Difference in Aroma Compounds and Quality Variation in Milled Rice from 1996 to 2001

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Abstract: Changes in old rice smell of milled rice were examined with focus on the percentage composition of carbonyl and sulfur compounds. Such study has not yet been published. The rice samples (Oryza sativa L. var. japonica co. Nihonbare) were produced in Shiga Prefecture, Japan, and harvested from 1996 to 2001. The analysis focused on six carbonyl compounds, 1-propanal (1), 1-butanal (2), ethyl methyl ketone (3), 1-pentanal (4), 1-hexanal (5) and 1-heptanal (6), all of which are recognized as a contributing factor to old rice smell, and eight sulfur compounds. Aroma distinction analysis by the Aromalizer revealed a clear relationship between the age of the rice and old rice smell. We found a clear relationship between changes in the properties of cooked rice and the harvest year from the evaluation of cooked rice samples by aroma analysts.

Key words: old rice smell, chemical component, sensory evaluation, carbonyl compound, sulfur compound

1 Introduction

Recently, many of commercial rice products have been developed in response to the various market needs in Japan. In general, after husking, rice is stored as brown rice (1, 2). It is then milled immediately before consumption (3, 4). Old rice of inferior quality is characterized by a strong bran smell that is caused by the oxidation of fats in bran due to long-term storage (5-7). The aroma compounds in old rice have been characterized by recently developed analytical methods (8-12). Approximately 150 to 170 aroma compounds in cooked rice or aromatic rice have been identified. Intensive studies have been carried out and many patent applications have been made. However, as far as we know there are no reports on the factors contributing to the changes in old rice smell, such as the year of harvest and the changes in the percentage composition of sulfur compounds. Therefore, we milled brown rice of Nihonbare (the standard rice variety in Japan) harvested in Shiga Prefecture from 1996 to 2001 at the milling yield of 90% (equivalent to milled rice available on the market), investigated the changes in the percentage composition of carbonyl compounds and sulfur compounds (13-15), which are considered to be the factors contributing to old rice smell, and clarified the relationship between the deterioration of rice quality and these compounds. Based on the data obtained and through the sensory evaluation of harvested rice samples with the Aromalizer as new aroma distinction equipment, we report here in our new findings.

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2 Materials and Methods

2.1 Material
Rice (Oryza sativa L. var. japonica co. Nihonbare) was harvested from 1996 to 2001 in Shiga Prefecture, Japan (supplied by Pearl Rice Shiga, Ltd.).

2.2 Preparation Method
Each brown rice sample (200 g) was milled at 90% milling yield by a test-milling machine (Satake MC-250). Each sample (1 g) was ground (Kett TQ-100) and placed in a vial with a septum, and the vial was sealed.

2.3 Analysis of Aroma Compounds (GC and GC-MS)
Each sample in a vial was heated at 60°C for 10 min in an aluminum block thermostatic bath, and the headspace gas was introduced into a fiber for SPME (solid-phase micro extraction)(16). Then, the aroma compounds were analyzed by GC method (Hewlett Packard 5890 Series II, column: DB-W AX, 60 m × 0.25 mm, 40°C (4 min hold) -4°C/min − 200°C, injector: 260°C, detector: 220°C) and GC coupled with mass spectrometry (GC-MS) (Hewlett Packard 5872 Series).

2.4 Analysis of Sulfur Compounds
Sulfur compounds were measured by GC (Hewlett Packard 5890 Series II, column: DB-1, 60 m × 0.25 mm, 40°C (4 min hold) -6°C/min − 260°C, injector: 260°C, detector: 220°C) equipped with an SCD (sulfur chemiluminescence detector).

2.5 Aroma Distinction Analysis
An Aromalizer (Bran-Luebbe 1800 model) was used for analyzing differences in the aroma of rice samples according to the year of harvest. Rice sample (2.0 g) ground by a Kett grain test grinder was placed in a 10 ml vial, and heated at 80°C for 10 min. The headspace gas (2500 µl) was extracted with an auto-sampler and then analyzed by the aromalizer, which consisted of 18 types of metal-oxide-semiconductor sensors, at room temperature (20 ± 3°C). Analysis was repeated five times for each rice sample.

2.6 Sensory Evaluation (3)
A milled rice sample (90% milling yield) from each harvest year was cooked. The aroma of the cooked rice was evaluated 1) immediately after cooking, 2) 20 min after cooking and 3) 60 min after cooking.

3 Results and Discussion
Rice Nihonbare harvested in Shiga Prefecture is recognized as the standard rice for tasting and sensory evaluation by the Japan Grain Inspection Association. The rice samples used in this study had been stored under the same conditions in the order of harvest year from 1996 to 2001. Focusing on the relationship between old rice smell and changes in the aroma components and the quality of the rice samples, the following are discussed.

3.1 Changes in Percentage Composition of Carbonyl Compounds
To evaluate check the deterioration of rice quality (3, 4), we measured the changes in the percentage composition of carbonyl compounds as they are known to be a contributing factor to the aroma of old rice. In this study, 30 compounds including carbonyl compounds were examined for the changes in the rice samples. Figure 1 shows GC charts of the aroma compounds of the rice samples harvested in 1996 and 2001, for which the largest differences were found. Table 1 lists the percentage composition of carbonyl compounds in the rice samples. The aroma components contributing to old rice smell, namely, 1-propanal (1) (GC figure ; R.T. after cooking and 3) 60 min after cooking.

![Figure 1](image-url)
Difference in Aroma Compounds and Quality Variation

<table>
<thead>
<tr>
<th>Year</th>
<th>Compound (Peak No.)</th>
<th>Percentage Composition (%)</th>
<th>Carboxyl Compounds in Total</th>
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<tr>
<td>1996</td>
<td>(1) 1-Propanal (2) 1-Butanal (3) Ethyl methyl ketone (4) 1-Pentanal (5) 1-Hexanal (6) Heptanal</td>
<td>0.60±0.09 (3.68±0.91) 0.50±0.07 (3.06±0.71) 0.80±0.10 (4.90±0.61) 2.51±0.21 (15.38±0.92) 11.53±0.36 (70.65±1.06) 0.38±0.06 (2.33±0.22)</td>
<td>16.32±0.15</td>
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<td>1997</td>
<td>0.58±0.11 (2.52±0.82) 0.60±0.09 (2.61±0.41) 0.92±0.16 (4.00±0.38) 3.24±0.76 (14.08±1.33) 17.27±2.08 (75.05±4.39) 0.40±0.09 (1.74±0.44)</td>
<td>23.01±0.55</td>
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<td>1998</td>
<td>0.47±0.11 (2.97±0.96) 0.46±0.08 (2.90±0.75) 0.69±0.12 (4.36±1.01) 2.19±0.76 (13.83±2.01) 11.64±2.01 (73.48±3.26) 0.39±0.04 (2.46±0.94)</td>
<td>15.84±0.52</td>
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<tr>
<td>1999</td>
<td>0.58±0.22 (4.05±1.01) 0.50±0.19 (3.49±0.92) 0.82±0.31 (5.72±1.16) 1.87±0.81 (13.04±2.26) 10.10±1.21 (70.43±3.06) 0.47±0.11 (3.27±0.84)</td>
<td>14.34±0.48</td>
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<tr>
<td>2000</td>
<td>0.30±0.09 (2.64±0.89) 0.24±0.06 (2.11±0.82) 0.30±0.06 (2.64±0.74) 1.11±0.27 (9.76±1.08) 9.11±1.81 (80.12±2.91) 0.31±0.09 (2.73±1.01)</td>
<td>11.37±0.40</td>
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<tr>
<td>2001</td>
<td>0.16±0.08 (1.22±0.26) 0.10±0.05 (0.76±0.21) 0.32±0.10 (2.44±0.98) 0.46±0.14 (3.51±1.04) 11.73±1.26 (89.47±5.61) 0.34±0.07 (2.60±0.92)</td>
<td>13.11±0.28</td>
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Fig. 1 Percentage Composition of Carbonyl Compounds.

Table 1 Percentage Composition of Carbonyl Compounds.

1) Percentage Composition (%) (The average value of three replicates).
2) Figures in parentheses are the percentages.

The rice sample harvested in 2001 had the lowest percentage composition of carbonyl compounds, whereas the samples harvested before 1999 had markedly high percentage composition. Five carbonyl compounds other than the above-mentioned compounds were also analyzed. The compounds detected in the milled rice samples from the early harvest years were 2-pentyl furan (R.T. 28.192 min), comprising 11.7 to 12.9% of the rice samples harvested from 1996 and 1997; and 1-pentanol (R.T. 32.474 min), comprising 15.6 to 15.7% of the samples harvested from years 1997 to 1998. It was also found that for 1-hexanol (R.T. 34.037 min), the earlier the harvest year, the higher its percentage composition (approximately 3.3%). 1-octanol (R.T. 45.733 min) and hexanoic acid (R.T. 51.088 min) were present only in trace levels (trace: 0.53% or less) in the recently harvested rice sample. These compounds contribute to old rice smell. Therefore, the compositions of the carbonyl compounds fol-
low the composition system described in empirical reports (2, 6) in relation to the deterioration of fat and protein contents in rice during storage.

3.2 Change in Percentage Composition of Sulfur Compounds (13, 15)

The relationship between the percentage composition sulfur compounds and old rice smell was examined. The GC chart of the sulfur compounds in the 2001 sample is shown in Fig. 3, and the structures of the sulfur compounds are shown in Fig. 4. Table 2 compares the percentage composition of sulfur compounds (7) to (20) in the rice samples by harvest year. That hydrogen sulfide (7) (5.01 ± 0.45 to 9.44 ± 0.62%), methanethiol (8) (5.17 ± 0.36 to 27.05 ± 0.72%), (10) (1.93 ± 0.20 to 5.70 ± 0.51%) and (20) (2.13 ± 0.09 to 11.91 ± 1.16%). Thus, these sulfur compounds contribute to the aroma of old rice. In contrast, in the more recent harvest years, higher percentages of dimethyl disulfide (14) and 3-thiophenaldehyde (16) were detected. The rice sample harvested in 2001 contained (14) at 47.10% ± 1.96% and (16) at 26.99% ± 2.21%. Compared to those in the earlier harvest years, the percentage composition of these two compounds was much lower. Thus, it is probable that these sulfur compounds contribute to the aroma of fresh rice.

3.3 Aroma Distinction Analysis

The results of sensory evaluation may vary depending on individual differences. Thus, the aromalizer was used for objective and accurate measurement and the results are shown in Fig. 5. Rice aroma on the horizontal axis is plotted against the hardness of rice kernel by

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<tbody>
<tr>
<td>1996</td>
<td>9.44±0.62</td>
<td>27.05±0.72</td>
<td>3.43±0.71</td>
<td>5.70±0.51</td>
<td>1.09±0.21</td>
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<td>5.38±0.92</td>
<td>1.03±0.26</td>
<td>0.99±0.04</td>
<td>1.06±0.26</td>
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<tr>
<td>1997</td>
<td>13.44±0.48</td>
<td>20.43±0.49</td>
<td>3.10±0.52</td>
<td>3.75±0.34</td>
<td>1.18±0.17</td>
<td>5.57±0.62</td>
<td>2.67±0.11</td>
<td>16.09±1.02</td>
<td>3.69±0.26</td>
<td>4.39±0.76</td>
<td>1.40±0.11</td>
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<td>11.23±1.32</td>
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<tr>
<td>1998</td>
<td>15.00±1.21</td>
<td>22.07±1.01</td>
<td>5.95±0.34</td>
<td>3.83±0.46</td>
<td>1.23±0.20</td>
<td>9.40±1.01</td>
<td>15.30±0.92</td>
<td>10.62±1.16</td>
<td>3.31±0.21</td>
<td>1.16±0.08</td>
<td>0.98±0.11</td>
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<td>5.04±0.76</td>
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<td>1999</td>
<td>7.88±0.68</td>
<td>5.19±0.28</td>
<td>3.11±0.41</td>
<td>2.07±0.21</td>
<td>0.79±0.09</td>
<td>4.93±0.61</td>
<td>40.89±1.46</td>
<td>3.21±0.74</td>
<td>19.38±1.06</td>
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<td>—</td>
<td>—</td>
<td>3.65±0.49</td>
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<tr>
<td>2000</td>
<td>5.59±0.76</td>
<td>12.46±0.82</td>
<td>2.52±0.32</td>
<td>2.58±0.29</td>
<td>0.57±0.04</td>
<td>3.48±0.34</td>
<td>0.81±0.08</td>
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<td>17.56±1.15</td>
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<tr>
<td>2001</td>
<td>5.01±0.45</td>
<td>5.17±0.36</td>
<td>6.94±0.47</td>
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<td>2.37±0.21</td>
<td>47.10±1.96</td>
<td>0.46±0.07</td>
<td>26.99±2.21</td>
<td>0.29±0.04</td>
<td>—</td>
<td>—</td>
<td>2.13±0.09</td>
<td>1.26±0.06</td>
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</tr>
</tbody>
</table>

1) Percentage Composition (%).  2) Trace.
variety on the vertical axis. The data derived from the early harvest years tended to localize at the right side, whereas those from the more recent years, at the left side. All the rice samples were of Nihonbare variety and thus the hardness of rice kernel by variety did not appear to differ. The discrepancy in rice aroma in the data obtained in 1996 and 1997 is probably due to the fact that the storage conditions of the 1997 sample were poor in terms of temperature and humidity.

### 3.4 Sensory Evaluation

Figure 6 summarizes the aroma of each rice sample as evaluated by aroma analysts immediately, 20 min and 60 min after cooking. At all the time points after cooking, all the rice samples harvested four or more years earlier were evaluated as having a strong old rice smell. Regardless of the time point, the rice samples harvested in 2000 and 2001 received positive evaluations for preference and freshness. Sweetness or fruitiness of the rice samples was generally preserved up to the two years after harvest, and was lowered, with increasing number of harvest years. The grassy aroma of the rice samples harvested after 1999 and evaluated immediately after cooking was weak, whereas the rice samples examined 20 min and 60 min after cooking had a strong grassy aroma.

### 4 Conclusion

Old rice smell in the same variety of rice harvested in different years was investigated, and the following were clarified. As regards carbonyl compounds (1), (2), (3) and (4), which are known to be a contributing factor to old rice smell, the percentage composition was found to increase as the harvest year became earlier (1996 in comparison with 2001). The percentage composition in the earlier harvest years two-to four fold that of 2001. On the other hand, one new finding of this research is that the percentage composition of sulfur compounds (7), (8) and (20) was low and that of compounds (14) and (16) was high in the newly harvested rice (2001). Moreover, in the evaluation of old rice smell by the Aromalizer as new aroma distinction equipment, the sensors to be used were pre-tested on each compound that is considered to be a contributing factor to old rice smell, and the most suitable combination of sensors was determined. As a result, the conditions for the accurate determination of the age (harvest year) of milled rice

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were found, as expected. It was confirmed that tour results agree with those obtained by the sensory evaluation of cooked rice by aroma analysts.

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References