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unlocking the potential of hops

ADVANCES IN HOP AROMA RESEARCH – HOW MUCH DO WE KNOW TODAY ?

AGENDA

- Hop aroma from hops to beer
- How to assess aroma activity?
- How much do we know today?
- Other factors to consider
- Putting the pieces together

FACOTRS INFLUENCING HOP AROMA

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variety
time of harvest
crop year, kilning

→

Point of addition
solubility/
evaporation

→

adsorption/
transformation/
interactions

→

dry hopping
(with/out yeast)
duration, temp,
agitation etc,

aroma in hops

to hoppy aroma in beer

harvest → brewhouse → fermentation → Lagering

plus…..filtration….bottling…storage

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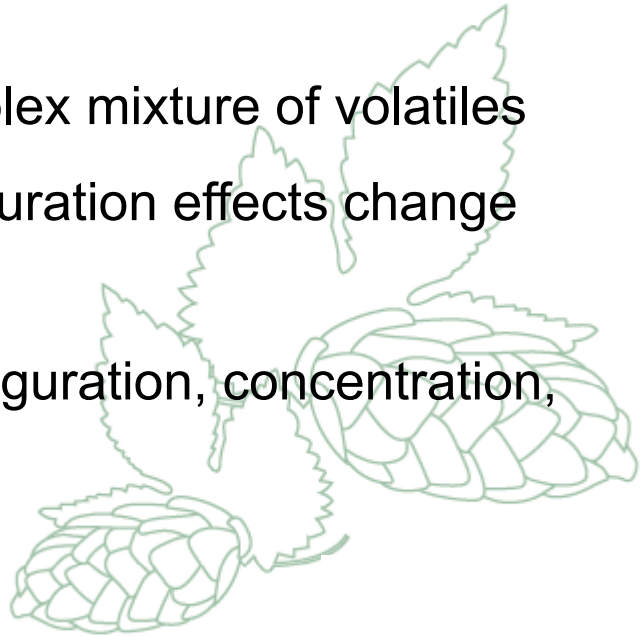
Aroma activity value = concentration of compound

threshold value

- Threshold values of volatiles have a high standard deviation
- There is no linear context for aroma activity
- A characteristic aroma is caused by a complex mixture of volatiles
- Additive, masking, synergistic, adaption, saturation effects change perception
- Quality of aroma changes according to configuration, concentration, individual perception, and matrix of the food
- Aroma is connected with emotions



HOW DID HOP AROMA RESEARCH CHANGE OVER TIME ?

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- How has brewing and hopping practice changed ?
- Which tools are available today for analysis ?
- What is the right approach for sensory evaluation ?
- How do hop varieties from the past compare to the varieties today ?
- What varieties will be important in the future ?

US 1990	Germany 1990	US 2012	Germany 2012
Cluster	**Hallertauer**	**Cascade**	**Perle**
Cascade	**Hersbrucker**	**Willamette**	Hallertauer Tradition
High Alpha	Spalter	Simcoe	Spalter Select
Willamette	Hüller	**Cluster**	**Hersbrucker**
Tettnanger	**Perle**	Centennial	**Hallertauer Mittelfrüh**
Fuggle	Norther Brewer	CTZ	**Tettnanger**
Perle	Orion	Summit	Saphir
	Tettnanger	Super Galena	Magnum
		Nugget	Herkules
		Apollo	Taurus

HOP OIL COMPONENTS

440 COMPOUNDS IDENTIFIED, 1000 + ARE LIKELY !

(Hopfen- vom Anbau bis zum Einsatz in Bier, Hans Carl Verlag)

Substance Group	Concentration
Monoterpenes (myrcene, pinene etc.)	approx. 40 %
Sesquiterpenes (ß-caryophyllene, α-humulene)	approx. 40 %
Carboxylicacid-esters (methyl-esters)	approx. 15 %
Carboxylicacids	approx. 1 %
Monoterpenoxides (linalool, geraniol etc.)	approx. 1 %
Sesquiterpenoxides (humullenol II, humulen epoxides)	approx. 1 %
Aldehydes, Ketones (hexenal, epoxydecenal, undecanone, octadienone)	approx.1 %
Aliphatic hydrocarbons	< 1 %
Sulfur containing compounds (4-MMP, 3-M-4-MP)	< 0,1 %
Glycosidically bound aroma compounds	?

SENSORY DESCRIPTIONS

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- Floral
- Citrus
- Spicy/ Herbal
- Woody
- Fruity
- Green

Descriptor	This includes the following aromas:
Menthol	Mint, melissa, sage, metallic, camphor, pine
Tea	Green tea, camomile tea, black tea
Green fruits	Pear, quince, apple, gooseberry, wine yeast, ethereal, grape
Citrus	Grapefruit, orange, lime, lemon, bergamot, lemon grass, ginger, mandarin
Green	Green-grassy, tomato leaves, green peppers, nettel, thuja, basil, parsley
Vegetal	Celeriac, leek, onion, artichoke, garlic, wild garlic
Cream caramel	Butter, chocolate, yoghurt, gingerbread, honey, cream, caramel, toffee, coffee
Woody aromatic	Tobacco, cognac, barrique, hay, leather, tonka, woodruff, incense, myrrh, resin
Spicy/herbal	Lovage, pepper, chilli, curry, juniper, marjoram, tarragon, dill, lavender, aniseed, liquorice, fennel, thyme, rosemary, clove
Red berries	Cassis, blueberries, raspberries, blackberries, strawberries, redcurrants, forest berries
Sweet fruits	Banana, watermelon, honeydew melon, peach, apricot, passion fruit, lychee, dried fruit, plum, pineapple, white jelly bears, cherry, kiwi
Floral	Elderflower, camomile blossom, lily of the valley, jasmine, apple blossom, rose, geranium, carnation, elder

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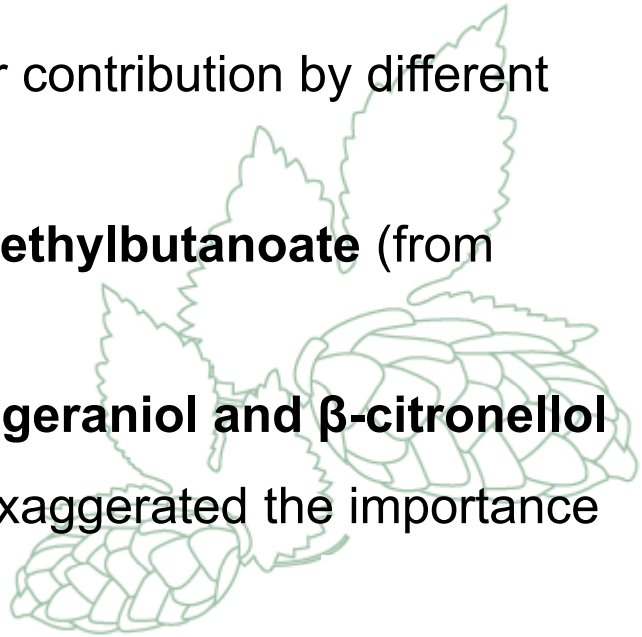
- Peacock 1980; **linalool** relevant to hop aroma in beer (200 ppb in american beer)
- Peacock 1981; **linalool**, **geraniol**, and to a lesser extent **geranyl isobutyrate** are responsible for most of the floral aroma (Cascade hops)
- Lam 1986; geraniol, linalool, and **citronellol** are mainly responsible for the **floral/citrus note**
- Kaltner 2000 **linalool (R and S)** and its flavour contribution by different brewing techniques etc
- Kishimoto 2006; **β-ionone 2-phenylethyl 3-methylbutanoate** (from fermentation) (floral)
- Takoi 2010; synergistic effect among **linalool**, **geraniol and β-citronellol**
- Peacock 2010; the emphasis on linalool has exaggerated the importance
- Van Opstaele 2011; **myrcene, 2-undecanone**



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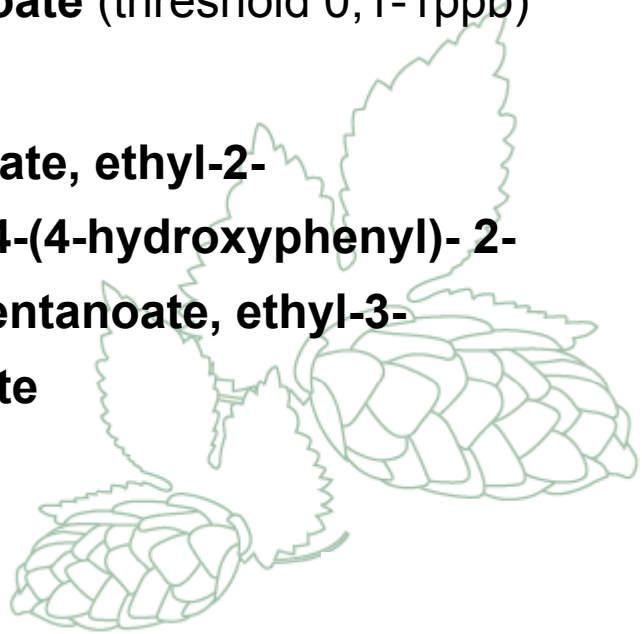
- Lam 1986; a **grapefruit-like fruity flavor** detected in beers brewed with extensively aged hops.
- Kishimoto 2006; **(Z)-3-hexen-1-ol** in combination with others
- Nielsen 2007; **cis-rose oxide**, **fruity/herbal/lychee** (from citronellol?) threshold 0,5-50 ppb, **ethyl-2-methylpropionate, ethyl-2-methylbutyrate, ethyl-3-methylbutyrate, ethyl-4-methylpentanoate** (threshold 0,1-1ppb) **(citrus, apple, pineapple)**
- Kishimoto 2006; **linalool, ethyl-3-methylbutanoate, ethyl-2-methylbutanoate, ethyl-2-methylpropanoate, 4-(4-hydroxyphenyl)- 2-butanone (citrus, raspberry), ethyl-4-methylpentanoate, ethyl-3-methylbutanoate and ethyl-4-methylpentanoate**



FRUITY THIOLS !

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- All thiols show very low sensory thresholds, chemically labile
- Steinhaus, Kishimoto 2006; **4-MMP,** blackcurrant, muscat, boxtree
- Nielsen 2007, **4-MMP**, **4-methoxy-2-methyl-2-mercaptobutane, Grapefruit mercaptan**
- Kishimoto 2008; **3-mercaptohexan-1-ol**, (55 ng/l) is esterified to **3-mercaptohexyl acetate** (5 ng/l)
- Takoi 2009; **3-mercapto-4-methylpentan-1-ol (3-M-4-MP) and 3-mercapto-4-methylpentyl acetate (3-M-4-MPA) (grapefruit, rhubarb, Sauvingon Blanc)**

Onion, burnt, rubber, cat urine ⟷ **grapefruit, rhubarb, black currant, muscat, ribes, grapes**

depending on configuration, concentration, interaction and perception

bad ⟷ good

SPICY/WOODY/HERBAL

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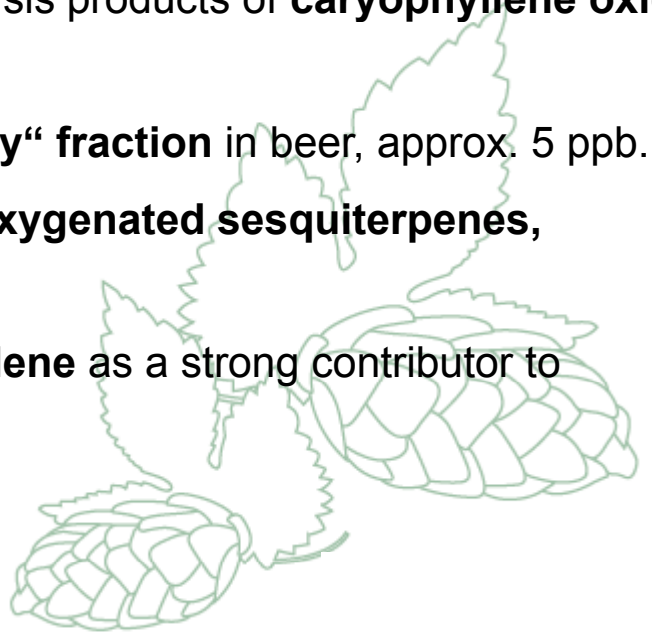
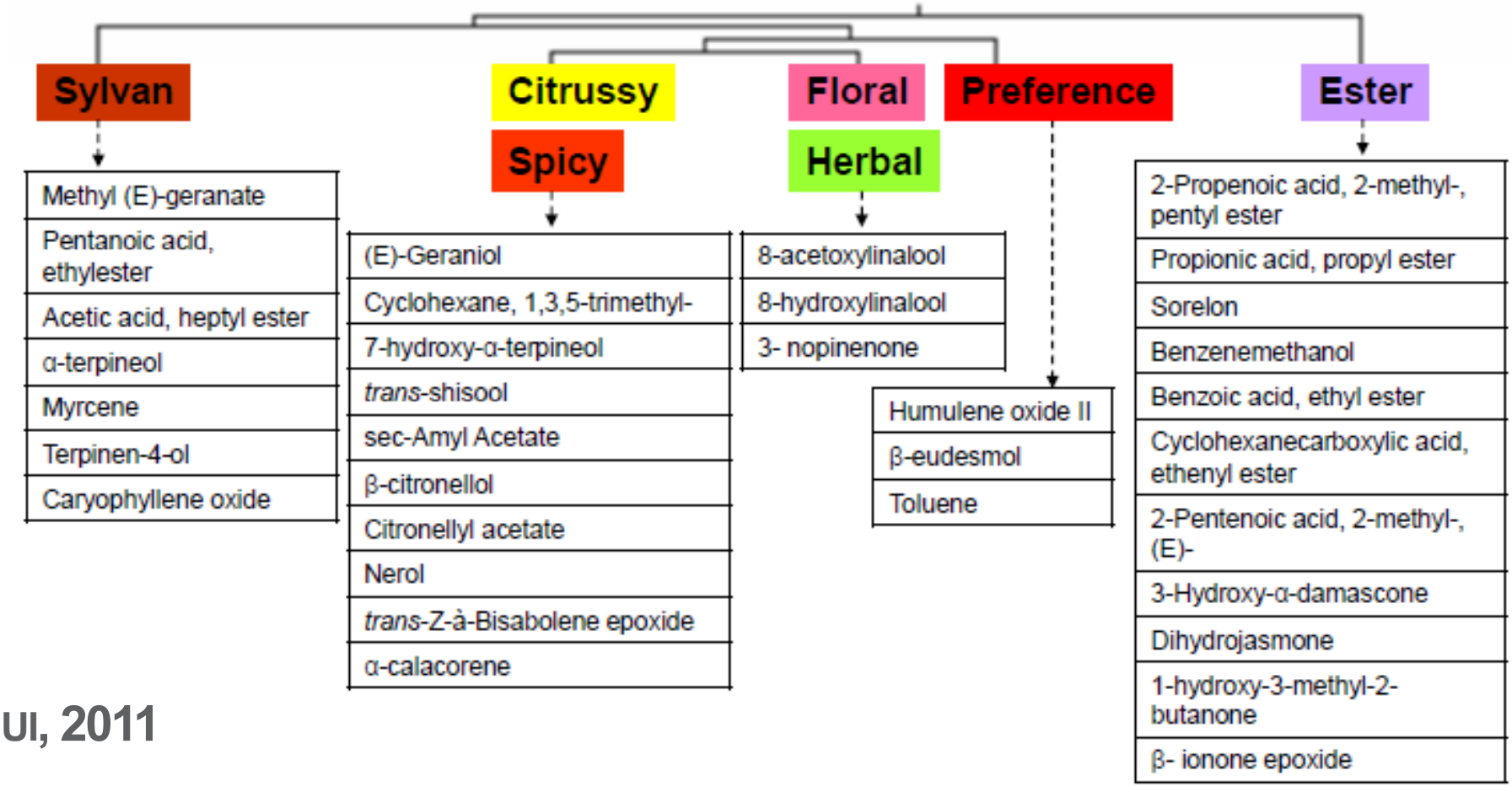
- Peacock 1980; α**-terpineol** less important, **humulenol II** in part responsible. Conclusion: **oxidation products of humulenes collectively** are important for a characteristic hoppy aroma ("noble")
- Tressl et al. 1979; **humulene epoxide I** contributes to hop aroma in beer
- Lam 1986; oxidation products of α**-humulene**, especially the **humulenol I** and **humulene diepoxides**, contribute to the **herbal/spicy** note in beer.
- Yang, 1993; the total concentration of the identified hydrolysis products of **caryophyllene oxide** in the beer samples may add to the **hop flavour**
- Goiris 2002; the approximate flavour threshold of the „**spicy" fraction** in beer, approx. 5 ppb.
- Eyres 2006; **intense cedar, woody** aroma coming from **oxygenated sesquiterpenes,** identification challenging
- Eyres 2007, was able to identify **14-hydroxy-ß-caryophyllene** as a strong contributor to **woody notes**
- Van Opstaele 2011, γ**-cadinene, α-calacorene, calarene**



The key aroma compounds related to hop aroma characteristics in beer



INUI, 2011

MOST AROMA ACTIVE HOP AROMA COMPONENTS IN BEER

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Compound	aroma description	threshold in ug/l
4-MMP	muscat, blackcurrant	0,002
3-MHA	muscat, blackcurrant	0,005
3-MH	muscat, blackcurrant	0,05
ß-damascenone	apple, peach	0,02
3-M-4-MP	rhubarb, grapefruit	0,07
(E,Z)-2,6-nonadienal	cucumber, green	0,5
cis-rose oxide	fruity, herbal	0,5-50
ß-ionone	floral, violet, berries	0,6
ethyl-4-methylpenatonate	citrus, pineapple	1-18
Sesquisterpenoid essence	spicy resinous	5
ethyl-2-methylbutanoate	citrus, appel	1-45
linalool	lavendar, floral	2-80
ethyl-3-methylbutanoate	citrus, appel	2
geraniol	floral, rose	4-300
ethyl-2-methylpropanoate	citrus ,pineapple	6-164
ß-citronellol	lime, lychee	9-40
myrcene	resinous, herbal, green	9-1000

MOST AROMA ACTIVE HOP AROMA COMPONENTS IN BEER

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Compound	aroma description	threshold in ug/l
humulenepoxid I	hay	10
(z)-3-hexenal	green, leaves	20
4-(4-Hydroxyphenyl)-2-butanone	citrus, rasperry	21
nerol	floral, lime, citrus	80-500
Humulenol II	pineapple, mugwort	150-2500
ß-caryophyllene	cedar, spicy, cloves	160-420
alpha-terpineol	lilac, resinous, rose	330
1-hexanal	green, leaves	350
limonene	citrus, green	1493
humulenepoxide II	cedar, lime	450
humulene	floral, grassy	747
humuladienone		100
geranyl isobutyrate		450
farnesene		550
eudesmol		10000

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AROMA INTERACTION IN BINARY MIXTURES

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µg/l	linalool	geraniol	humulen	caryo.	nerol	terp.	myr.	far.
linalool	27	104[a]; 133[b]						493[c]
geraniol	104a; 133b	90						2304 [d]
humulene			3483	4346[e]	1843[f]	5668 [g]		
ß-Caryophyllene			4346[e]	239	147[h]	1297[i]		
nerol			1843[f]	147[h]	1206	2699[j]		
α-Terpineol			5668[g]	1297[i]	2699[j]	1076		
myrcene							119	
farnesene	493[c]	2304[d]						2020

Single components
Synergism
additive
masking

These interactions also occur with fermentation volatiles !

Hanke 2009

WHAT IS THE ROLE OF THE YEAST ?

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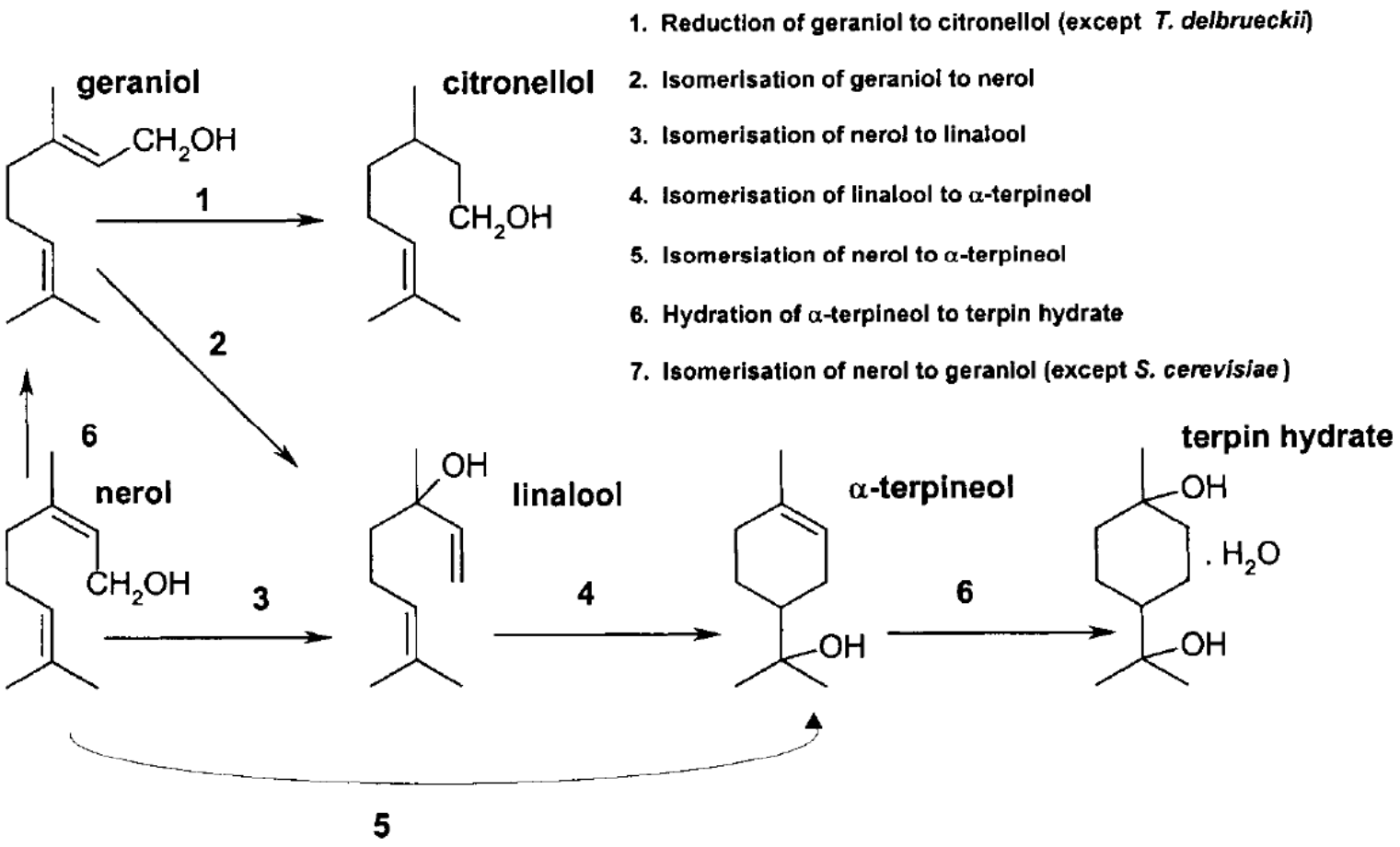

Figure 3. Scheme showing the monoterpenoid biotransformation reactions catalysed by *S. cerevisiae*, *T. delbrueckii* and *K. lactis*

King, 2000, Yeast 2000; 16: p.499±506.

WHAT IS THE ROLE OF THE YEAST ?

GLYCOSIDICALLY BOUND AROMA COMPONENTS

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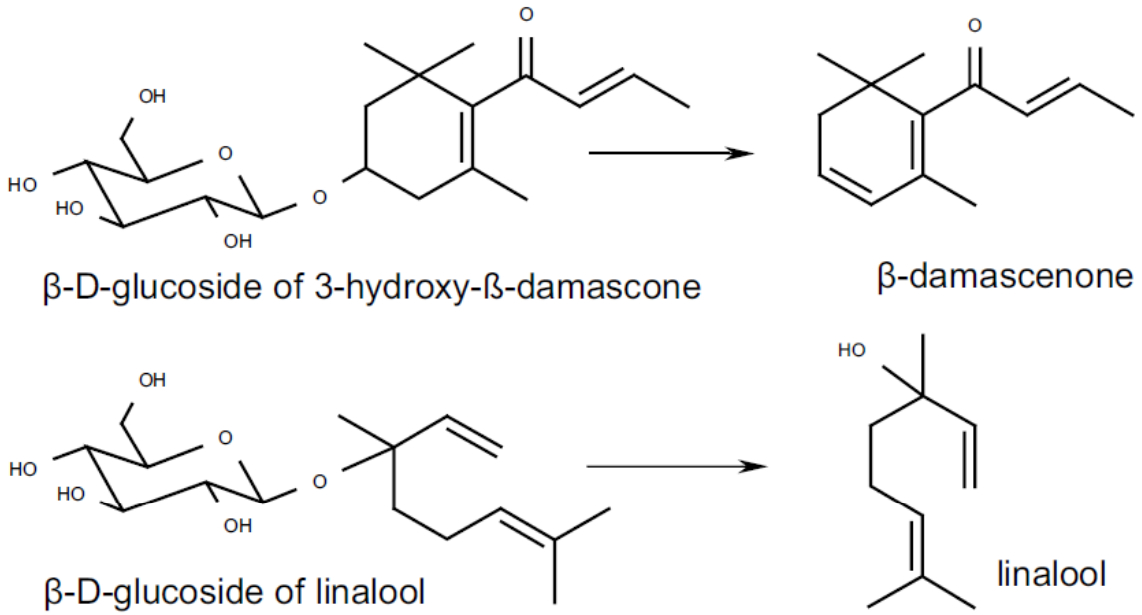

Kollmansberger, 2006

- Daenen 2008; pronounced exo-ß-glucanase activity in Saccharomyces brewing yeasts leads to a higher release of certain aglycones. Brettanomyces brewing yeasts hydrolyses glycosidically bound volatiles of hops.
- Ting 2009 ; named 28 hydrolysis products by ß-glucosidase from glycosides

ARE THERE APPARENT VARIETY SPECIFICS ?

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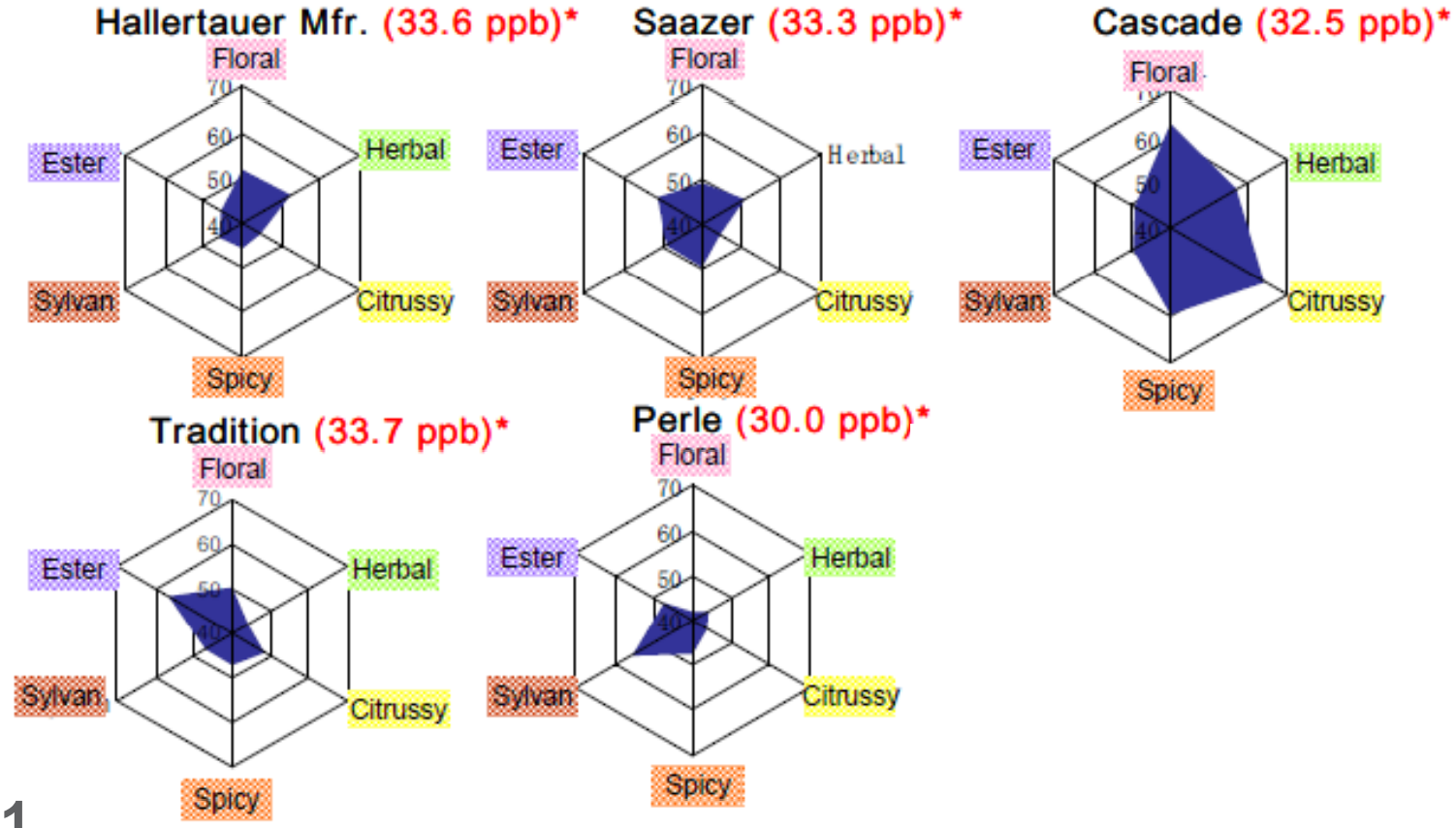
- All hops contain more or less the same components (in different concentrations)
- It is maybe the different composition of low concentration compounds that is responsible for variety unique aroma
- 4-MMP is important for some US and AUS varieties
- Geraniol seems to be more dominant in US varieties
- A higher concentration of sesquiterpenes is typical for European varieties
- Sensory data show the influence of crop years and the growing location
- other thiols seem to be of importance e.g. for Nelson Sauvin and Tomahawk: 2-methylbutyl isobutyrate (apple, apricot), 3-mercapto-4-methylpentan-1-ol (3-M-4-MP) and 3-mercapto-4-methylpentyl acetate (3-M-4-MPA) (grapefruit, rhubarb, Sauvigngon Blanc)

Results of organoleptic evaluation and preference of beer samples



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*The concentration of Linalool in beer

WHAT COMPOUNDS ARE IMPORTANT IN OTHER FRUITS (HERBS)?

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white wine	3-mercapto-hexan-1-ol 3-mercaptohexylacetate	4MMP
pine apple juice	ethyl-2-methyl-propanoate 4-hydroxy-2,5dimethyl 3(2h)furanone ß-damascenone	1-E,Z-3-5-undecatriene ethyl-2methyl-butanoate methyl-2methyl-butanoate
apple juice	1-butanol ethyl-2methyl-butanoate ethyl-butanoate dimethylsulfid	ß-damascenone hexanal 1-hexanol 1-octen-3one
apricots	γ-decalactone ß-damascenone δ-decalactone Linalool E,Z,2-6-nondienal Z,1,5-octadien-3-one (z)-3-hexanal	ß-ionone 1-octen-3-one hexyl-acetate gamma-dodecalactone acetaldehyde 3-methyl-2,4-nonandione

orange juice	linalool octanal ethyl-2-methylbutanoate limonene α-pinene	ethyl-butanoate myrcene acetaldehyde decanal ß-Damascenone
durian pulp	ethyl-propanoate ethyl-2-methylpropanoate 3,5-dimethyl-1,2,4-trithiolane	ethane-1.1-dithiol
passion fruit	2-methyl-4-propyl-1,3-oxathiane	3-mercapto-1-hexanol
lychee	β-citronellol ethyl isobutyrate β-damascenone furaneol linalool geraniol	cis-rose oxide ethyl-isohexanoate isoamylacetate isobutyl acetate

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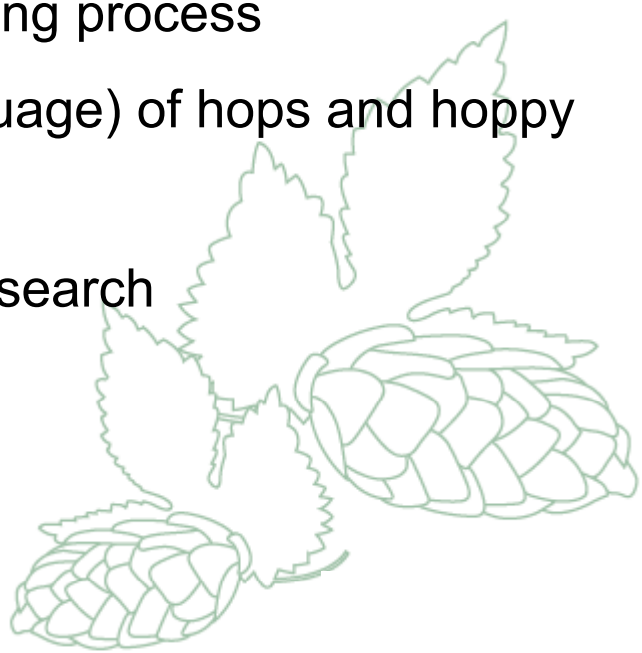
- Over the last 30 years a lot of data on hop aroma (in beer) has been collected
- still unknown/unidentified components
- No single character impact compound, complex mixture of components
- Genes, climate and location influence the composition and aroma
- Numerous components in beer have been identified and can be attributed to certain aroma characteristics
- Certain variety aroma characteristics (in beer) cannot be explained currently
- aroma interaction, configuration, reactivity of compounds, changes in concentration can have a big aroma (flavour) impact in beer

OUTLOOK

- More emphasis on correlating aroma analysis with sensory assessment
- Human aroma perception should be included in research
- Combine research efforts
- Single variety beers with standardised brewing process
- Standardised sensory assesment (one language) of hops and hoppy beers
- Every hop variety basically merits its own research



….WE KNOW A LOT, BUT NOT ENOUGH! THE FUTURE OF HOP AROMA RESEARCH LOOKS BRIGHT !

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