4-Vinyl syringol and other flavouring phenols (issued from hop & malt)

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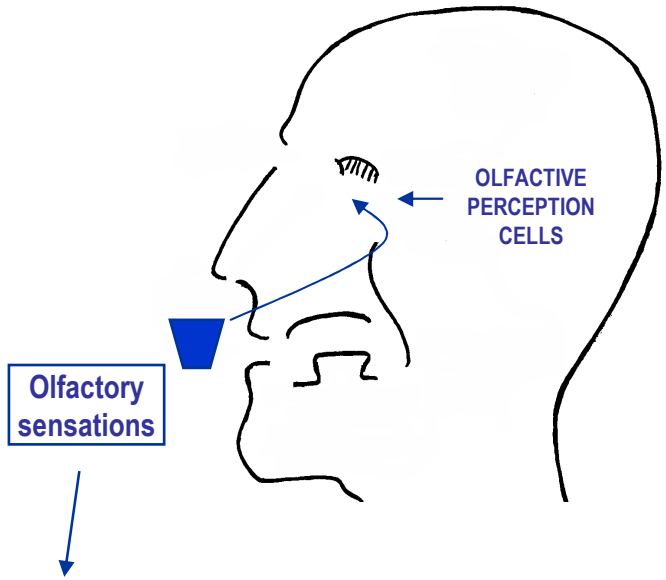
Work published during PhD thesis
PhD advisor Prof. S. Collin

Fonds InBev-Baillet Latour

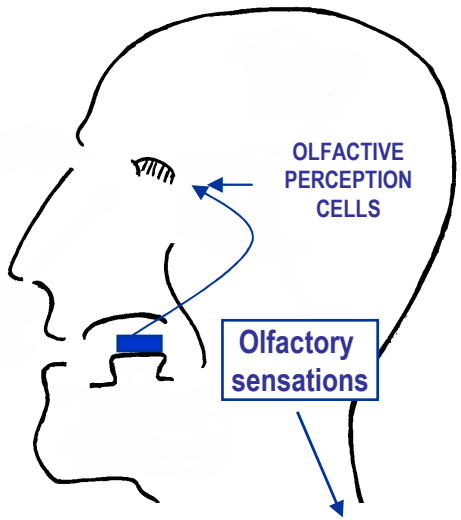
J. De CLERCK CHAIR – session: Polyphenols as flavour precursors
7-10 September 08 - Louvain-la-Neuve, Belgium

The odour



Nasal direct perception « ODOUR »

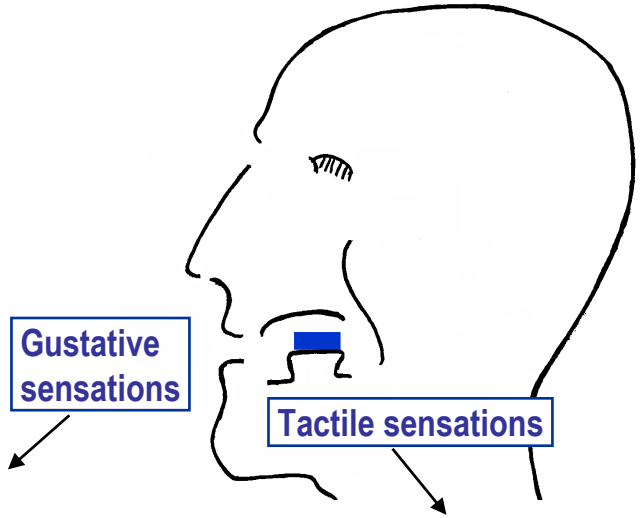
The aroma



Back of the nose perception « Aroma »

ODOUR + AROMA = FLAVOUR

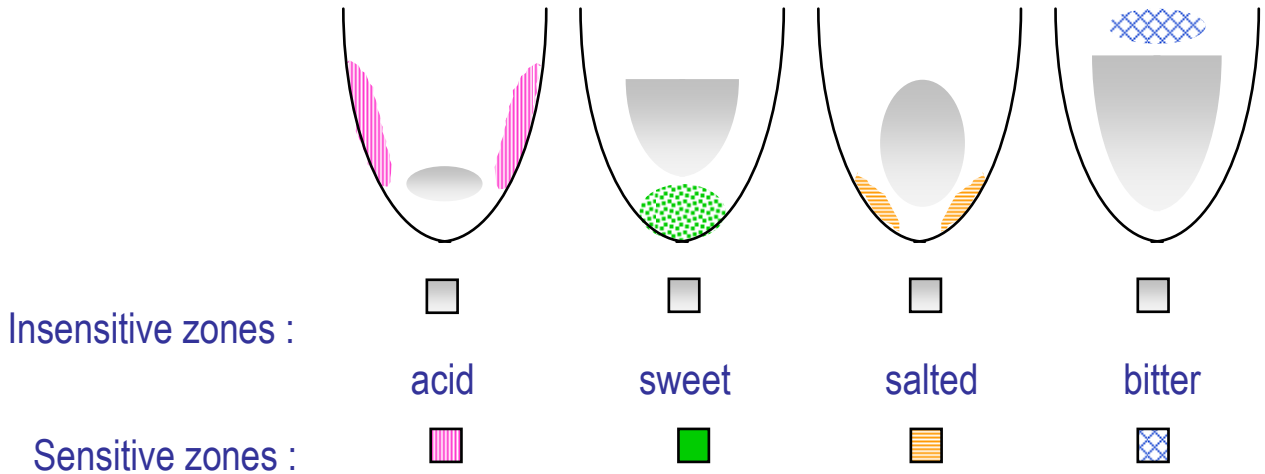
The taste



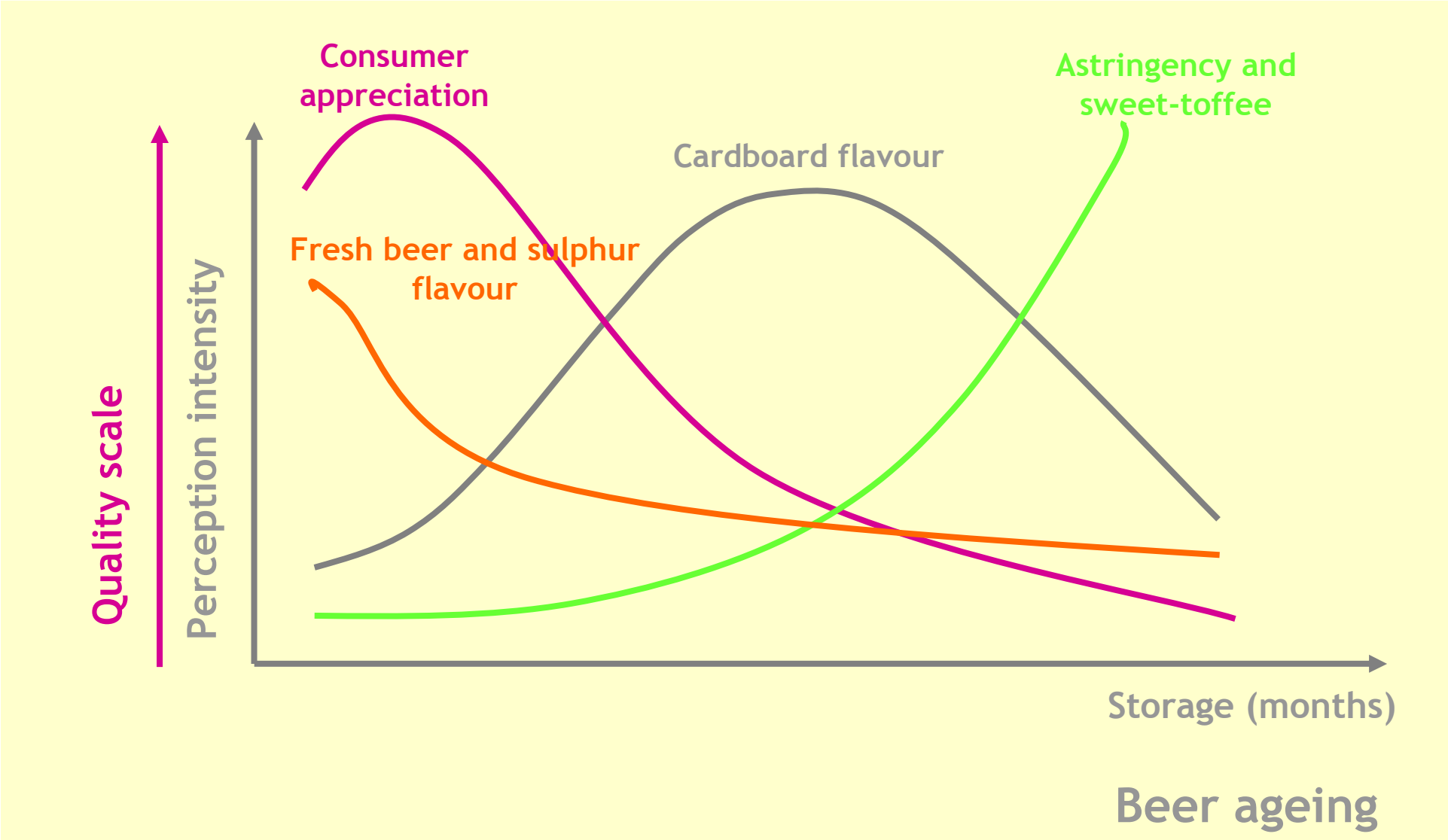
5 « TASTES »

sweet, salted, bitter, acid, umami

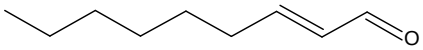
astringency and metallic



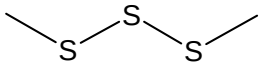
Beer profile changes



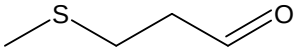
Compounds responsible of beer flavour: mechanisms already investigated

***trans*-2-Nonenal** 

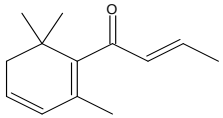
Cardboard 

Dimethyltrisulfide 

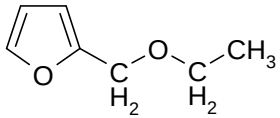
Onion, cabbage 

Methional 

⇨Potato 

β-Damascenone 

Red fruit 

2-Furfurylethylether 

Solvent 

Factors: pH, oxygen, precursors, storage conditions, …

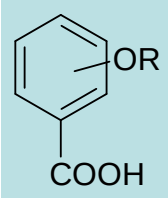
Other compounds can be responsible

of beer flavour

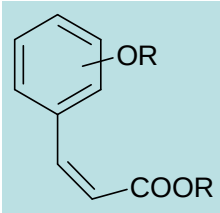
Polyphenols: potential sources of flavouring compounds

Phenolic acids

→ **Benzoic acid**



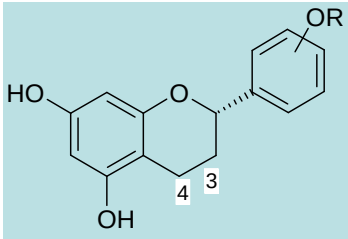
→ **Cinnamic acid**



Antioxidant, flavour precursors

Flavonoids

→ **Flavanoids**



Flavanones
Flavones
Neoflavanes
Flavan-3-ols
3,4-Flavanediols
Isoflavones

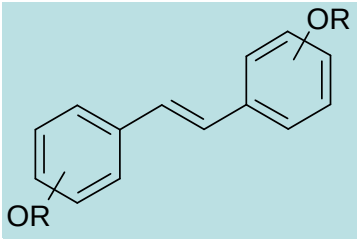
→ **Flavonols**

→ **Prenylchalcones**

→ **Anthocyanidins**

Antioxidant, astringency, color, haze, health benefits (cardioprotector, estrogenic activities,…)

Stilbenes



Health benefits (cardioprotector, anti-carcinogenic, anti-inflammatory,…)

Very few data concerning phenolic acids

and their impact on beer flavour…

1. *Literature overview on hydroxybenzoic, hydroxycinnamic acids, and derived compounds*

2. *New data*

Review accepted to be published in Food Reviews Int.

Submitted to *Food Reviews International*

Review Title

STRUCTURE, ORGANOLEPTIC PROPERTIES, QUANTIFICATION METHODS AND STABILITY OF PHENOLIC COMPOUNDS IN BEER – A REVIEW

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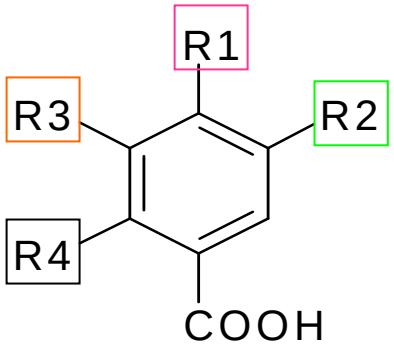
Unité de Brasserie et des Industries Alimentaires, Université catholique de Louvain, Croix du Sud, 2/bte 7, B-1348 Louvain-la-Neuve, Belgium

RUNNING TITLE HEADER: *Phenolic compounds in beer*

TABLE OF CONTENTS

Hydroxybenzoic acids **occurrence**

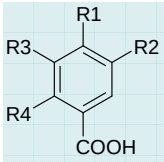
Structure	Compounds	R1	R2	R3	R4
	*p*-Hydroxybenzoic acid	OH	H	H	H
	m-Hydroxybenzoic acid	H	H	OH	H
	Protocatechuic acid	OH	H	OH	H
	Gallic acid	OH	OH	OH	H
	Vanillic acid	OH	H	OCH_3	H
	Syringic acid	OH	OCH_3	OCH_3	H
	Gentisic acid	H	OH	H	OH

Callemien & Collin, Review, Food Reviews International, accepted 2008

Malt is richer in gentisic acid, **hop** in vanillic and syringic acids.

In beer, *p*-Hydroxybenzoic, gallic, and vanillic acids reach a few ppms.

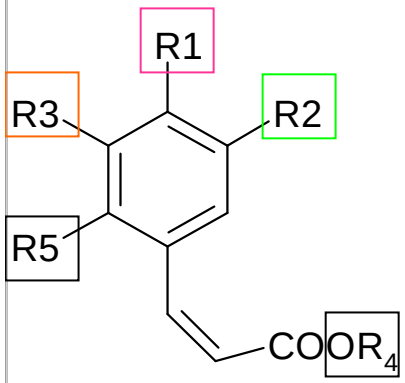
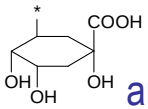
Hydroxybenzoic acids have also been found as **glycosides or other bound forms**.



Compounds	Malt (mg/kg)	Hop (mg/kg)	Beer (mg/l)
p-Hydroxybenzoic acid	**1.0-1.7** (Wackerbauer *et al.*, 1982)	**1.6-2.5** (Wackerbauer *et al.*, 1982)	**0.4-3.09** (Wackerbauer and Kramer, 1982); **0.3-1.8** (McMurrough *et al.*, 1984); **0.017-0.068** (Montanari *et al.*, 1999); **0.092** (Bartolomé *et al.*, 2000); **16.84** (Floridi *et al.*, 2003)
m-Hydroxybenzoic acid	-	-	**0.324** (Floridi *et al.*, 2003)
Protocatechuic acid	**0.1-0.5** (Wackerbauer *et al.*, 1982)	-	**0.01-2.7** (Wackerbauer and Kramer, 1982); **0.2-1.2** (McMurrough *et al.*, 1984); **0.007-0.020** (Montanari *et al.*, 1999); **0.840** (Floridi *et al.*, 2003); **<0.1** (Nardini and Ghiselli, 2004); **0.66-5.1** (Garcia *et al.*, 2004)
Gallic acid	**0.01-0.3** (Wackerbauer *et al.*, 1982)	**0.5-1** (Wackerbauer *et al.*, 1982)	**0.01-1.79** (Wackerbauer and Kramer, 1982); **0.3-3.5** (McMurrough *et al.*, 1984); **0.015-0.034** (Montanari *et al.*, 1999); **2.9** (Gorinstein *et al.*, 2000); **0.593** (Floridi *et al.*, 2003)
Vanillic acid	**0.7-2.3** (Wackerbauer *et al.*, 1982); **7** (McMurrough *et al.*, 1984)	**59** (McMurrough *et al.*, 1984)	**0.01-3.15** (Wackerbauer and Kramer, 1982); **1.5-12.7** (McMurrough *et al.*, 1984); **1.42-1.79** (Hayes *et al.*, 1987); **1-10** (Moll, 1991); **3.6** (Achilli *et al.*, 1993); **0.062-0.097** (Montanari *et al.*, 1999); **0.477** (Bartolomé *et al.*, 2000); **0.737** (Floridi *et al.*, 2003); **0.59-0.85 and 0.37-1.25*** (Nardini and Ghiselli, 2004)
Syringic acid	**0.02-0.5** (Wackerbauer *et al.*, 1982); **3** (McMurrough *et al.*, 1984)	**1.3-1.8** (Wackerbauer *et al.*,1982); **30** (McMurrough *et al.*, 1984)	**0.35-1.3** (Wackerbauer and Kramer, 1982); **0.7-2.2** (McMurrough *et al.*, 1984); **0.68-1.16** (Hayes *et al.*, 1987); **0.5** (Achilli *et al.*, 1993); **0.017-0.027** (Montanari *et al.*, 1999); **0.237** (Floridi *et al.*, 2003); **<0.1-0.23 and <0.1-0.26*** (Nardini and Ghiselli, 2004)
Gentisic acid	**26-312** (Wackerbauer *et al.*, 1982	-	**0-1.5** (Moll, 1991); **0.376** (Floridi *et al.*, 2003)

- Not determined; * Total amount measured after hydrolysis (free + bound forms occurring as esters, glycosides or bound complexes).

Hydroxycinnamic acids **occurrence**

Structure	Compounds	R1	R2	R3	R4
	*p*-Coumaric acid	OH	H	H	and R5 = H
	o-Coumaric acid	H	H	H	H and R5 = OH
	m-Coumaric acid	H	H	OH	and R5 = H
	Caffeic acid	OH	OH	H	and R5 = H
	Ferulic acid	OH	OCH_3	H	and R5 = H
	Sinapic acid	OH	OCH_3	OCH_3	and R5 = H
	Chlorogenic acid	OH	OH	H	 and R5 =H

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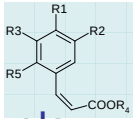
Hop is an important source of *p*-coumaric, caffeic, and ferulic acids (more than 10 ppm).



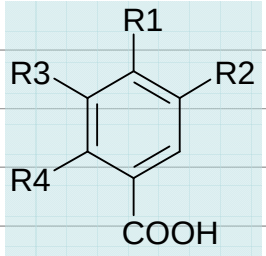
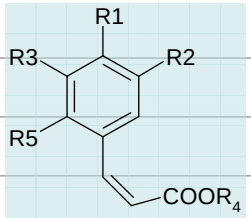
In malt, *p*-coumaric, caffeic, ferulic, sinapic, and chlorogenic acids were quantified at ppm levels. *p*-Coumaric and ferulic acids are **esterified with arabinoxylans in malt**. They can be both water-extracted and enzymatically solubilized by cinnamoyl esterases. After mashing, an additional release of ferulic acid may occur during fermentation, due to yeast cinnamoyl esterases.

Compounds	Malt (mg/kg)	Hop (mg/kg)	Beer (mg/l)
p-Coumaric acid	**0.3-1.3** (Wackerbauer *et al.,* 1982); **3** (McMurrough *et al.,* 1984)	**2.2-2.8** (Wackerbauer *et al.*,1982); **13** (McMurrough *et al.,* 1984)	**0.06-0.27** (Kenyhercz and Kissinger, 1977); **0.21-1.45** (Wackerbauer and Kramer, 1982); **0.6-4.6** (McMurrough *et al.,* 1984); **0.57-0.92** (Hayes *et al.*, 1987); **0.027-0.129** (Montanari *et al.,* 1999); **2.1** (Gorinstein *et al.,* 2000); **0.77** (Bartolomé *et al.,* 2000); **1.36** (Floridi *et al.,* 2003); **0.34-0.76** and **0.15-1.62*** (Nardini and Ghiselli, 2004); **0.11-0.73** (Garcia *et al.,* 2004); **1.41 and 1.67*** (Vanbeneden *et al.,* 2006b)
o-Coumaric acid	-	-	**0.15-0.18** (Montanari *et al.,* 1999); **1.73** (Floridi *et al.,* 2003)
m-Coumaric acid	-	-	**0.07-0.33** (Montanari *et al.,* 1999); **0.22** (Floridi *et al.,* 2003)
Caffeic acid	**0.29-2.13** (Wackerbauer *et al.,* 1982); **1** (McMurrough *et al.,* 1984)	**1.7-3.6** (Wackerbauer *et al.*,1982); **38** (McMurrough *et al.,* 1984)	**0.01-0.98**** (Wackerbauer and Kramer, 1982); **Trace-1** (McMurrough *et al.,* 1984); **0.13-0.29** (Hayes *et al.,* 1987); **0.006-0.019** (Montanari *et al.,* 1999); **0.074** (Bartolomé *et al.,* 2000); **0.566** (Floridi *et al.,* 2003); **0.15-0.20 and 0.94-1.01***(Nardini and Ghiselli, 2004); **0.19-0.41** (Garcia *et al.,* 2004)
Ferulic acid	**7.8-12.8** (Wackerbauer *et al.,* 1982); **14** (McMurrough *et al.,* 1984)	**13.2-14.1** (Wackerbauer *et al.*,1982); **24** (McMurrough *et al.,* 1984)	**0.15-0.61** (Kenyhercz and Kissinger, 1977); **5.6-13.1** (Wackerbauer and Kramer, 1982); **1.1-10.8** (McMurrough *et al.,* 1984); **1.07-1.90** (Hayes *et al.,* 1987); **6.5** (Achilli *et al.,* 1993); **0.7-6.6** (McMurrough *et al.,* 1996a); **0.116-0.274** (Montanari *et al.,* 1999); **6.8** (Gorinstein *et al.,* 2000); **1.305** (Bartolomé *et al.,* 2000); **2.41** (Floridi *et al.,* 2003); **1.36-2.31** and **10.75-15.39*** (Nardini and Ghiselli, 2004); **0.66-2.4** (Garcia *et al.,* 2004); **1.2-14.2** (Coghe *et al.,* 2004); **2.22 and 16.18*** (Vanbeneden *et al.*, 2006b)
Sinapic acid	**1.0-4.3** (Wackerbauer *et al.*,1982)	**4.1-5.1** (Wackerbauer *et al.*,1982)	**0.056-1.04** (Kenyhercz and Kissinger, 1977); **2.4-4.5** (Wackerbauer and Kramer, 1982); **0.2-3.0** (McMurrough *et al.,* 1984); **0.15-0.24** (Hayes *et al.*, 1987); **0.09** (Bartolomé *et al.,* 2000); **0.15** (Floridi *et al.,* 2003); **0.20-0.84 and 2.8-5.32*** (Nardini and Ghiselli, 2004); **0.24 and 2.74** *(Vanbeneden *et al.,* 2006b)
Chlorogenic acid	**0.3-6.6** (Wackerbauer *et al.*,1982)	**4-7** (Wackerbauer *et al.*,1982)	**0.01-7.77** (Wackerbauer and Kramer, 1982); **0.028-0.089** (Montanari *et al.,* 1999); **0.21-0.26** (Nardini and Ghiselli, 2004); **0.901** (Floridi *et al.*, 2003)

letermined; * Total amount measured after hydrolysis (free + bound forms occuring as esters, glycosides or bound complexes).

Organoleptic properties

Hydroxybenzoic and hydroxycinnamic acids are characterized by relatively **high flavour thresholds** (> ppm, mainly bitter taste and astringency).

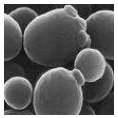
Phenolic compounds		Organoleptic characteristics	Threshold (mg/L)
Hydroxybenzoic acids			
	4-Hydroxybenzoic acid	Bitter	20 * and 2**
	Protocatechuic acid	Bitter, astringent	>50* and 5**
	Gallic acid	Astringent	50* and 5**
	Vanilic acid	Astringent	20* and 10**
	Syringic acid	Bitter	10* and 5**
	Gentisic acid	Bitter, astringent	20* and 2**
Hydroxycinnamic acids			
	*p*-Coumaric acid	Astringent	50* and 5**
	Caffeic acid	Astringent, bitter	20* and 2**
	Ferulic acid	Astringent	20* and 10**
	Sinapic acid	Bitter, bitter-sweet	20* and 5**

In beer*, in 5% aqueous ethanol (adapted from Dadic and Belleau, 1973) and in water ***(Counet, 2004).**

On the other hand, the hydroxycinnamic acids decarboxylated derivatives can impart very strong flavour to beer.

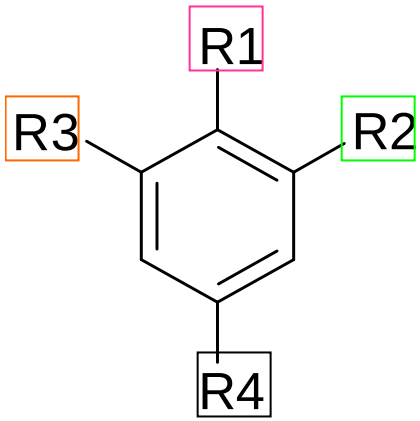
Formation of the hydroxycinnamic acids derived compounds

The decarboxylation of **Hydroxycinnamic acids** can occur either:

- by **thermal degradation** during malt kilning and in the boiling kettle 
- or **during fermentation** 

Decarboxylation is catalyzed by the phenylacrylic acid decarboxylase found in *Saccharomyces cerevisiae* strains displaying the Pof$^+$ phenotype (**Phenolic-Off-Flavor**) and in some contaminating microorganisms like *Brettanomyces/Dekkera* spp. or *Enterobacteriacea*.

Hydroxycinnamic acids derived compounds occurrence

Structure	Compounds	R1	R2	R3	R4
	Ferulic acid derived compounds				
	4-Vinylguaiacol	OH	OCH_3	H	$CHCH_2$
	4-Ethylguaiacol	OH	OCH_3	H	CH_2CH_3
	4-Methylguaiacol	OH	OCH_3	H	CH_3
	Guaiacol	OH	OCH_3	H	H
	4-Allylguaiacol	OH	OCH_3	H	CH_2CHCH_2
	4-Propenylguaiacol	OH	OCH_3	H	$CHCHCH_3$
	Vanillin	OH	OCH_3	H	CHO
	Acetovanillone	OH	OCH_3	H	CCH_3O
	***p*-Coumaric acid derived compounds**				
	4-Vinylphenol	OH	H	H	$CHCH_2$
	4-Ethylphenol	OH	H	H	CH_2CH_3
	4-Methylphenol	OH	H	H	CH_3
	Phenol	OH	H	H	H

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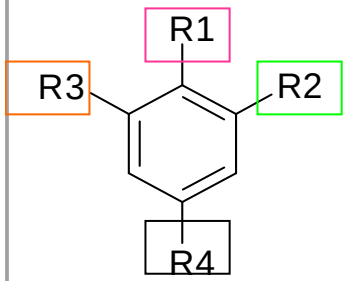
4-Vinyguaiacol was detected in **malt and hop**.

Up to 6.2 ppm in 4-vinylguaiacol and up to 3.2 ppm in **4-vinylphenol** were reported in **wheat beers**. Both can be further degraded to **vanillin, 4 - ethylguaiacol, guaiacol, and 4-ethylphenol**.

Compounds	Malt (mg/kg)	Hop (mg/kg)	Beer (mg/l)
Ferulic acid derived compound			
4-Vinylguaiacol	Detected (Fickert and Schieberle, 1998)	Detected (Steinhaus and Schieberle, 2000)	**0.05-0.55** (Tressl *et al.,* 1975 -1976); **0.007-0.074** (Wackerbauer *et al.,* 1977); **0.19-4.3***** (Wackerbauer and Kramer, 1982); **0.098*, 2.51***, 0.2****** (Wackerbauer *et al.,* 1982); **0.49-6.17***** (Kieninger *et al.,* 1984); **0.051-0.17** (Villareal *et al.,* 1986); **0.05-0.55** (Moll, 1991); **0.12-0.53*, 0.9***** (Schieberle, 1991); **0.04-0.07*, 0.68***** (Madigan *et al.,* 1994); **0-0.09*, 0.57***** (McMurrough *et al.,* 1996a); **0-0.28*, 0.16-2.23**, 0.15-2.42***** (Coghe *et al.,* 2004); **0.1390** (Vanbeneden *et al.,* 2006b)
4-Ethylguaiacol	**0.40** (Kieninger and Boeck, 1977)	-	**<0.01** (Tressl *et al.,* 1975 -1976); **0-0.6***** (Wackerbauer and Kramer, 1982); **0*and ***, 0.13***** (Wackerbauer *et al.,* 1982)
4-Methylguaiacol	**0.80** (Kieninger and Boeck, 1977)	-	**0-0.15***** (Wackerbauer and Kramer, 1982); **0*, 0.04***, 0.5****** (Wackerbauer *et al.,* 1982)
Guaiacol	**0.12** (Kieninger and Boeck, 1977)	-	**0.01-0.02** (Tressl *et al.,* 1975-1976); **0-0.3 0-0.3***** (Wackerbauer and Kramer, 1982); **0.014*, 0.02***, 0.42****** (Wackerbauer *et al.,* 1982)
4-Allylguaiacol	-	-	**0-0.2***** (Wackerbauer and Kramer, 1982); **0.01*, 0***, 0.2****** (Wackerbauer *et al.,* 1982)
4-Propenylguaiacol	**3.30** (Kieninger and Boeck, 1977)	-	**<0.01** (Tressl *et al.,* 1975 -1976); **0-0.16***** (Wackerbauer and Kramer, 1982); **0*, 0.04***, 0****** (Wackerbauer *et al.,* 1982)
Vanillin	-	-	**<0.01** (Tressl *et al.,* 1975 -1976) ; **0.030*, < 0.005*** and ****** (Wackerbauer *et al.,* 1982) ; **1.6** (Achilli *et al.,* 1993); **0.028** (Bartolomé *et al.,* 2000)
Acetovanillone	-	-	**<0.01** (Tressl *et al.,* 1975 -1976); **0-0.5***** (Wackerbauer and Kramer, 1982); **0.01*, 0.01***, 0.35****** (Wackerbauer *et al.,*1982); **0.01-0.3** (Moll, 1991)
***p*-Coumaric acid derived compounds**			
4-Vinylphenol	-	-	**0.04-0.15** (Tressl *et al.,* 1975 -1976); **0.005-0.172** (Wackerbauer *et al.,* 1977) ; **0.2-2.7***** (Wackerbauer and Kramer, 1982); **0.01*, 1.25***, 0.2****** (Wackerbauer *et al.,* 1982); **0.3-3.17***** (Kieninger *et al.,* 1984) ; **0.0453** (Vanbeneden *et al.,* 2006b)
4-Ethylphenol	**4.41** (Kieninger and Boeck, 1977)	-	**0-0.1***** (Wackerbauer and Kramer, 1982); **0 *and ***, 0.51****** (Wackerbauer *et al.,* 1982)
4-Methylphenol	-	-	**0-0.03***** (Wackerbauer and Kramer, 1982)
Phenol	**0.16** (Kieninger and Boeck, 1977)	-	**0-0.03***** (Wackerbauer and Kramer, 1982); **0.03*, 0.7***** (Wackerbauer *et al.,* 1982)

- Not determined; * Pils, ** White beers made with unmalted wheat, German beers made with malted wheat: ***Weizen beers and **** Rauchbeers.

Hydroxycinnamic acids derived compounds occurrence

Structure	compounds	R1	R2	R3	R4
	**Sinapic acid derived compounds**				
	4-Vinylsyringol	OH	OCH_3	OCH_3	$CHCH_2$
	4-Ethylsyringol	OH	OCH_3	OCH_3	CH_2CH_3
	4-Methylsyringol	OH	OCH_3	OCH_3	CH_3
	4-Propylsyringol	OH	OCH_3	OCH_3	$CH_2CH_2CH_3$
	4-Allylsyringol	OH	OCH3	OCH_3	CH_2CHCH_2
	4-Propenylsyringol	OH	OCH_3	OCH_3	$CHCHCH_3$
	Syringol	OH	OCH_3	OCH_3	H
	Syringaldehyde	OH	OCH_3	OCH_3	CHO

Callemien & Collin, Review, Food Reviews International, accepted 2008

Sinapic acids derived compounds were detected in beer. No data concerning their occurrence in malt and hop are available in the literature.

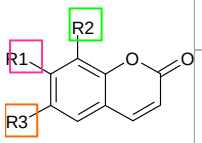
Compounds	Malt (mg/kg)	Hop (mg/kg)	Beer (mg/l)
Sinapic acid derived compounds			
4-Vinylsyringol	-	-	**<0.01** (Tressl *et al.*, 1975 -1976) **0.9-0.6*** ** (Wackerbauer and Kramer, 1982) **0.04*, 0.2***, 0.14**** ** (Wackerbauer *et al.*, 1982)
4-Ethylsyringol	-	-	**<0.01** (Tressl *et al.*, 1975 -1976) **0*, 0***, 0.042**** ** (Wackerbauer *et al.*, 1982)
4-Methylsyringol	-	-	**<0.01** (Tressl *et al.*, 1975 -1976) **0*, 0***, 1.1**** ** (Wackerbauer *et al.*, 1982)
4-Propylsyringol	-	-	**0* and ***, 0.9**** ** (Wackerbauer *et al.*, 1982)
4-Allylsyringol	-	-	**0* and ***, 0.14**** ** (Wackerbauer *et al.*, 1982)
4-Propenylsyringol	-	-	**<0.01** (Tressl *et al.*, 1975 -1976) **0* and ***, 0.36**** ** (Wackerbauer *et al.*, 1982)
Syringol	-	-	**0* and ***, 2.3**** ** (Wackerbauer *et al.*, 1982)
Syringaldehyde	-	-	**<0.01** (Tressl *et al.*, 1975 -1976) **0.7** (Achilli *et al.*, 1993)

- Not determined; * Pils, ** White beers made with unmalted wheat, German beers made with malted wheat: ***Weizen beers and **** Rauchbeers.

Hydroxycinnamic acids derived compounds occurrence

Three coumarins issued from orthohydroxycinnamic acid cyclization have been found in beer.

No data concerning their occurrence in malt and hop are available in the literature.

Structure	compounds	R1	R2	R3	R4	Malt (mg/kg)	Hop (mg/kg)	Beer (mg/l)
	Umbelliferon	OH	H	H	/	-	-	0.5-5 (Moll, 1991)
	Scopoletin	OH	H	OCH_3	/	-	-	< 0.1 (Moll, 1991)
	Daphnetin	OH	OH	H	/	-	-	0.5-5 (Moll, 1991)

Callemien & Collin, Review, Food Reviews International, accepted 2008

Organoleptic properties

Decarboxylated derivatives can impart **very strong phenolic/clove/smoked flavours** to beer because of their low threshold values (ppb order).

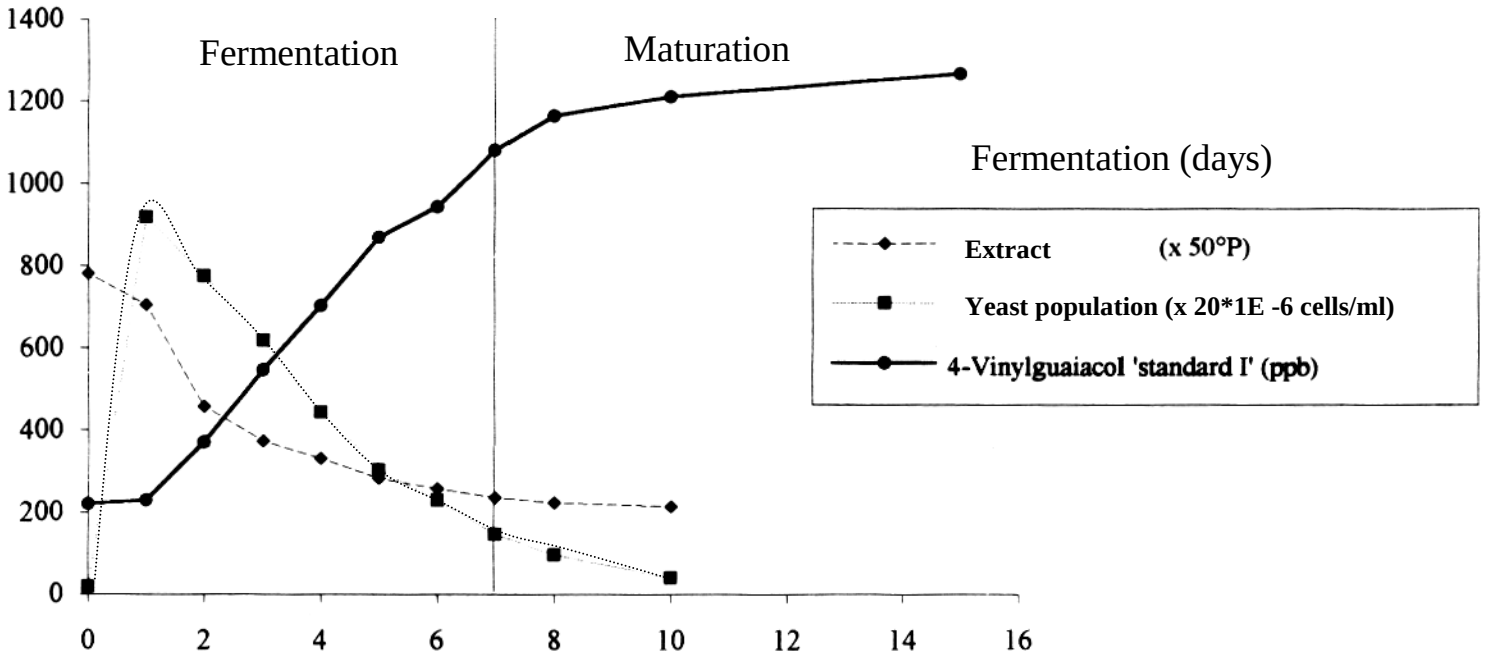
4-Vinylguaiacol: specificity of **Belgian white beers** (made with unmalted wheat) and **German Rauch and Weizen beers** (made with malted wheat).

4-Vinylguaiacol can lead either to strong pharmaceutical off-flavour defects or to pleasant clove flavours, whilst **4-vinylphenol** is always considered to be an off-flavour.

Phenolic compounds	Organoleptic characteristics	Threshold in beer (mg/l)
4-Vinylguaiacol	Clove, phenolic, bitter	0.25*; 0.30** and ***
4-Ehylguaiacol	Clove, phenolic, sweet	0.13* and **
4-Methylguaiacol	Medicinal, burned	0.20*
Guaiacol	Phenolic, burned	0.70*
Eugenol or 4-Allylguaiacol	Clove, dental, disinfectant	0.20*
4-Propenylguaiacol	Clove, dental, disinfectant	0.10*
Vanillin	Vanilla	0.50*
Acetovanillone	Vanilla	0.50*
4-Vinylphenol	Phenolic, bitter, astringent	0.20*
4-Ethylphenol	Cresol	0.10*
4-Methylphenol	Medicinal, phenolic	0.20*
Phenol	Phenolic, cresol	0.30*
4-Vinylsyringol	Smoked, burned	0.50*
4-Ethylsyringol	Smoked, burned	0.50*
4-Methylsyringol	Smoked, burned	0.50*
4-Propylsyringol	Smoked, burned	0.50*
4-Allylsyringol	Smoked, burned	0.50*
4-Propenylsyringol	Smoked, burned	0.25*
Syringol and syringaldehyde	-	-

- Not determined; * Wackerbauer *et al.*, (1982); ** Meilgaards (1975); *** Moll (1991).

4-Vinylguaiacol and 4-Vinylphenol



In Belgian white beer production:

- The enzymatic decarboxylation of ferulic acid occurs linearly through fermentation at a rate close to 140 ppb/day.
- The rate decreases strongly during secondary fermentation, down to 20 ppb/day.

Collin, Unpublished data

Optimal concentration of ferulic acid in beer

Phenolic acids	Wort (ppm)	Beer (ppm)
Ferulic acid	4.1	2.6
p-Coumaric acid	1.2	1.2

Phenolic acids	Wort (ppm)	Beer (ppm)
Ferulic acid	1.2	0.2
p-Coumaric acid	1.0	0

Compared to *p*-coumaric acid, ferulic acid is preferentially degraded by yeast.

p-Coumaric acid remains unmodified until the ferulic acid concentration reaches 2 ppm

if [ferulic acid] < 2 ppm:

- decarboxylation of *p* - coumaric acid
- ➔ **4-vinylphenol** formation (off - flavour)

Collin, Unpublished data

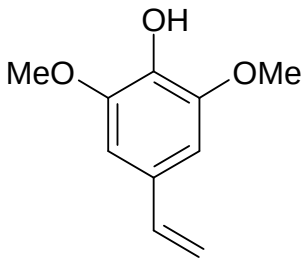
How to identify other phenolic compounds

responsible of the most potent flavours of beer?

e.g.: 4-Vinylsyringol

Callemien, Dasnoy and Collin, Journal of Agricultural and Food Chemistry, 54, 1409-1413, 2006

Flavour stability: "Cinnamic" – derived phenols
With a strong "stale-beer" odour



4-Vinylsyringol

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2006,** *54,* 1409–1413 **1409**

Identification of a Stale-Beer-like Odorant in Extracts of Naturally Aged Beer

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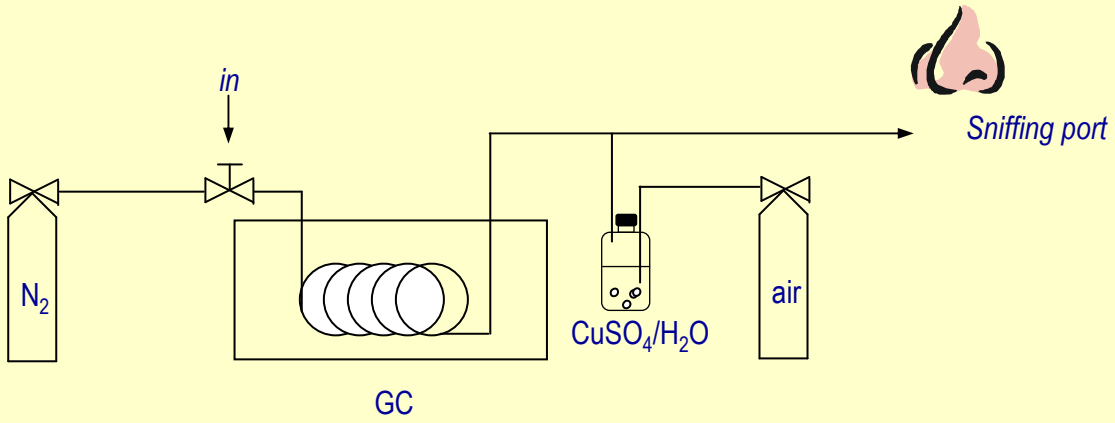
For a long time, beer staling has been a prime concern in brewery research. Yet, to improve flavor stability, better knowledge of all chemicals involved is still needed. From our aroma extract dilution analyses (AEDA) applied to naturally aged lager beers emerged an old-beer-like odorant at $RI_{CP-SIL\ 5\ CB} = 1532$ and $RI_{FFAP} = 2809$, with a FD value close to that of *trans*-2-nonenal (the well-known cardboard off-flavor found in aged beers). Specific phenol extraction, GC cold trapping, and mass spectrometry (electron impact and chemical ionization) enabled us to identify it as 4-vinylsyringol. Although already mentioned in some fresh beers, this compound had never been highlighted as involved in the aging process of lager beers.

KEYWORDS: Beer; storage; aging; stale; flavor; GC olfactometry; 4-vinylsyringol

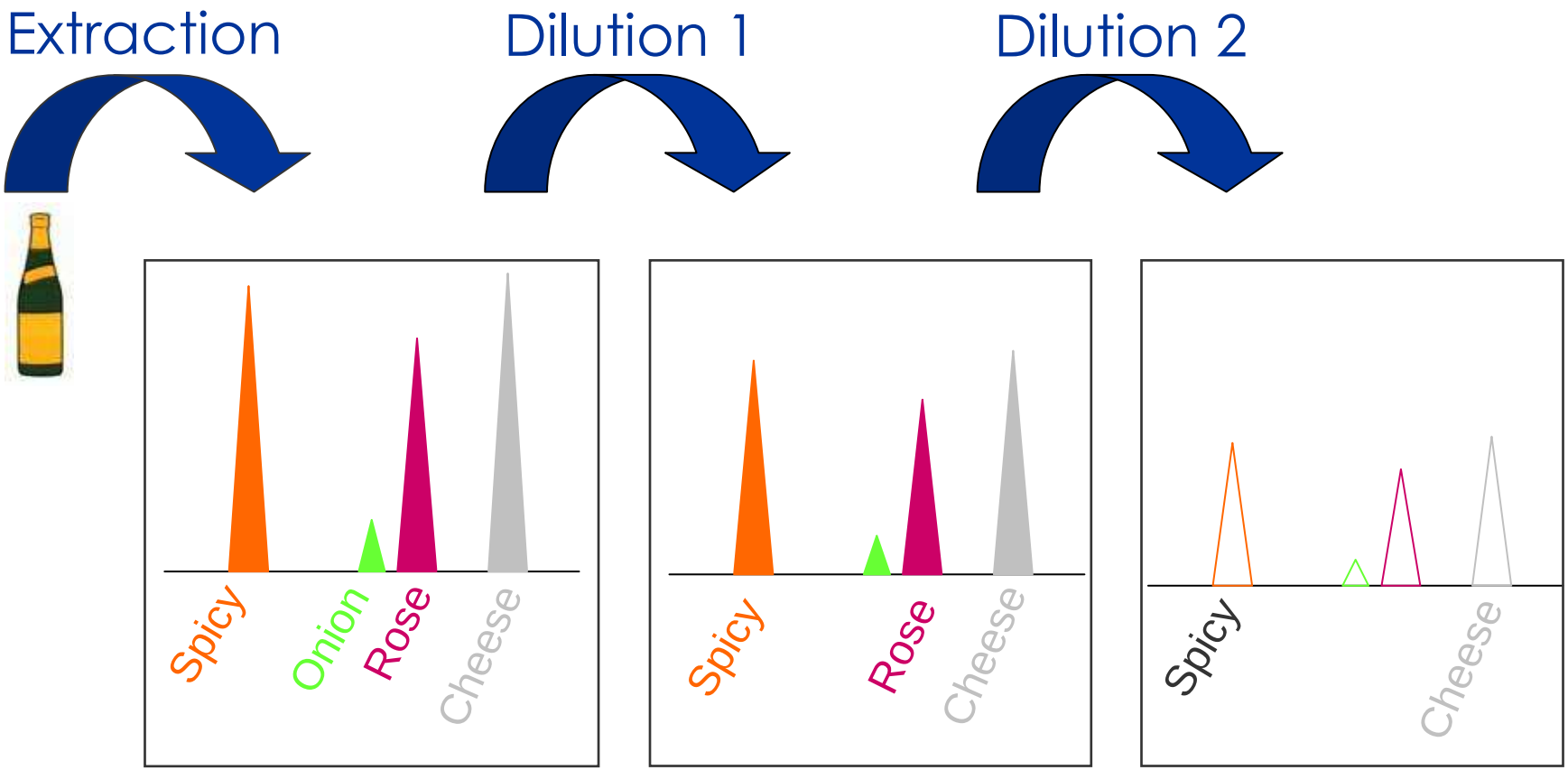
Organoleptic profile of fresh and aged beers by AEDA

Use of **GC-O / AEDA** method to determine key-flavours of beer extracts (fresh, aged for 3 and 6 months) obtained with the Amberlite XAD - 2 resin



AEDA - *Aroma Extract Dilution Analysis*

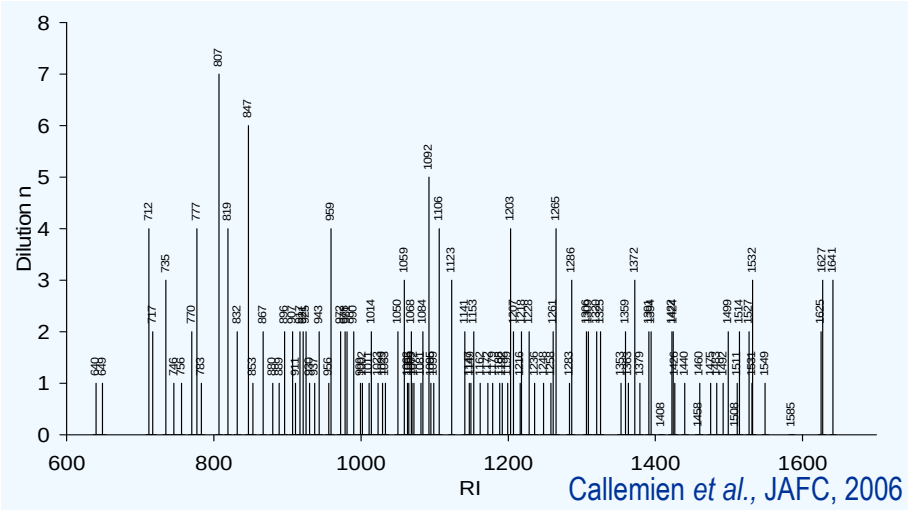
Callemien *et al.*, JAFC, 2006



FD = d $^{n-1}$ with

d dilution factor

n number of dilutions required for no odour to be perceived



Callemien *et al.*, JAFC, 2006

7 compounds revealed to be key-flavours of naturally aged beers

Lager beers FD			Odour	Compounds
FB	N3	N6		
2187	2187	2187	hop	Isopentenylmercaptan
729	2187	243	nutty	2 – Methyl – 3 - furanthiol
27	27	27	potato	Methional
81	243	729	cabbage	Dimethyltrisulfide
27	27	243	curry	Sotolon
81	243*	729*	floral	β – Phenylethanol + Linalool *
27	81	243	cardboard	*trans* – 2 - Nonenal
81	243	81	honey	2‘ - Aminoacetophenone
81	81	81	smoked	4 - Vinylguaiacol
27	81	81	red fruits	β – Damascenone
27	243	243	smoky, old	Unknown $RI_{CP\text{-}Sil\ 5}$ = 1532

« […] at least as important as *trans*-2-nonenal » (Gijs *et al.*, 2002)

Callemien *et al.*, JAFC, 2006

Unknown with IK = 1532 and a smoky-old beer flavour

⇨ First data:

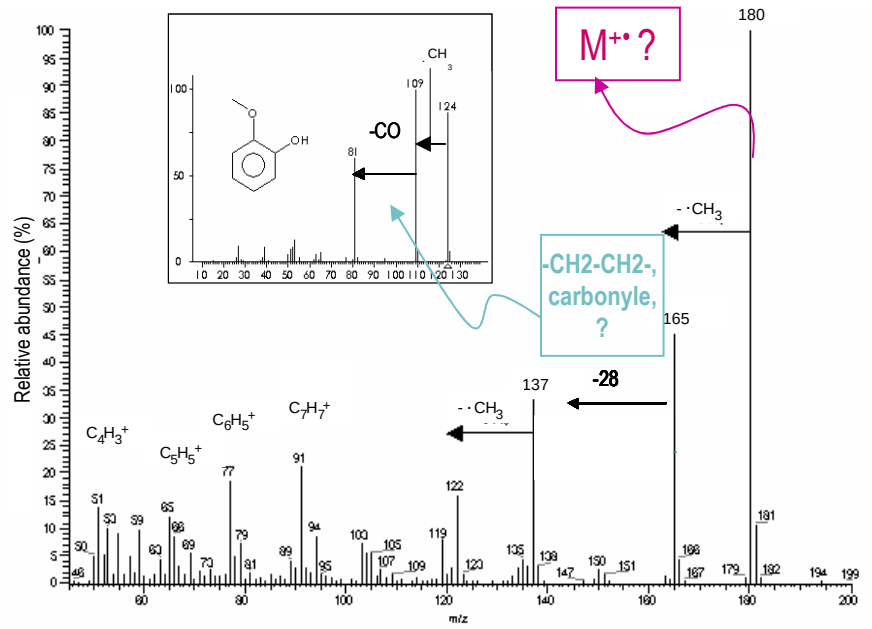
- FD = 27 (FB), 243 (N3-6), 243 (A)

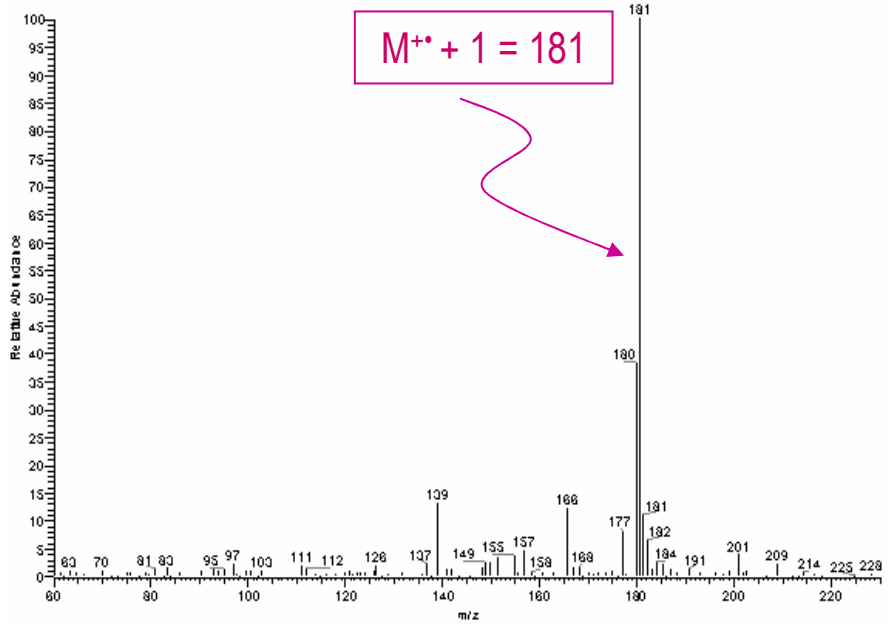
- RI = 1532 (CP-Sil 5), 2809 (FFAP)

- description at the sniffing-port = smoky-old beer

Callemien *et al.*, JAFC, 2006

Analyses by GC-MS in EI and CI





- ✓ Aromatic
- ✓ CH_3 terminal
- ✓ M+• stable

- ✓ Mw = 180

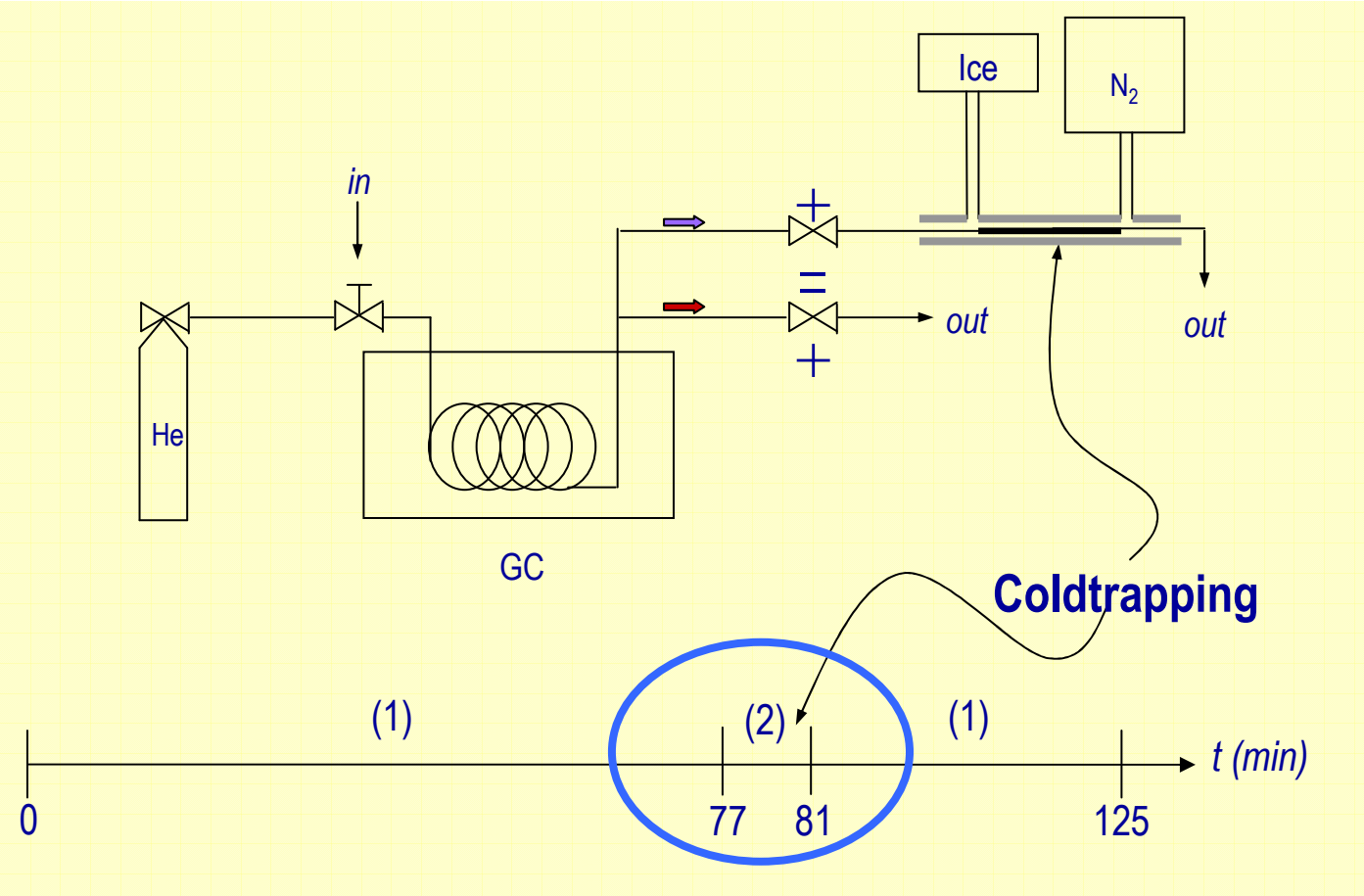
Callemien *et al.*, JAFC, 2006

Part of the effluent is isolated in a cold trap

Information

- RI = 1532 (CP-Sil 5)

  RI = 2809 (FFAP)
- Smoky, old; tobacco ↗ ↗
- Aromatic
- CH_3 terminal
- $M^{+\bullet}$ stable
- Mw = 180



✓ Confirmation of GC - MS peak

✓ And odour tobacco / aged beer (GC-O) ➔ phenol ? ➔ specific extraction : yes

Callemien *et al.*, JAFC, 2006

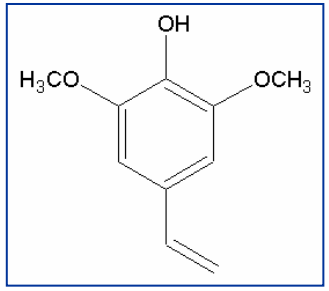
Preparation of the hypothetic structure

Information

- RI = 1532 (CP-Sil 5)

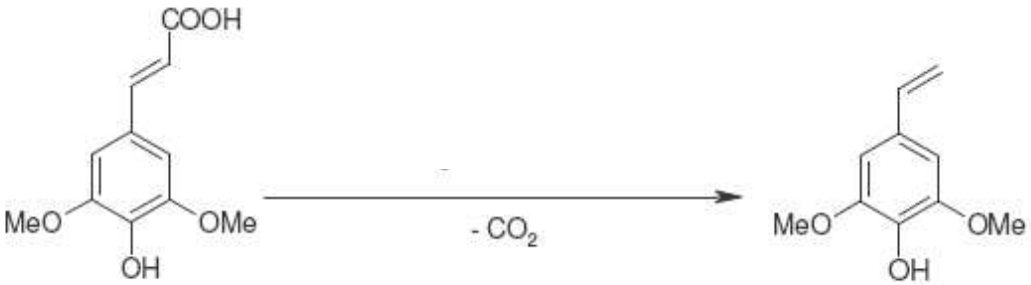
  RI = 2809 (FFAP)
- Smoky, old; tobacco ↗ ↗
- Aromatic
- CH_3 terminal
- $M^{+\bullet}$ stable
- Mw = 180
- Phenolic compound

Tobacco flavours « smoky-old»



4-vinylsyringol

(Mw = 180)



Sinapic acid

4-Vinylsyringol

Callemien *et al.*, JAFC, 2006

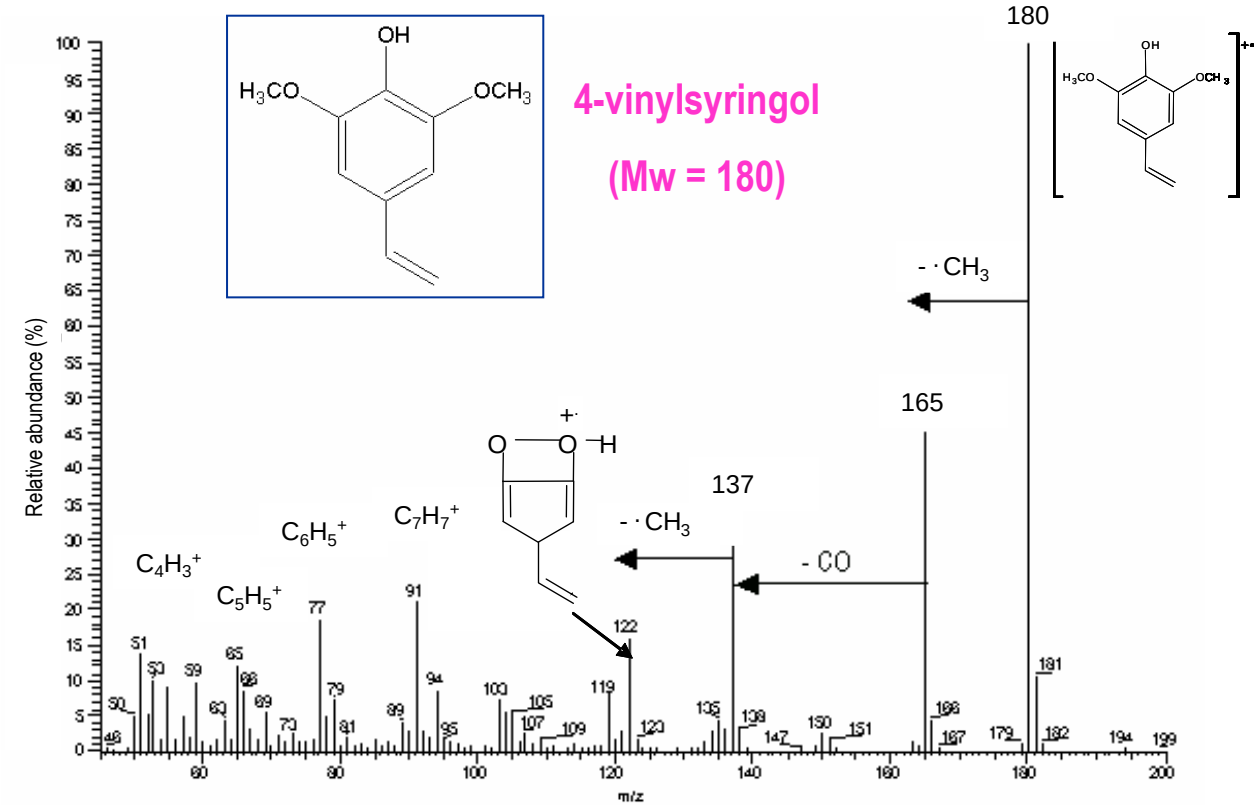
Identification of the unknown has been achieved

Information

- RI = 1532 (CP-Sil 5)

  RI = 2809 (FFAP)
- Smoky, old; tobacco ↗ ↗
- Aromatic
- CH_3 terminal
- $M^{+\bullet}$ stable
- Mw = 180
- Phenolic compound

Tobacco flavours « smoky-old»

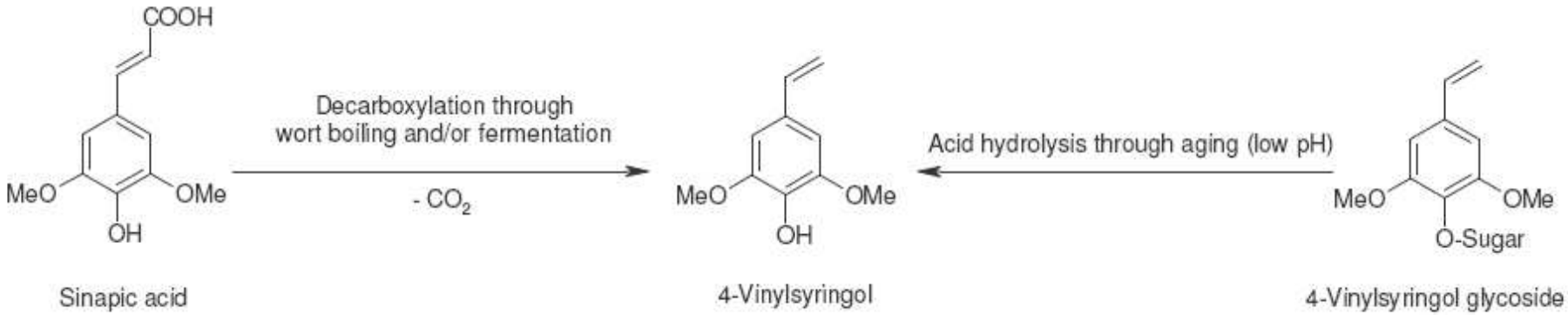


Already identified in a fresh beer but with no relation to ageing

Callemien *et al.*, JAFC, 2006

Hypothesis of its pathway synthesis in beer

- Sinapic acid
- Glycoside (observed in tobacco)
- Adducts with polyphenols (observed in Wine)



Callemien *et al.*, JAFC, 2006

Conclusions and next steps

- **Literature overview :**

Ferulic and *p*-coumaric acids release 4-VG and 4-VP, respectively. Both impacting the flavour of beer.

- **New data obtained on aged beer:**

Identification of 4-VS

➢ **Next steps:** identify the precursors/presence in malt and hop

Special thanks to

- Professeur Sonia Collin & INBR team
- La fondation InBev-Baillet Latour & Inbev
- La laboratoire de Spectrométrie de Masse, UCL

- Baxter R&D Nivelles

Thank you for your attention

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