Fermentation-derived aroma compounds and grape-derived monoterpenes

Leigh Francis
Flavours from yeast

Volatile phenols
Volatile fatty acids
Higher alcohols
Volatile acidity

‘Barrel-fermented Chardonnay’

Sulfides

MEDICINAL
SPIRITOUS
CHEESY/SWEATY
SULFIDIC

VINEGAR

2-phenylethanol
2-phenylethyl acetate
Ethyl esters
Acetate esters

Polyfunctional thiols

‘Tropical Sauvignon blanc’

Confectionary
Fruity
Tropical
Floral
Sulfidic
Cheesy/Sweaty
Medicinal
Vinage

Adapted from Cordente et al Flavour-active yeasts
## Fermentation derived volatiles: fatty acids

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Aroma Description</th>
<th>Aroma Threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyric acid</td>
<td>rancid, cheese</td>
<td>2300</td>
</tr>
<tr>
<td>Isovaleric acid</td>
<td>sweat, rancid</td>
<td>33</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>pungent, vinegar</td>
<td>200 000</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>rancid, cheese, vomit</td>
<td>173</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>sweat</td>
<td>420</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>sweat, cheese</td>
<td>500</td>
</tr>
<tr>
<td>Decanoic acid</td>
<td>rancid, fat</td>
<td>1000</td>
</tr>
</tbody>
</table>

Reactions in fermentation can produce volatile fatty acids (VFA), such as acetic, propionic, and butyric acids, which can contribute to the aroma profile of wine. The table above lists some common fatty acids found in wine along with their aroma threshold values. The chemical structure of octanoic acid (C8:0) is also shown below:

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}
\]
### Fermentation derived volatiles: alcohols

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aroma Descriptors</th>
<th>Aroma Threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutanol</td>
<td>Solvent, harsh</td>
<td>40000</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>whiskey, malt, burnt</td>
<td>30000</td>
</tr>
<tr>
<td>2-Phenylethyl alcohol</td>
<td>rose, lilac</td>
<td>14000</td>
</tr>
</tbody>
</table>
Fatty acids and higher alcohols

- Formation from amino acids, and glucose via pyruvate (BAT1 and BAT2 genes)
- Higher alcohols tend to be promoted with:
  - higher temperature
  - higher nitrogen
  - aerobic conditions
  - higher Brix must

![Chemical reactions diagram]

- From amino acid to \( \alpha \)-keto acid via transamination
- From \( \alpha \)-keto acid to fusel aldehyde via decarboxylation
- Fusel aldehyde can be oxidized to fusel acid or reduced to fusel alcohol.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Aroma Description</th>
<th>Aroma Threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl isobutyrate</td>
<td>fruity</td>
<td>15</td>
</tr>
<tr>
<td>Ethyl 2-methylbutyrate</td>
<td>apple</td>
<td>18</td>
</tr>
<tr>
<td>Ethyl isovalerate</td>
<td>fruit</td>
<td>3</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td>apple</td>
<td>20</td>
</tr>
<tr>
<td>Ethyl hexanoate</td>
<td>apple peel, fruit, pineapple</td>
<td>14</td>
</tr>
<tr>
<td>Ethyl octanoate</td>
<td>fruit, fat</td>
<td>5</td>
</tr>
<tr>
<td>Ethyl decanoate</td>
<td>grape</td>
<td>200</td>
</tr>
<tr>
<td>Isoamyl acetate</td>
<td>banana</td>
<td>30</td>
</tr>
<tr>
<td>Phenylethyl acetate</td>
<td>rose, honey</td>
<td>250</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>fruity, solvent</td>
<td>12264</td>
</tr>
</tbody>
</table>
Fermentation derived volatiles: Esters

- fatty acid ethyl esters, acetate esters
- \( EEB1, EHT1 + ATF1, ATF2 \) genes
  - slower rate of fermentation, increase in esters
    - ie lower temp

- Higher acetate esters
  - higher Brix must
  - Higher nitrogen
  - 20 °C optima

- yeast strain
- juice composition: amino acid pattern
- undergo chemical hydrolysis/reaching chemical equilibrium with storage: rapid decrease in first year in bottle

\[
R_1\text{COOH} + R_2\text{OH} \rightleftharpoons R_1\text{COOR}_2 + \text{H}_2\text{O}
\]
Grape C6 levels contribute to acetate ester formation

Published in: Eric G. Dennis; Robert A. Keyzers; Curtis M. Kalua; Suzanne M. Maffei; Emily L. Nicholson; Paul K. Boss; *J. Agric. Food Chem.* 2012, 60, 2638-2646.
DOI: 10.1021/jf2042517
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Grape derived monoterpenes

- Linalool
- Geraniol
- Wine lactone
Grape derived monoterpenes: unlocking flavour

Formed in plant cells: geranyl pyrophosphate
❖ ~ 70 compounds identified, aromas may be additive

Three classes of monoterpenes
1. Free aroma compounds
   ▪ low aroma thresholds eg linalool, geraniol, nerol
2. Polyhydroxylated forms
   ▪ free odourless polyols
   ▪ some are reactive and can break down easily to give other pleasant volatiles eg rose oxide
3. Glycoside conjugates
   ▪ Attached to sugars
   ▪ released by enzyme or acid hydrolysis
Glycoside precursors

- enzyme hydrolysis
  - inhibited by glucose
  - Yeast/bacteria
  - Exogenous enzymes

- Acid-catalysed hydrolysis and rearrangements during wine processing and ageing

<table>
<thead>
<tr>
<th>Compound</th>
<th>Odour Descriptor</th>
<th>Detection threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linalool</td>
<td>Muscat, fresh, floral, lavender, sweet</td>
<td>25 µg/L</td>
</tr>
<tr>
<td>Nerol</td>
<td>Rose</td>
<td>300 µg/L</td>
</tr>
<tr>
<td>Geraniol</td>
<td>Spicy, flowery, citrus</td>
<td>30 µg/L</td>
</tr>
<tr>
<td>α-Terpineol</td>
<td>Floral, citrus, sweet</td>
<td>250 µg/L</td>
</tr>
<tr>
<td>Citronellol</td>
<td>Spicy, flowery</td>
<td>100 µg/L</td>
</tr>
<tr>
<td>cis-Rose Oxide</td>
<td>Lychee, rose</td>
<td>100 µg/L</td>
</tr>
<tr>
<td>Wine Lactone</td>
<td>Coconut, lime</td>
<td>0.01 µg/L</td>
</tr>
<tr>
<td>1,8-Cineole</td>
<td>Eucalyptus</td>
<td>3.2 µg/L</td>
</tr>
</tbody>
</table>
Geraniol
Rose, geranium
(30 μg/L)

Nerol
Rose
(300 μg/L)

Linalool
Floral, lavender
(25 μg/L)

α-Terpineol
Floral, lilac
(250 μg/L)

trans-Rose oxide
Rose, floral
(80 μg/L)

cis-Rose oxide
Rose, lychee
(0.2 μg/L)

1,8-Cineole
Eucalyptus, medicinal
(3 μg/L)
Monoterpenes

- **linalool** floral, lemon
  - threshold ~25 μg/L, in Muscat wine up to 500 μg/L

- **‘wine lactone’**
  - ‘coconut’, ‘lime’, ‘woody’ and ‘sweet’
  - very potent: threshold 0.01 μg/L, in wine ~0.1 μg/L, aged wines
  - First isolated in Koala urine (1975)

- **cis-rose oxide** roses, lychee 0.2 μg/L, in wine up to 20 μg/L, esp. Gewürztraminer
Loss of monoterpenes over time

Concentration (µg/L) vs. Time (months)

- Linalool
- Nerol
- Geraniol
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