New technologies for development of citrus-based ready-to-drink (RTD) alcoholic beverages that maintain freshness

Asahi Breweries, Ltd.
Development Laboratories for Alcoholic Beverages

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1. Introduction
2. New value “freshness”
3. Flavor components
4. Antioxidants
5. Summary
1. Introduction
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3. Flavor components
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5. Summary
Japanese beer market

The quantity of beer consumption is decreasing

From 2000 to 2017 × 0.8 ↓

Source: National Tax Agency “taxable shipping volumes” (partly estimated by Asahi breweries)
Japanese alcohol market

RTD is increasing every year

From 2000 to 2017

\[ \times 3.2 \uparrow \]

Source: National Tax Agency “taxable shipping volumes” (partly estimated by Asahi breweries)
What is RTD?

■ RTD stands for “Ready To Drink“ beverages with low alcohol (alcopop)
■ RTD was inspired by freshly squeezed lemon cocktails

- Vodka + lemon juice + carbonation
  - bar > canned (1984)
  - home

RTD
Why is RTD growing? ① “Price”

Tax and retail price of RTD are less than beer

- Retail price and alcohol tax (350ml)

<table>
<thead>
<tr>
<th></th>
<th>Beer</th>
<th>RTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retail price</td>
<td>2.01</td>
<td>1.37</td>
</tr>
<tr>
<td>Alcohol tax</td>
<td>0.70</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Retail price at convenience stores (including 8% consumption tax)

109.5 JPY/USD
Why is RTD growing? ② “Variety”

RTDs can meet a wide range of customer needs

**Flavor**
- citrus
- Soft fruits
- plain

**Alcohol**
- 9%
- 6%
- 3%

**Function**
- Non Sugar
- Low calories
Why is RTD growing? ② “Variety”

RTDs can meet a wide range of customer needs

- **Flavor**
  - citrus
  - Soft fruits
  - plain

- **Alcohol**
  - 9%
  - 3%
  - 6%

- **Function**
  - Non Sugar

pairs with any meals
Why is RTD growing? ② “Variety”

RTDs can meet a wide range of customer needs

Flavor
- citrus
- Soft fruits
- plain

Alcohol
- 9%
- 6%
- 3%

Function
- Non Sugar
- like juice
Why is RTD growing? ② "Variety"

RTDs can meet a wide range of customer needs

**Flavor**
- citrus
- plain

**Alcohol**
- 9%
- 3%
- 6%

**Function**
- Non Sugar
- Low calories

200 new RTD products every year (60 new beer products)
Why is RTD growing?

Many consumers have changed from beer to RTDs

Beer

High price

Few flavors

5-6% alcohol

Unhealthy image

RTD

Low price

Various flavors

3-9% alcohol

Healthy image
Our brewery in Ibaraki

Beer and RTDs have many points in common in production and sales process.
Strategy of Asahi breweries

Become the “No.1 alcohol beverage company in Japan”
⇒ Develop brands as No.1 in all alcohol beverage categories
RTD market in Japan

- RTD (Ready to Drink) market is growing while beer is decreasing

- The reasons why RTD is growing are
  1. Tax and retail price of RTD are cheaper than beer
  2. Various RTDs can meet a wide range of customer needs
1. Introduction

2. New value “freshness”

3. Flavor components

4. Antioxidants

5. Summary
The most important flavor of RTDs

Citrus-based RTDs are popular in Japan, and lemon taste RTDs are 30% of sales ⇒ We focused on lemon taste RTDs

Flavor shares of RTDs in 2016

- Lemon
- Grape fruit
- Plain
- Japanese plum
- Red grape
- Peach
- Lime & Lemon
- Flat lemon
- Orange
- Others

Source: INTAGE “RTD Landscape review 2016”
We pursued RTD’s needs for consumers

According to market research, ideal RTDs for consumers have a fresh feeling

Q. What is ideal RTDs for you?

A. Match with any food!
A. Light & refreshing!
A. Freshly squeezed!

Squeezed lemon alcohol beverage
We pursued RTD’s needs for consumers

We propose ”fresher feeling of fruit juice” in RTDs

Ideal RTDs

Squeezed lemon beverage → Natural

Fresh

Rich
Key flavor component “citral”

- Citral is important flavor component, contribute to freshness
- Citral is unstable in beverages and converts into off-flavors

![Chemical structures of citral and its derivatives](image)

Off-flavor

heat, light
Problem

Fresh flavor (Citral etc.)

Off-flavor
Strategy ①

1. Strengthen “freshness”

Fresh flavor (Citral etc.)

Off-flavor
Strategy ②

① Strengthen “freshness”

Fresh flavor (Citral etc.)

② Preserve “freshness”

Off-flavor
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Lemon-based RTDs (prototypes, commercial products)

The freshest Prototype

- lemon juice contents: high, low
- characteristics of flavor: fruity, juicy, ...
- taste: sweet, sour...

Search key flavor components contribute to freshness in sample A
The freshest Prototype

CATA (Check-all-that-apply) sensory evaluation
(Adams, Williams, Lancaster (2007))

Check all attributes that describe this sample:

- Citral
- Peel
- Floral
- Green
- Fatty
- Fruity
- Vitamin C
- Gasoline
- Brunt

Non-target GC-MS
with multivariate analysis software
Sample A (the freshest RTD) is characterized by “green”

Mapping of CATA (n=40)
Result ② flavor component analysis

Methylheptenone is highly contribute to characteristics of sample A (the freshest RTD)

SBSE (Stir Bar Sorptive Extraction)

□ multivariate analysis: MPP (Mass Profiler Professional) software
Result ③ Stability of methylheptenone

Methylheptenone is very stable

Survival rate (%)

<table>
<thead>
<tr>
<th></th>
<th>Start</th>
<th>37°C1W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylheptenone</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>Citral</td>
<td>29</td>
<td>0</td>
</tr>
</tbody>
</table>

Chemical structures:
- Methylheptenone
- Citral

Equation:
\[ \text{Methylheptenone} + \text{Citral} \]
Methylheptenone is considered to improve and maintain a feeling of freshness, combined with citral.

\[
\text{Freshness-improving effect of methylheptenone}\]

\[
\text{Freshness score (control)}
\]

\[
\text{Analyze software: Optimus (Response surface method) Analyze method: RBF}
\]
Methylheptenone is considered to improve and maintain a feeling of freshness, combined with citral.

**Freshness-improving effect**

Result ④ freshness-improving effect of methylheptenone

- Methylheptenone is considered to improve and maintain a feeling of freshness, combined with citral.

- Analyze software: Optimus (Response surface method)
  - Analyze method: RBF

- Freshness score
  - 5.0
  - 4.5
  - 4.0
  - 3.5
  - 3.0 (control)

*Note: The diagram illustrates the relationship between methylheptenone and citral concentrations and their freshness score.*
Methylheptenone is considered to improve and maintain a feeling of freshness, combined with citral.

Freshness-improving effect of methylheptenone

Freshness score

※Analyze software: Optimus
(Response surface method)
Analyze method: RBF
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Key flavor component “citral”

Citral is instable in beverages and converts into off-flavors

Cyclization in acid condition (pH of RTD: 3.0~3.5)

Oxidation etc.

Geranial + Neral

Citral

Off-flavor

- p-Cymene (gasoline-like)
- p-Methylacetophenone (bitter-almond-like)
- p-Cresol (phenolic)
Key flavor component “citral”

Citral is unstable in beverages and converts into off-flavors

Cyclization in acid condition (pH of RTD: 3.0~3.5)

Antioxidants

Oxidation etc.

Off-flavor

- p-Cymene (gasoline-like)
- p-Methylacetophenone (bitter-almond-like)
- p-Cresol (phenolic)
Some plant extracts were found to have a inhibitory effect on off-flavor generation

Rate of change : off-flavor generation without antioxidants = 100
We developed “Mogitate” by using new methods.

Mogitate

Strengthen freshness

Methylheptenone

Maintain freshness

Antioxidants
“Mogitate” maintains the fresh feeling even after storage.
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Summary

We pursued needs for RTD’s consumer, and found that is “fresher feeling of fruit juice.”

We developed new RTD by new methods of:

① Usage of flavor components to strengthen freshness
② Antioxidants usage to prevent citrus off-flavor formation

Fresh flavor (Citral etc.)

Before

Off-flavor

After

①

②
<table>
<thead>
<tr>
<th>Flavor component</th>
<th>Threshold (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citral</td>
<td>20</td>
</tr>
<tr>
<td>Methylheptenone</td>
<td>Less than 100</td>
</tr>
<tr>
<td>$p$-Cymene</td>
<td>130</td>
</tr>
<tr>
<td>$p$-Methylacetophenone</td>
<td>22</td>
</tr>
<tr>
<td>$p$-Cresol</td>
<td>20</td>
</tr>
</tbody>
</table>
## Polyphenol materials

<table>
<thead>
<tr>
<th>Extracts</th>
<th>Primary Ingredient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilberry</td>
<td>Procyanidin</td>
</tr>
<tr>
<td>Sweet tea</td>
<td>Ellagitannin</td>
</tr>
<tr>
<td>Olive fruits</td>
<td>Hydroxytyrosol</td>
</tr>
<tr>
<td></td>
<td>Verbascoside</td>
</tr>
<tr>
<td>Red wine mash</td>
<td>Procyanidin</td>
</tr>
<tr>
<td>Grapeseeds</td>
<td>Procyanidin</td>
</tr>
<tr>
<td></td>
<td>CATA</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Training</td>
<td>unnecessary</td>
</tr>
<tr>
<td>Intensity</td>
<td>no measure</td>
</tr>
<tr>
<td>Number of panels</td>
<td>More than 40</td>
</tr>
</tbody>
</table>
SBSE (Stir Bar Sorptive Extraction)

<table>
<thead>
<tr>
<th>Pre-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>* Sample 1.0g + 10ppm internal standard (linalool-d5) 200μl → × 50 dilution</td>
</tr>
<tr>
<td>* Adsorption reaction with (40 °C 2hour)</td>
</tr>
</tbody>
</table>

**GC-MS**

*Programmed Temperature Vaporizing Injection Port* (CIS4, Gerstel社製)

*Thermal Desorption Unit (TDU, Gerstel)*

*GC System (7890B, Agilent Technologies)*

*Mass Selective Detector (5977, Agilent Technologies社製)*

**condition of injection**

*TDU*: 20 °C (1 min) - (720 °C / min) - 250 °C (3 min)

*CIS*: -50 °C (1.5 min) - (12°C / sec) – 240 °C (45 min)

**condition of column**

*LTM column* (1st: DB-WAX, 20 m × 0.18 mm; 0.3 μm, 2nd: DB-5, 10 m × 0.18 mm; 0.4 μm, Agilent Technologies)

*1st temperature*: 40 °C (3 min) - (5 °C / min) – 180 °C (0 min)

*2nd column temperature*: 40 °C (31 min) - (5 °C / min) – 180 °C (0 min)
Response Surface Methodology (RSM) :
modeling and analysis of programs in which a response of interest is
influenced by several variables and the objective is to optimize this
response.
Material

lemon-based RTD (prototype, commercial products) A~G

-ranking evaluation of Fresh feeling-

Evaluation item: fresh feeling of lemon juice
n=8

The most fresh Prototype
Flow of alcohol categories share

RTD market is growing because of inflow from beers, distilled spirits, wine and wiskey.

Source: Intage SCI
Previous period: 2015/1-12
Current period: 2016/1-12

Based on monetary amounts