Effect of hop harvest date on the thiol contents in hop cones

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SAPPORO BREWERIES LTD.
Agenda

- Introduction
- Materials and Methods
- Results
- Summary and Perspective
Agenda

✓ Introduction
✓ Materials and Methods
✓ Results
✓ Summary and Perspective
About SAPPORO BREWRIES LTD.

- In 1876, established in Sapporo, Hokkaido
- 6 breweries in Japan
  - Hokkaido
  - Sendai
  - Chiba
  - Nasu
  - Shizuoka
  - Kyushu-Hita

Our Varieties
- SORACHI ACE
- Furano No. 18
- Furano Special
- Furano Beauty
- Furano Magical

SAPPORO is the only company which breeds both barley and hops all over the world.
Effect of harvest date

Variation of characteristics depends on harvest date

Mellowed fruit
Banana
Mangos etc.

Wine
Spätlese (Late harvest grape)

How about the effect of harvest date in hop cones?

yield

Essential oils
Volatile thiols

3-sulfanylhexan-1-ol \( 3\text{SH} \)

\[
\text{CH}_3 \quad \text{CH}_3
\]

4-methyl-4-sulfanylpentan-2-one (4MSP)

\[
\text{CH}_3 \quad \text{CH}_3
\]

3-sulfanyl-4-methylpentan-1-ol (3S4MP)

\[
\text{CH}_3 \quad \text{SH}
\]

3-sulfanyl-4-methylpenty acetate (3S4MPA)

\[
\text{SH} \quad \text{CO}
\]

Representative varieties including thiols

Nelson Sauvin  Citra®  Mosaic®
Volatile thiols

4MSP  (4-methyl-4-sulfanylpentan-2-one)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{SH} \\
& \quad \text{O}
\end{align*}
\]

Odor: Black currant-like

Threshold: 1.5 ppt

3S4MP  (3-sulfanyl-4-methylpentan-1-ol)

\[
\begin{align*}
\text{CH}_3 & \quad \text{OH} \\
\text{SH}
\end{align*}
\]

Odor: Grapefruit-like

Threshold: 70 ppt

4MSP and 3S4MP have major influences on the flavor of beer.

We focused on these two volatile thiols.
The relationship between the harvest date and the contents of thiols has never been researched.

✔ To clarify the relationship between the harvest date and the thiol contents
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Materials and Methods

Raw materials

Cascade

Furano Beauty

Furano Magical®

bred by SAPPORO BREWERIES LTD.

Both hops give unique varietal aroma to finished beer

Harvest date

‘45 days‘ after flowering (Normal)

‘65 days‘ after flowering

‘75 days‘ after flowering

‘85 days‘ after flowering
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Results

Result 1  Sensory evaluation using hop boiled water extraction method (Koie et al., J.ASBC 2016)

Result 2  Analysis of α-acids and essential oils in hop cones

Result 3  Analysis of thiols in hop cones

Result 4  Analysis of thiols in trial beer

Result 5  Sensory evaluation of trial beer
Results

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(Koie et al., J.ASBC 2016)

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Sensory evaluation using hop boiled water extraction method

**Result 1**

**Furano Beauty**
- The scores of fruit and flower are increased by late harvest.

**Furano Magical**
- The balance of aroma are changed by late harvest.
**Results**

**Result 1**  Sensory evaluation using hop boiled water extraction method (Koie et al., J.ASBC 2016)

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**Result 4**  Analysis of thiols in trial beer

**Result 5**  Sensory evaluation of trial beer
Essential oils

With the delaying harvest date, the content of essential oils are increased.

α-acids

Depending on the date of harvest, the content of alpha acids are not almost changed or slightly increased.

### Result 2

**Analysis of α-acids and essential oils**

#### Essential oils (ppm)

<table>
<thead>
<tr>
<th></th>
<th>Cascade 45 days</th>
<th>Cascade 65 days</th>
<th>Cascade 75 days</th>
<th>Furano Beauty 45 days</th>
<th>Furano Beauty 65 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myrcene</td>
<td>5,157</td>
<td>6,062</td>
<td>10,158</td>
<td>8,917</td>
<td>13,338</td>
</tr>
<tr>
<td>Linalool</td>
<td>48</td>
<td>65</td>
<td>88</td>
<td>70</td>
<td>110</td>
</tr>
<tr>
<td>Geraniol</td>
<td>14</td>
<td>14</td>
<td>31</td>
<td>66</td>
<td>84</td>
</tr>
</tbody>
</table>

### α-acids (%)

<table>
<thead>
<tr>
<th></th>
<th>Furano Beauty 45 days</th>
<th>Furano Beauty 65 days</th>
<th>Furano Magical 45 days</th>
<th>Furano Magical 65 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-acids</td>
<td>10.7</td>
<td>10.6</td>
<td>5.0</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Results

Result 1  Sensory evaluation using hop boiled water extraction method (Koie et al., J.ASBC 2016)

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**Result 3**

**Analysis of thiols in hop cones**

<table>
<thead>
<tr>
<th></th>
<th>45 days</th>
<th>65 days</th>
<th>75 days</th>
<th>85 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furano Beauty</td>
<td>45 days</td>
<td>65 days</td>
<td>75 days</td>
<td>85 days</td>
</tr>
<tr>
<td>Furano Magical</td>
<td>45 days</td>
<td>65 days</td>
<td>75 days</td>
<td>85 days</td>
</tr>
<tr>
<td>Cascade</td>
<td>45 days</td>
<td>65 days</td>
<td>75 days</td>
<td>85 days</td>
</tr>
</tbody>
</table>

**Furano Beauty, Cascade**

The contents of 4MSP are not changed.

**Furano Magical**

The content of 4MSP is decreased by late harvest.
Result 3
Analysis of thiols in hop cones

The contents of 3S4MP are increased by several times in all varieties.
Result 3
Analysis of thiols in hop cones

With delaying harvest date,
the balance of these thiols are significantly changed
the thiol’s balance of Furano Magical ‘65days’ shows similar to Mosaic®
3S4MP is increased by several times, while 4MSP is maintained.

Furano Beauty ‘75 days’ and ‘85 days’ shows higher contents of 3S4MP than that of Nelson Sauvin with delaying harvest date.
Results

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### Result 4
Analysis of thiols in trial beer

<table>
<thead>
<tr>
<th></th>
<th>4MSP (ppt)</th>
<th>3S4MP (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furano Beauty 45 days</td>
<td>10</td>
<td>37</td>
</tr>
<tr>
<td>Furano Beauty 65 days</td>
<td>8</td>
<td>174</td>
</tr>
</tbody>
</table>

Over threshold

<table>
<thead>
<tr>
<th></th>
<th>4MSP</th>
<th>3S4MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furano Magical 45 days</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>Furano Magical 65 days</td>
<td>42</td>
<td>148</td>
</tr>
</tbody>
</table>

Over threshold

- **4MSP**: Not changed
- **3S4MP**: Increased by several times

It is possible to increase 3S4MP selectively by delaying harvest date
Results

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Sensory evaluation of trial beer

**Furano Beauty**

The scores of fruity, flowery and citrus are increased by late harvest.

**Furano Magical**

The balance of aroma is changed by late harvest.
**Result 5**

Sensory evaluation of trial beer

**In both varieties, the scores of ‘Freshness’ and ‘Light taste’ is increased**

The increase of 3S4MP might contribute to increase these scores
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Summary and Perspective

Summary

With delaying harvest date,

- the balance of these thiols are significantly changed
- the content of 3S4MP in hop cones are increased by several times
- the scores of ‘Freshness’ and ‘Light taste’ increase in trial beer
- It is possible to increase 3S4MP selectively in trial beer

The flavor of beer can be appropriately controlled by ‘hop harvest date’

Perspective

- Investigate of the effect of late harvest on yield
- Establish the “Spätlese” for flavor hops
Acknowledgement

SAPPORO BREWERIES LTD.

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