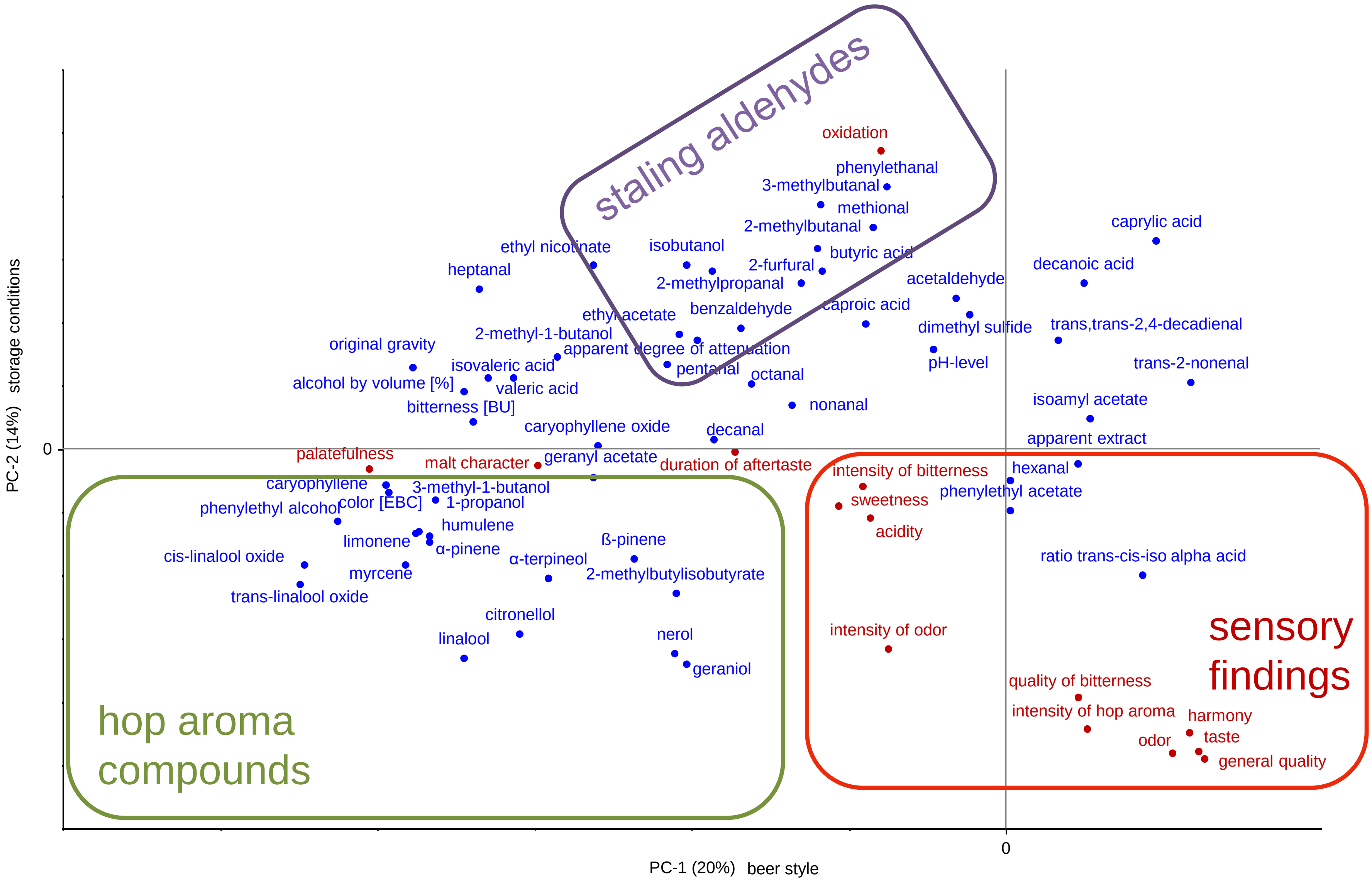


PC 2 represents the storage conditions

Hoppy, top fermented samples (Loadingsplot)



Hoppy, top fermented samples (Loadingsplot)



Principal component analysis (PCA)

Summary storage trials

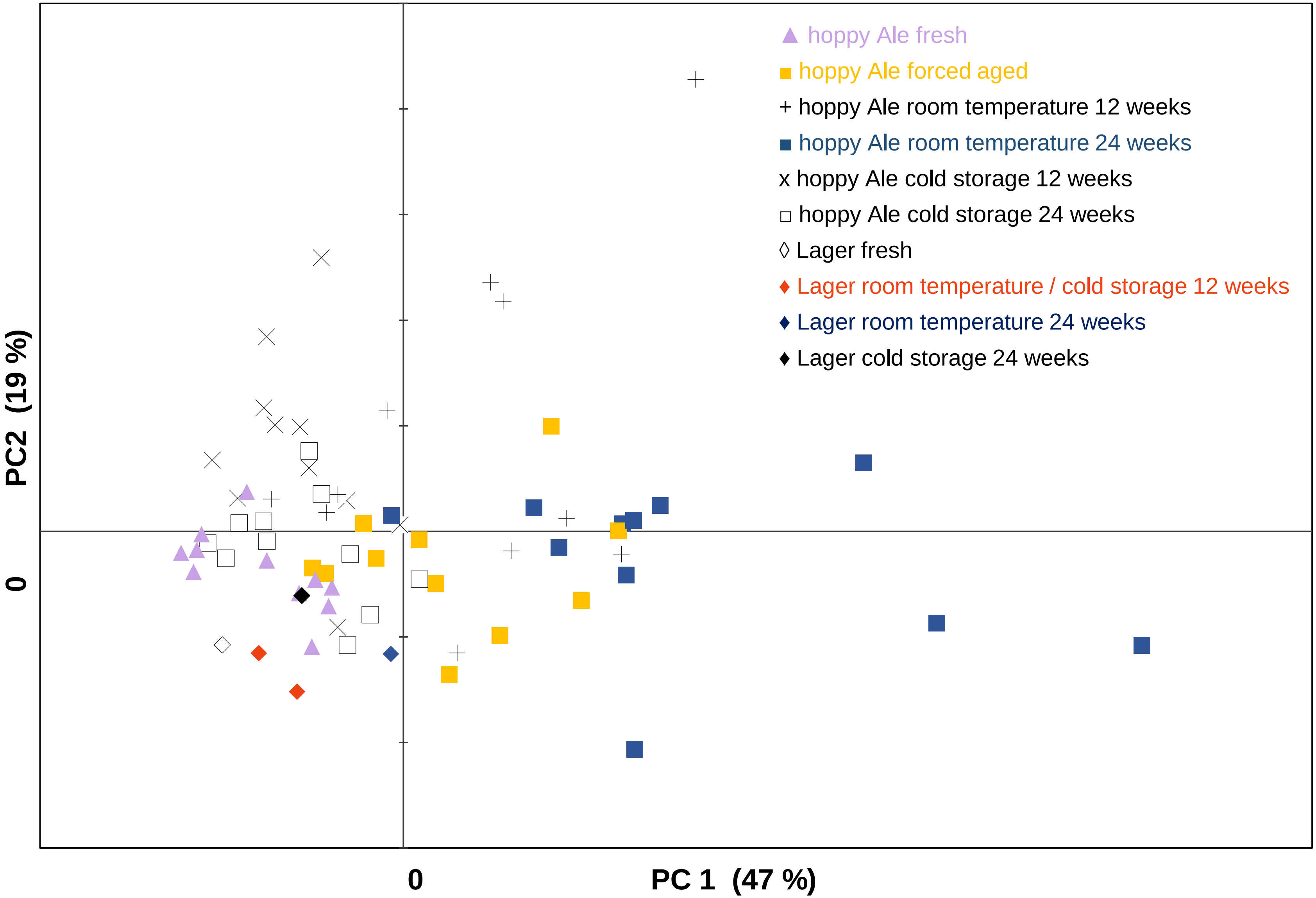
- beer styles are clustering (similar beer styles) or distinguish

- staling aldehydes correlate with storage conditions but sensory trials are not able to fully describe them

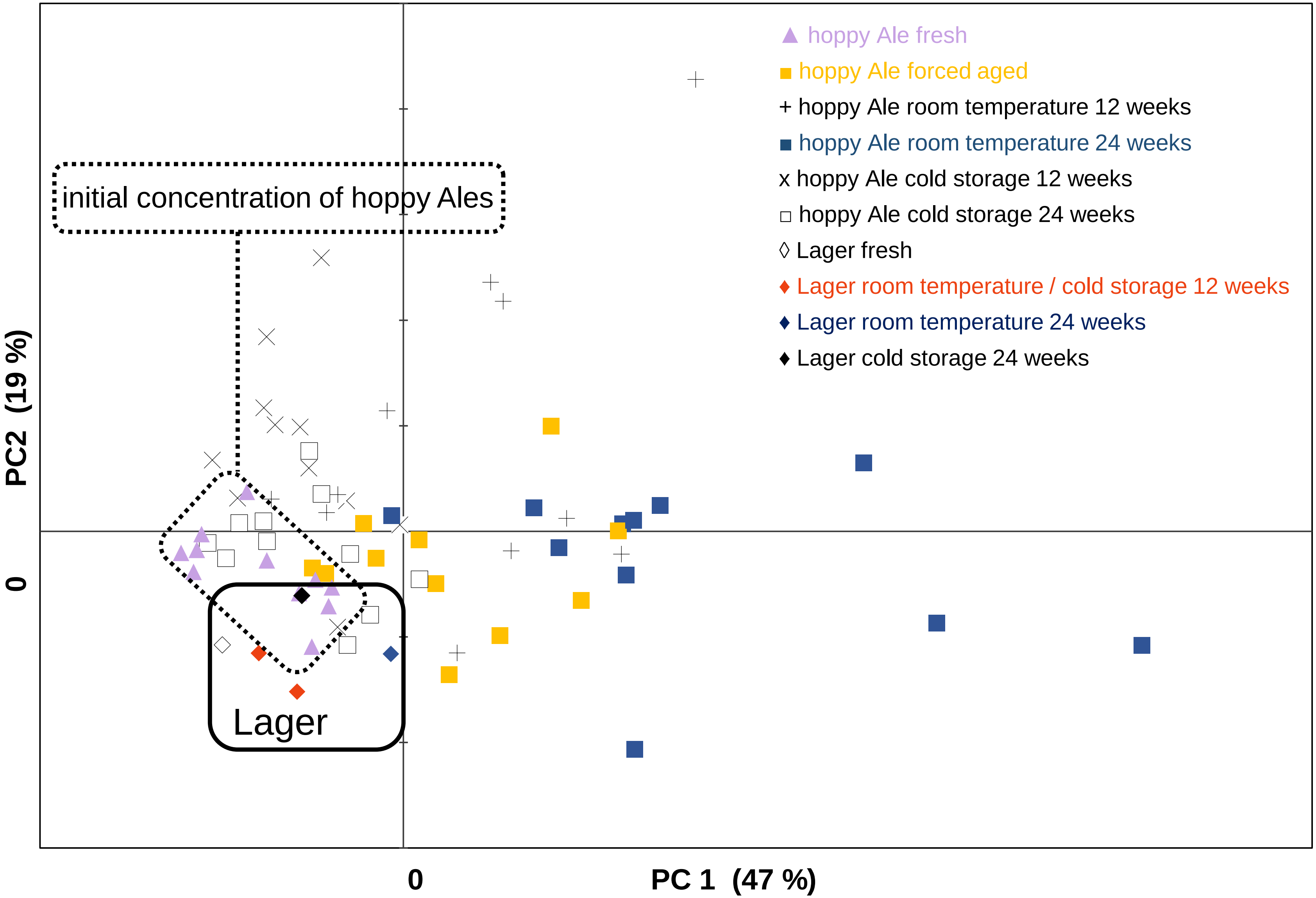
- beers react as expected under storage conditions
  - forced ageing test describes in a good way the behavior of ageing under room temperature conditions (12 – 24 weeks)

    → time savings for subsequent project steps

Staling Aldehydes



Staling Aldehydes



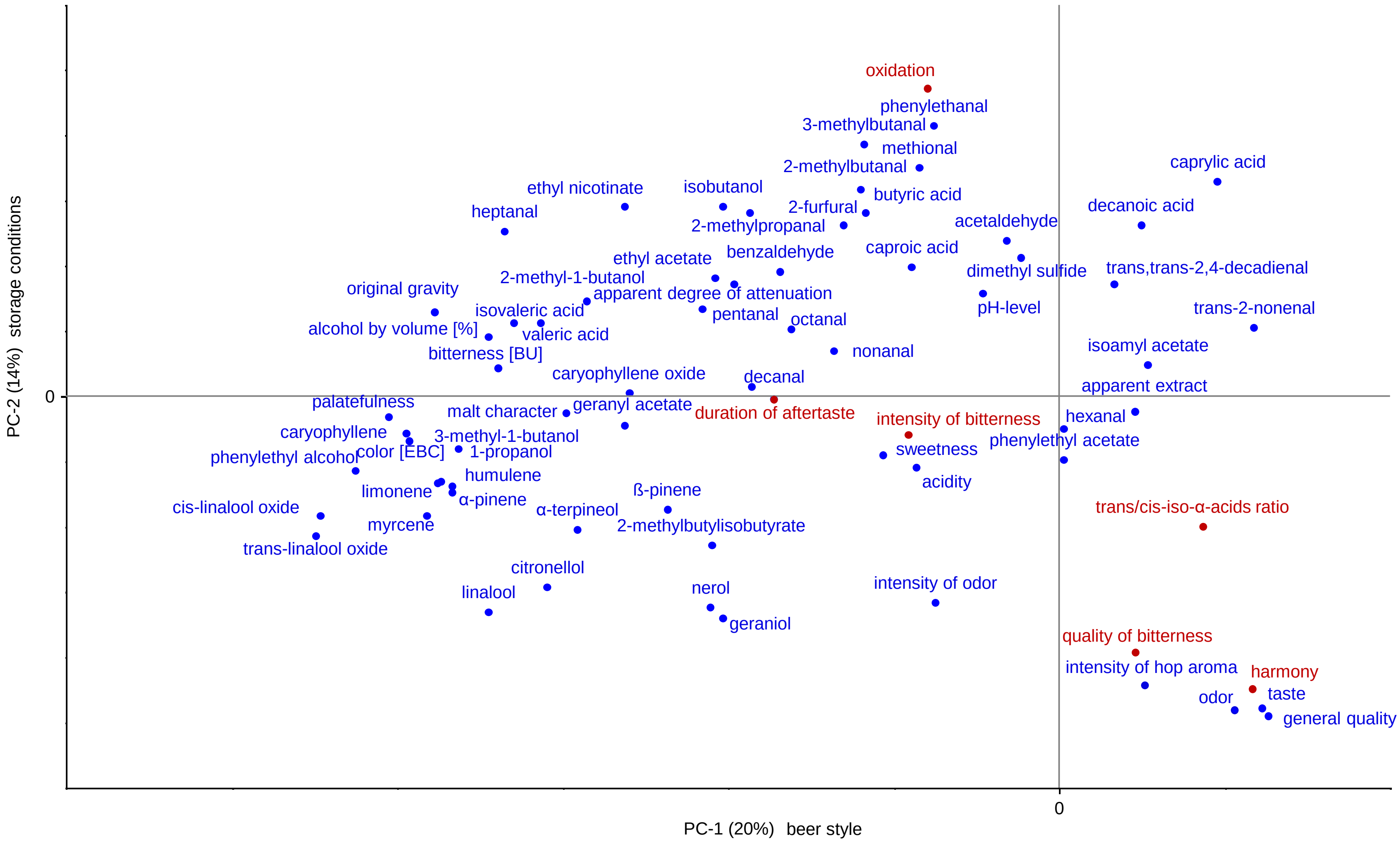
Summary staling aldehydes

- concentration of carbonyl compounds increase less in Lager style (compared to highly hopped beers)
  - nevertheless stale taste is noticeable early in Lager beer

- staling aldehydes in highly hopped beers started at a higher range than Lager reach after storage
  - no “ageing” characteristic was recognized in sensory trials of fresh products
  - they where noticed only after a high increase during storage
  - mainly as “oxidized” → harmony, odor, taste and general quality seem less affected

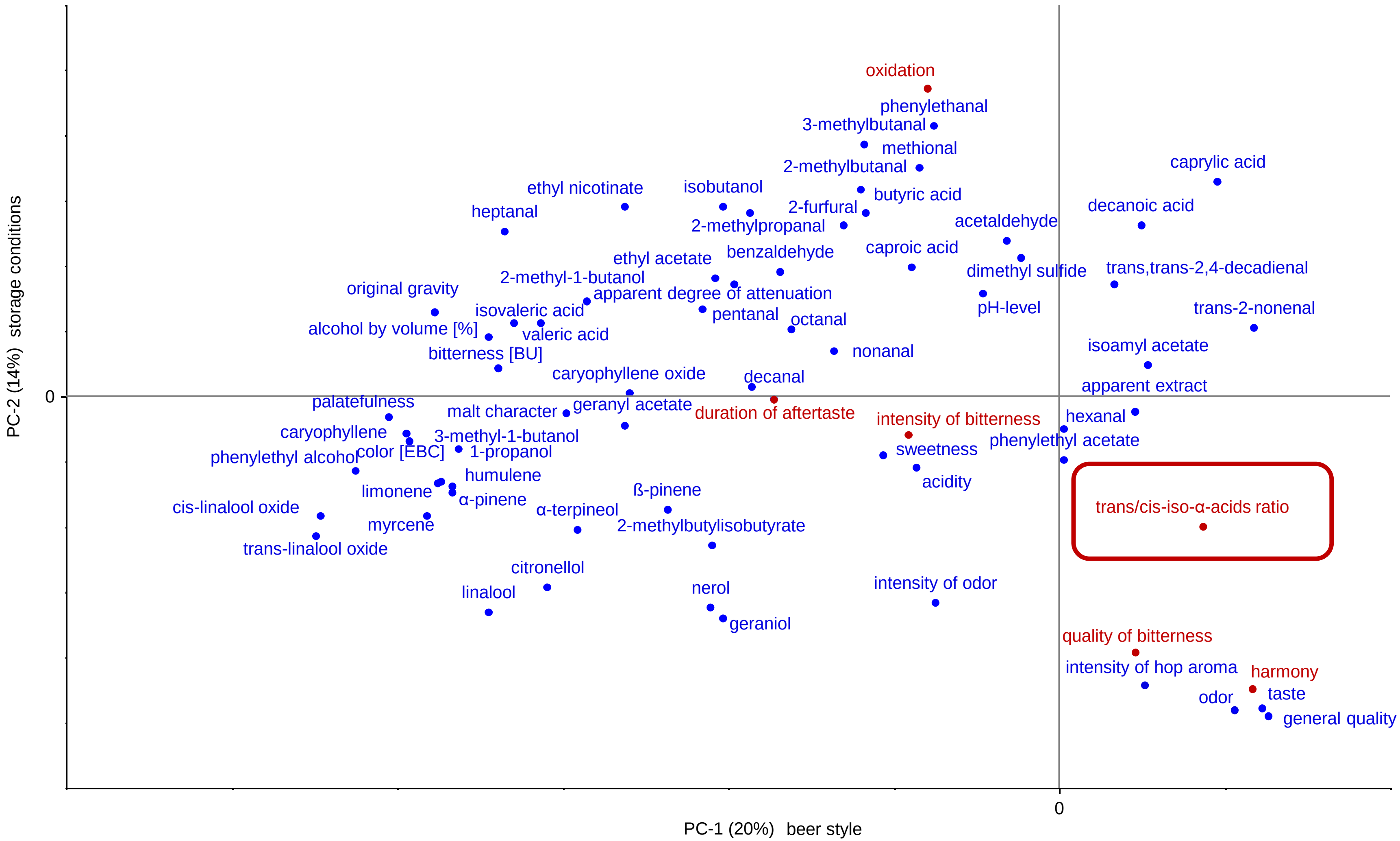
staling aldehydes are of interest in hop forward beers but they are not that crucial as they are in Lager style

Bitterness

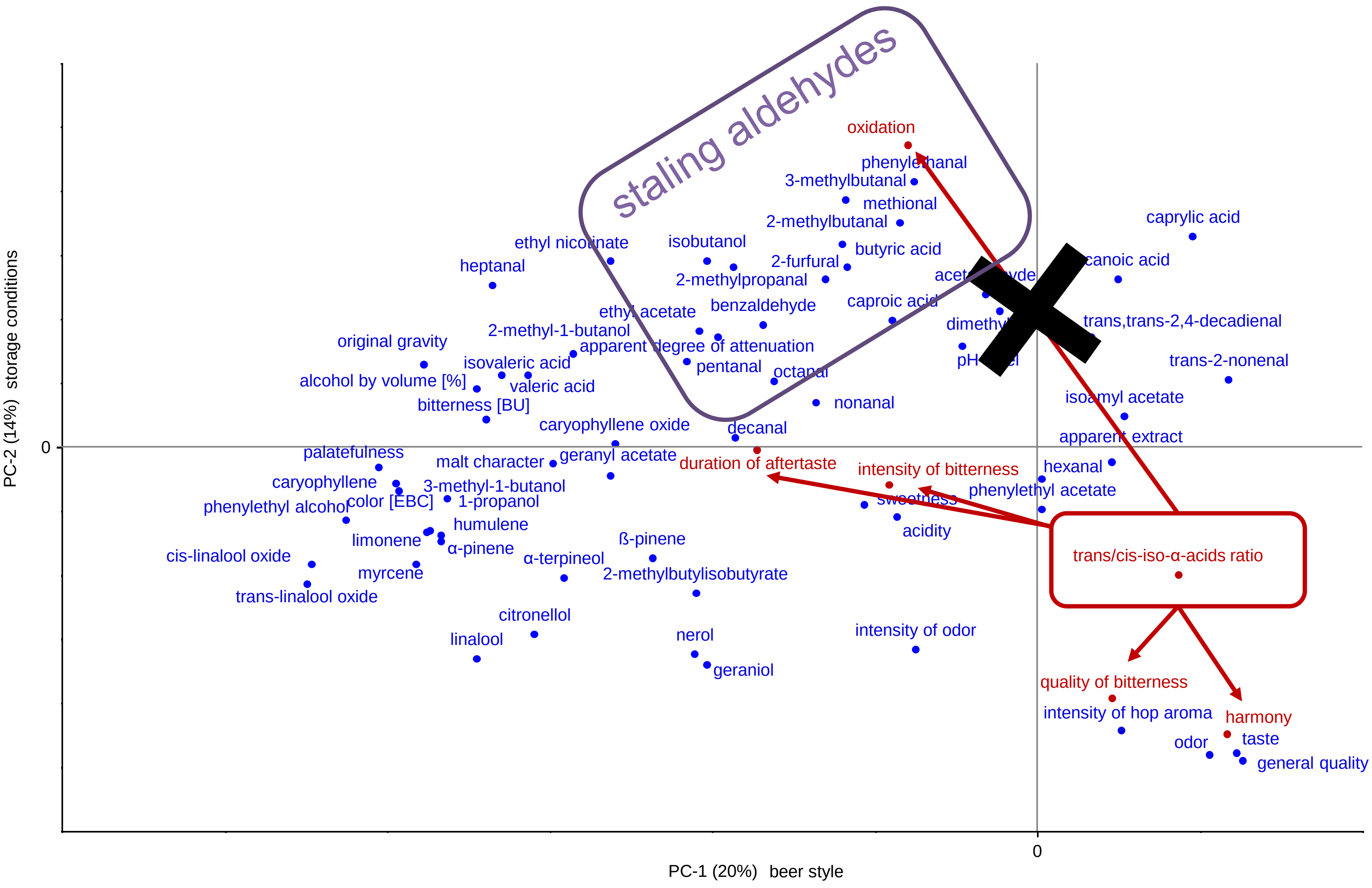


PC-2 (14%) storage conditions
PC-1 (20%) beer style
0
0
oxidation
phenylethanal
3-methylbutanal
methional
2-methylbutanal
caprylic acid
ethyl nicotinate
isobutanol
butyric acid
heptanal
2-furfural
decanoic acid
2-methylpropanal
acetaldehyde
ethyl acetate
benzaldehyde
caproic acid
2-methyl-1-butanol
dimethyl sulfide
trans,trans-2,4-decadienal
original gravity
apparent degree of attenuation
isovaleric acid
pentanal
octanal
pH-level
trans-2-nonenal
alcohol by volume [%]
valeric acid
bitterness [BU]
nonanal
isoamyl acetate
caryophyllene oxide
decanal
apparent extract
palatefulness
malt character
geranyl acetate
duration of aftertaste
intensity of bitterness
hexanal
caryophyllene
3-methyl-1-butanol
sweetness
phenylethyl acetate
phenylethyl alcohol
color [EBC]
1-propanol
humulene
acidity
limonene
ß-pinene
α-pinene
cis-linalool oxide
α-terpineol
trans/cis-iso-α-acids ratio
myrcene
2-methylbutylisobutyrate
trans-linalool oxide
citronellol
linalool
nerol
intensity of odor
geraniol
quality of bitterness
intensity of hop aroma
harmony
taste
odor
general quality

Bitterness


oxidation
phenylethanal
3-methylbutanal
methional
2-methylbutanal
caprylic acid
ethyl nicotinate
isobutanol
butyric acid
heptanal
2-furfural
decanoic acid
2-methylpropanal
acetaldehyde
ethyl acetate
benzaldehyde
caproic acid
2-methyl-1-butanol
dimethyl sulfide
trans,trans-2,4-decadienal
original gravity
apparent degree of attenuation
isovaleric acid
pH-level
trans-2-nonenal
pentanal
octanal
alcohol by volume [%]
valeric acid
bitterness [BU]
nonanal
isoamyl acetate
caryophyllene oxide
decanal
apparent extract
0
palatefulness
malt character
geranyl acetate
duration of aftertaste
intensity of bitterness
hexanal
caryophyllene
3-methyl-1-butanol
phenylethyl acetate
phenylethyl alcohol
color [EBC]
1-propanol
sweetness
humulene
acidity
limonene
ß-pinene
α-pinene
trans/cis-iso-α-acids ratio
cis-linalool oxide
α-terpineol
myrcene
2-methylbutylisobutyrate
trans-linalool oxide
citronellol
intensity of odor
linalool
nerol
geraniol
quality of bitterness
intensity of hop aroma
harmony
taste
odor
general quality
PC-2 (14%) storage conditions
PC-1 (20%) beer style
0

Bitterness



staling aldehydes
oxidation
phenylethanal
3-methylbutanal
methional
2-methylbutanal
caprylic acid
ethyl nicotinate
isobutanol
butyric acid
heptanal
2-furfural
2-methylpropanal
ethyl acetate
benzaldehyde
caproic acid
2-methyl-1-butanol
trans,trans-2,4-decadienal
original gravity
apparent degree of attenuation
isovaleric acid
trans-2-nonenal
alcohol by volume [%]
pentanal
octanal
valeric acid
isoamyl acetate
bitterness [BU]
nonanal
caryophyllene oxide
decanal
apparent extract
0
palatefulness
malt character
geranyl acetate
duration of aftertaste
intensity of bitterness
hexanal
caryophyllene
3-methyl-1-butanol
phenylethyl acetate
phenylethyl alcohol
color [EBC]
1-propanol
sweetness
humulene
acidity
limonene
α-pinene
ß-pinene
trans/cis-iso-α-acids ratio
cis-linalool oxide
α-terpineol
myrcene
2-methylbutylisobutyrate
trans-linalool oxide
citronellol
intensity of odor
linalool
nerol
geraniol
quality of bitterness
intensity of hop aroma
harmony
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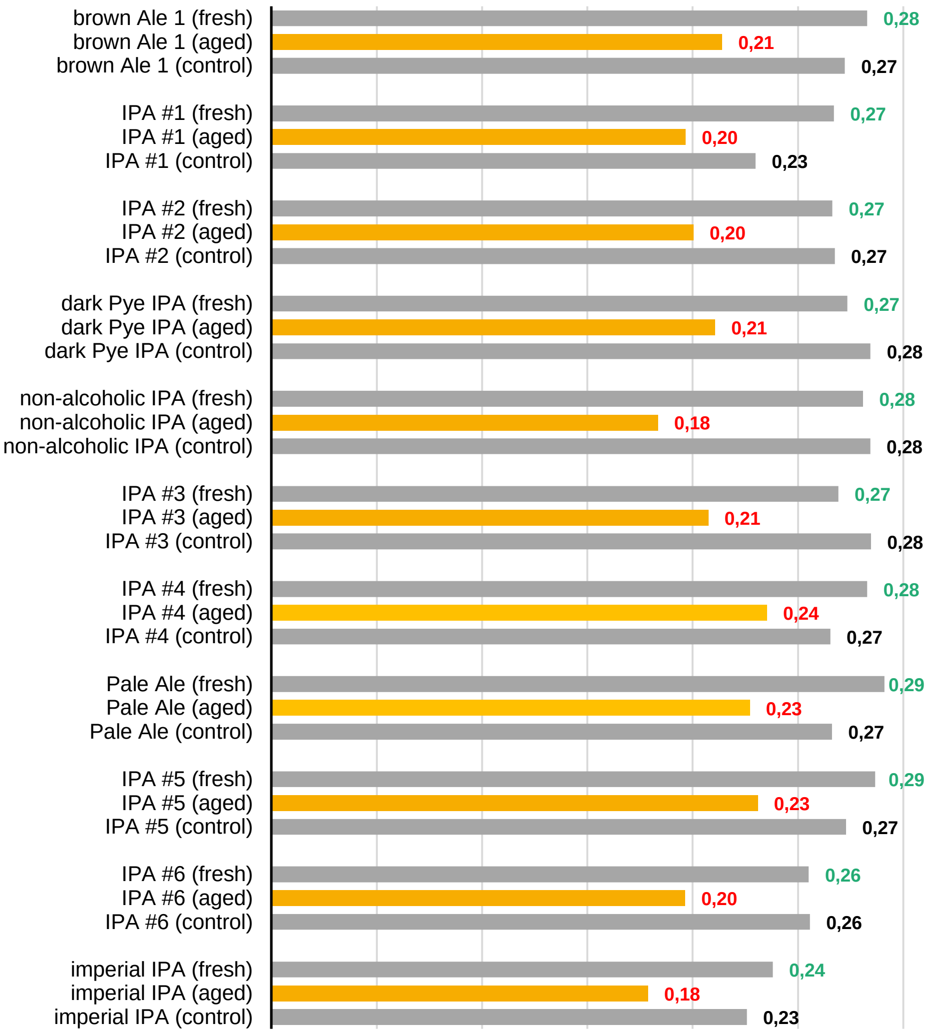
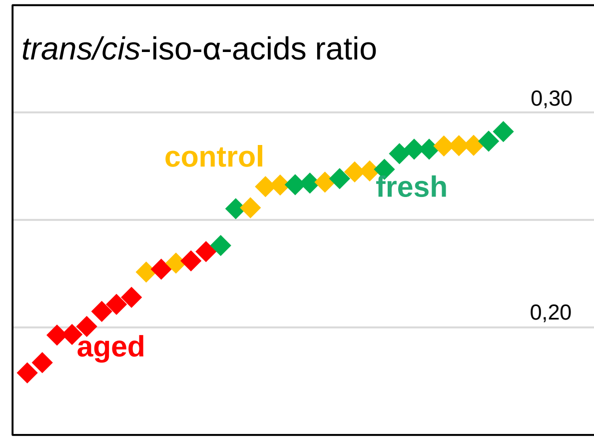
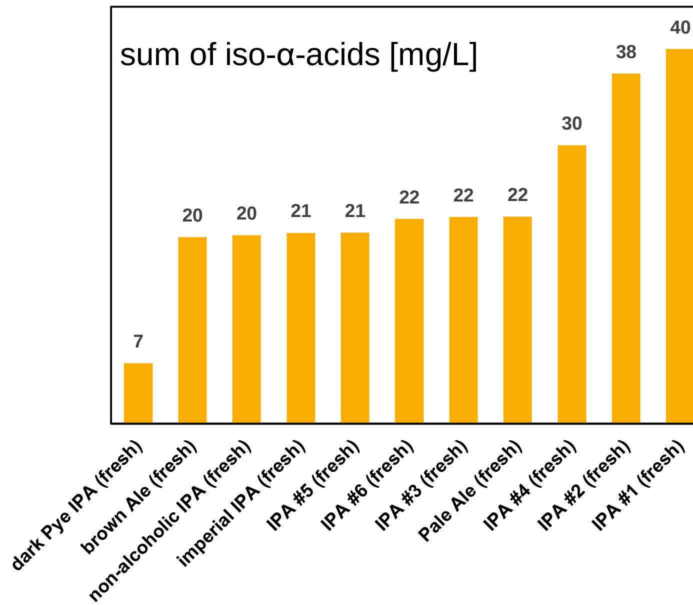
taste
general quality
PC-2 (14%) storage conditions
PC-1 (20%) beer style
0

trans/cis-iso-α-acids ratio



aged = 24 weeks and 20 °C / control = 24 weeks and 5 °C





Summary bitterness

- *trans/cis*-iso-α-acids ratio decreases during storage

- *trans/cis*-iso-α-acids ratio does not have the expected (high) influence on sensory attribute “oxidation”
  - sensory attribute “oxidation” is negative correlated to “quality of bitterness” and “harmony”
  - “oxidation” is only correlated to staling aldehydes

Summary stage one

+ more restricted beer samples are needed
  - for example only use IPA or Pale Ale
  - differences in one category of products are adequate
+ sampling times of fresh, forced aged, 12 weeks and 24 weeks storage parameters are sufficient
+ carbonyl compounds are not elementary off-flavors for hoppy, top fermented beers
  - focus more on hop aroma compounds (e.g. linalool or esters from hops)
+ combine oxidative processes analysis into one
(e.g. electron paramagnetic resonance)
+ sensory trials are good but not satisfactory at all
  - use other descriptors + ongoing training of panelists

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