Volatile monophenols in belgian special beers: identification of specific markers

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Volatile monophenols in belgian special beers

1. State of the art
Volatile phenols …

– Important flavor contributors in beverages
e.g: Weizen beers and Belgian white beers
Phenylpropanoid pathway (stress related) L-phenylalanine

monophenols

associated with lignins (ether or ester bound) or under hydroxycinnamic acids form (Li et al., 2008)

Glycoside forms

Lignin-carbohydrate complex in herbaceous straws (Buranov et al., 2008)

Lignin polymer (Gross et al., 2007)
<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>Concentration in</th>
<th>Threshold in beer (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Malt (ppm)</td>
<td>Hop (ppm)</td>
</tr>
<tr>
<td>Ferulic acid</td>
<td><img src="image" alt="Ferulic acid structure" /></td>
<td>7,8-12,8</td>
<td>13,2-14,1</td>
</tr>
<tr>
<td>p-Coumaric acid</td>
<td><img src="image" alt="p-Coumaric acid structure" /></td>
<td>0,3-1,3</td>
<td>2,2-2,8</td>
</tr>
<tr>
<td>Sinapic acid</td>
<td><img src="image" alt="Sinapic acid structure" /></td>
<td>1.0-4.3</td>
<td>4.1-5.1</td>
</tr>
</tbody>
</table>

(Wackerbauer and Kramer, 1982)
Little impact of hydroxycinnamic acids on beer profile!

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ferulic acid</th>
<th>p-Coumaric acid</th>
<th>Sinapic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure of Ferulic acid" /></td>
<td>7.8-12.8 ppm</td>
<td>0.3-1.3 ppm</td>
<td>1.0-4.3 ppm</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure of p-Coumaric acid" /></td>
<td>13.2-14.1 ppm</td>
<td>2.2-2.8 ppm</td>
<td>4.1-5.1 ppm</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure of Sinapic acid" /></td>
<td>5.6-13.1 ppm</td>
<td>0.21-1.45 ppm</td>
<td>2.4-4.5 ppm</td>
</tr>
</tbody>
</table>

(Wackerbauer and Kramer, 1982)
Phenylacrylic acid decarboxylase (POF + yeast)  
Saccharomyces cerevisiae  
Brettanomyces/Dekkera spp. ou  
Enterobacteriacea.  
(McMurrough et al., 1996, Suarez et al., 2007)
Thermic decarboxylation

- **Malting**
  - $T^\circ \uparrow$
  - Humidity $\downarrow$
  - Lignin pyrolysis

- **Brewing**
  - $T^\circ \uparrow$
  - Humidity $\uparrow$
Volatile monophenols in belgian special beers:

3. Material & methods
7 Commercial Belgian special beers
Green malt kilning

- 5 EBC
- 50 EBC
- 500 EBC
- 900 EBC
- 1500 EBC

PILSEN MALT TORREFACTOR step: until 225 °C

- 15 min – 125°C
- 10 min – 180°C
- 10 min – 225°C
- 20 min – 225°C
EBC method congress wort

Phenols

Ebullition

Malt

EBC Congress wort
4-Vinylguaiacol | Guaiacol
4-Methylphenol | 4-Methylguaiacol
4-Ethylphenol | 4-Ethylguaiacol
4-Vinylphenol | Apocynol
Vanilline
GC-MS analysis (SIM Mode)

- 4-Methylphenol
- Guaiacol
- 4-Ethylphenol
- 4-Vinylphenol
- 4-Ethylguaiacol
- 4-Vinylguaiacol
- Vanillin
- Apocynol
- 4-Methylguaiacol
Volatile monophenols in belgian special beers:

4. Results
A. Analysis of fresh beers
Thermal degradation of ferulic and p-coumaric acids + lignins during roasting
B. Special malts investigation
Malting procedure

Steeping

Germination

Kilning

ROASTER

TORREFACTOR

Caramel malt

Green malt

Pilsen malt

Chocolate malt
Green malt kilning

- 5 EBC
- 50 EBC
- 500 EBC
- 900 EBC
- 1500 EBC

PILSEN MALT TORREFACTOR step: until 225 °C

- 15 min – 125°C
- 10 min – 180°C
- 10 min – 225°C
- 20 min – 225°C
• Emergence of 3 specific profiles
Evolution 4-methylphenol, guaiacol and 4-methylguaiacol

Temperature of roasting (>250°C)

Specific to the use of torrefied malts
Evolution of vanillin, 4-ethylguaiacol, 4-ethylphenol and apocynol.
Evolution of 4-vinylphenol and 4-vinylguaiacol.
Phenols glucosides: vanillin?
Phenols glucosides: extraction procedure

- Washing with H₂O mQ, 5x5 ml Ether diéthylique
- Elution: 5x5mL méthanol

Dryness + 50 mL acetate buffer

β-D-glucosidase

3x L:L diethyl ether

Octyl-glucopyranoside 1ml – 1000ppm IST

Beer or EBC wort

XAD 2 Resin

Octanol

+ dodecane 1ml, 20ppm (EST)
Concentration to 500 µL
Abundance

Released IST
30201 µV.s

Vanillin
174266 µV.s

Time (min)

Abundance

Released IST
17446783 µV.s

Vanillin
1300600 µV.s

Time (min)
5. Conclusions
• As suspected by beer analysis

  – Use of dark specialty malts liberate specific phenolic compounds
  – These compounds are present in beers produced with torrefied malts
  – Malting process and thermic steps are key factors
  – Investigation of glucosides
Thank you for your attention...