Note

Differences in Aromatic Components of Ten Brands of Rice according to Annual Production

Kouichi Masumoto¹, Akiko Fujita², Kouji Kawakami², Takashi Mikami² and Masato Nomura¹*

¹Department of Biotechnology and Chemistry, School of Engineering, Kinki University, Umenobe, Takayama, Higashihiroshima, Hiroshima 739-2116, Japan
²Taste Research Laboratory, Products Development Engineering Division, Satake Corporation, Saijo-Nishihonmachi, Higashihiroshima, Hiroshima 739-8602, Japan

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The production of the high quality rice called brand rice is the increasing year by year with about one hundred thirty five kinds is known by the name of the place it is produced. We analyzed using GC and GC-MS the volatile components of ten kinds of rice harvested from 2000 to 2002 years. The results indicated that six kinds of carbonyl compounds; Propanal, 1-Butanal, Methyl Ethyl Ketone, 1-Pentanal, 1-Hexanal, and 1-Heptanal, were one causes of the old rice smell. Moreover, Methyl Ethyl Ketone and 1-Pentanal and Propanal were deeply involved in this smell, while 1-Butanal and 1-Heptanal were involved in a fresh rice smell. Furthermore, as for the quality of aroma and the change in strength, it was measured objectively using an Aromalizer (TM). That result, old rice-ization proceeded to have said since before, it was found that the aroma was strongly indicated to be the result of the quality analysis of the rice by the sensor.

Keywords: aromatic components of rice, carbonyl compound, aromalizer

Introduction

Rice is one of the three major grains in the world, the other two being wheat and corn, and is highly sustaining in Japan. However, due to recent changes in dietary habits among the Japanese, the demand for rice has tended to decrease. Under the circumstances, the development of new processed products and research and development in the efficient use of excess produced rice, such as use of rice flour instead of wheat flour in bread, are being actively conducted. Also, in response the new Agricultural Produce Inspection Law that went into effect beginning April 1, 2001 and allows private institutions to make inspections that were formerly done by the government authorities concerned, each manufacturer in the industry can modify existing inspection procedures for quality of rice and other grains and research and develop new equipment. Under this present trend, however, consumers still want varieties of rice with good taste. Various modifications and research have taken place over a long period, and, especially, there are many reports and theses on differences in aromatic components of rice or the qualities of new rice and old rice (Bechtel, et al., 2004; Champagne, et al., 2001; Jezussek, et al., 2002). Moreover, some previous research focused on the difference in aromatic components of rice and changes in quality in different harvest years, resulting in very interesting findings.

In this research, as connected to former studies, chemical components in ten easily obtainable varieties of rice after harvesting according to year of harvest (from 2000 to 2002) were investigated by gas chromatography (GC) and GC-MS analyses using the solid phase micro extraction (SPME) method and the relationship between change in composition rate of six kinds of carbonyl compounds (propanal, 1-butanal, methyl ethyl ketone, 1-pentanal, 1-hexanal, and 1-heptanal), which were expected to be the cause of the old rice odor, and the actual old rice odor was observed. The ten varieties of rice were: Miyagi-Sasanishiki, Okayama-Asahi, Miyagi-Hitomebore, Niigata-Koshihikari, Hokkaido-Kirara 397, Shiga-Nihonbare, Hiroshima-Hinohikari, Shiga-Kinuhikari, Aomori-Mutsuhomare and Akita-Akitakomachi. Also, in the previous report (Fujita, et al., submitted for publication), the Aromalizer, which was invented to make an objective judgment in odor distinction analysis, was employed as a new method of evaluating odor quality and level rather than a human olfactory evaluation. A relationship between deterioration of rice and aromatic components was demonstrated.

Materials and Methods

Sample materials The ten brands of sample rice (Miyagi-Sasanishiki, Okayama-Asahi, Miyagi-Hitomebore, Hiroshima-Hinohikari, Shiga-Kinuhikari, Shiga-Nihonbare, Hokkaido-Kirara 397, Niigata-Koshihikari, Aomori-Mutsuhomare, Akita-Akitakomachi) harvested in years 2000, 2001 and 2002 were obtained from the Shiga Pearl Rice Plant.

*To whom correspondence should be addressed.
E-mail: nomura@hiro.kindai.ac.jp
Preparation methods Two hundred gram samples of brown rice for each brand were milled at 90% milling yield by the Satake rice test milling machine (Satake Corporation, Model MC-250) and 1 g of each sample was ground (by Kett, Model TQ-100). Then, each sample was placed in a vial with a septum and sealed.

Aromatic component analysis (GC, GC-MS Method) After the prepared samples were heated at 60°C/10 min in an aluminum block thermostatic bath (Iwaki, Model MG-2000) and headspace gas was adsorbed into a fiber by the SPME (solid-phase micro extraction) method, the GC method (Hewlett Packard, 5890 Series II, column: DB-WAX, 60 m and 0.25 mm, 35°C [4 minute hold] to 220°C [4°C/min], injection: 260°C, detector: 220°C) and the GC-MS method (Hewlett Packard, 5872 Series, column: DB-WAX, 60 m and 0.25 mm, 35°C [4 minute hold] to 220°C [4°C/min], injection: 260°C, detector: 220°C) were applied.

Odor distinction determination The Aromalizer (PrimeTech, α-FOX4000) was employed as analysis equipment to identify odors of the ten brands according to harvest year. Two grams of the rice sample that was ground in advance (by Kett, Grinder for Grain Inspection) was placed in a 10 ml vial and heated at 80°C for 10 minutes. Then, injecting volatile components (2500 μl) extracted from the auto-sampler to the rice sample, odor distinction analysis was conducted by the Aromalizer (TM). The detection principle is based on a change in the electrical resistance or frequency of each individual sensor. Then, this time combined by 18 varieties of metal-oxide-semiconductor sensors (made of tin oxide) in a determination temperature of 20 ± 3°C.

Results and Discussion

Analysis of aromatic components There are a number of reports on the analysis of aromatic components of rice (Fujimaki, et al., 1977; Fujimaki, et al., 1978; Habu, et al., 1978; Hayashi, et al., 1979; Kato, et al., 1980; Kato, et al., 1983). However, all focus on a single harvest year based on evaluation of aromatic components concerning rice cooking as cooked rice aroma and old rice odor. Therefore, this research investigated the difference in aromatic components of the rice in three harvest years (from 2000 to 2002) among ten different brands of rice harvested in different places. Firstly, the gas chromatogram of the aromatic component analysis on Shiga Nihonbare, Japanese standard rice, harvested in 2000 and 2001 is shown in Fig. 1. While the rice harvested in 2000 contained compounds (3) (11.19%), (16) (5.92%) and (19) (10.05%) as major components, the proportion of these three components in rice harvested in 2001 remarkably decreased, being (3) (4.95%), (16) (1.35%) and (19) (1.77%). Also, compounds (2) and (7), which were expected to be responsible for the old rice odor, decreased in proportion (1.37% ~ 0.46%) and (1.11% ~ 0.46%), respectively. However, the following four compounds increased as the rice aged: compounds (8) (1.62% ~ 3.60%), (9) (0.35% ~ 1.77%), (11) (9.11% ~ 11.73%) and (21) (0.98 ~ 3.14%). Therefore, it can be considered that compounds
Fig. 2. The formation ratio of six carbonyl compounds in 10 brand rice.
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(2), (5), (11), (16) and (19) are old rice odor components and that compounds (8), (9) and (15) are aromatic components of new rice. These findings were also investigated by differences in the composition ratio of compounds that were expected to be old rice odor components of the other 9 brands as shown in Fig. 2. In addition, it was clearly confirmed, as to characteristics of these old rice odor components, that the proportions of the formation of propanal and methyl ethyl ketone in any rice variety increased as the rice aged and that there was abundant formation of 1-butanal and 1-heptanal in new rice.

**Odor distinction determination**

It is said that the sense of taste will be paralyzed if aroma is blocked because aroma is an important factor in the taste of food. The results of sensory evaluation by the human nose differ by individual, and physical and psychological conditions of the detectors greatly influence the results. Analysis of aroma is very difficult because aroma emanates from very small amounts of volatile compounds. A major fatty acid of rice is linoleic acid and oleic acid. This acid is easily oxidized by lipoxygenase and forms various aldehydes, which are responsible for old rice odor. Moreover, brown rice contains more linoleic acid than milled rice (100 – 98% milling yield).

In this research, in order to confirm the difference in odors of milled rice and old rice, the odor quality and level of ten brands of milled and brown rice by harvest year were analyzed by the Aromalizer(TM). This new equipment was expected to make a more objective judgment than the human nose. Also, regarding each aldehyde that was considered to be a component of old rice odor, metal-oxide-semiconductor sensors were selected followed by a pilot distinction experiment of concentration dependency with the Aromalizer(TM). The results are shown in Fig. 3 and Fig. 4. Old rice odor levels are on the horizontal axis and levels by rice variety are on the vertical axis. For the harvest years examined, 2002, 2001, and 2000, the plot of the old rice odor level of milled rice shifted to the right as the rice aged. It was also demonstrated in the same way for brown rice. In addition, although some difference is observed by the Aromalizer(TM) for brown rice, the brands strong in old rice odor level and levels by variety were indicated as weak and those weak in old rice odor level and levels by variety were shown as strong. In relation to the point that the brands of brown rice with weak odor were displayed as strong in odor of milled rice, negative correlation is perceived between the strength of aroma and linoleic acid content in brown rice, according to Shida, et al 1979. Therefore, weak odor is believed to occur in brown rice because of there being much more linoleic acid in the bran layer and that strong odor arises in milled rice due to removal of the bran layer in the whitening process. Also, concerning the point that the brands of brown rice with strong odor were indicated as weak in the odor of milled rice, because brown rice contains more amino acid than milled rice, it is logical that the amount of aldehyde in brown rice, which is one of the aromatic components formed by strecker decomposition of amino acid, will be greater than that of milled rice. Therefore, this is presumed to be the cause of the strong odor in brands of brown rice that were indicated as having a weak odor of milled rice.

**Summary**

Through the investigation of aromatic components of new and old rice in terms of six kinds of carbonyl compounds, we found that methyl ethyl ketone, 1-pentanal and the trace component, propanal, were largely responsible for the old rice odor and that 1-butanal and 1-heptanal contributed to the odor of new rice. Also, as a result of the analysis of ten varieties of brown and milled rice by harvest year with the application of the new evaluation equipment, the Aromalizer(TM) it was confirmed that odor of both milled and brown rice become stronger as rice ages.

---Sign explanation---
- Siga Nihonbare (NI)
- Miyagi Hitomebore (HT)
- Kirara397 (KR)
- Niigata Koshihikari (KO)
- Mutsuhomare (MU)
- Siga Kinuhikari (KN)
- Hiroshima Hinohikari (HN)
- Miyagi Sasanishiki (SA)
- Okayama Asahi (AS)
- Akitakomachi (AK)

2000 Year
2001 Year
2002 Year

Fig. 3. A result of an analysis in 2000–2002 milled rice by Aromalizer.
---Sign explanation---
Siga Nihonbare (NI)
Miyagi Hitomebore (HT)
Kirara397 (KR)
Niigata Koshihikari (KO)
Mutsuhomare (MU)
Siga Kinuhikari (KN)
Hiroshima Hinohikari (HN)
Miyagi Sasanishiki (SA)
Okayama Asahi (AS)
Akitakomachi (AK)

000 Year
001 Year
002 Year

Fig. 4. A result of an analysis in 2000-2002 brown rice by Aromalizer.

References