Studies on Cereals

Part V Stale Flavor of Stored Rice*

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When stored rice (40°C, two months) was cooked, the stale flavor (komai-shu) was clearly detected by sensory test. Direct gas chromatographic analysis of head space vapors over cooked rice showed three main peaks which corresponded to propionaldehyde or acetone, n-valeraldehyde and n-caproaldehyde. On the other hand, the content of linoleic and linolenic acids of the rice decreased during storage at 40°C. This means that the unsaturated fatty acids autoxidized during storage and gave rise to carbonyl compounds responsible for the stale flavor of cooked rice.

INTRODUCTION

When rice is stored at room temperature, many palatability factors are deteriorated gradually, so that most Japanese are not fond of cooked products of stored rice. The deteriorative changes on storage appear first in rheological properties of cooked rice and then in the characteristic stale flavor.1) Therefore, both the rheological change and stale flavor are responsible for the unacceptability of stored rice. Although several reports have been published on the deterioration of rheological qualities of rice, no work has been done on the off-flavor of stored rice.

On the other hand, recent development of highly sensitive detector system in the gas chromatography has made it possible to analyse volatile compounds of foods. For instance, off-flavor of peas,2) potato-granules3,4) and potato chips5) have been studied in detail. In the previous paper,6) we reported five carbonyl compounds existing in the vapor of cooked rice. The present investigation was undertaken to determine the quantitative and qualitative effects of storage temperature on the flavor of cooked rice by using gas chromatography. Because it is generally accepted that the rice keeps its flavor unchanged during storage at low temperature,1) this study will provide the differences in flavor between fresh rice and stored rice and also present the information to clarify the mechanism of the development of the stale flavor.

EXPERIMENTAL

Materials

Rice. Commercial milled rice was packed in polyethylene bags and separately stored at 5°C and 40°C for two months. n-Hexane, benzene, chloroform and methanol were purified by the methods of Schwartz et al.7,8) Acidic hydrosxylamine solution

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* This report was presented at the Meeting of Kansai Division of the Agricultural Chemical Society of Japan, Kyoto, Sept. 18, 1965.
2) B. Bengtsson and I. Bosund, Food Tech., 18, 773 (1964).
6) K. Yasumatsu, S. Moritaka and S. Wada, This Journal, 30, 470 (1965).
was prepared by the method of Bassette et al.  

**Methods**  

a) Direct gas chromatography of cooked rice.  
One hundred gram of rice and 120 ml of distilled water were put into a 300 ml flask fitted with a 30 cm Liebig condenser. After the flask had been heated in boiling water for 20 min, the condenser was taken off and the flask was immediately closed with a rubber bung lapped with aluminum-foil. Vapor sample was taken up by inserting a hypodermic syringe through a rubber bung into the head space gas above the cooked rice. Ten ml of head space gas was injected into the gas chromatography apparatus, Yanagimoto Co. Model GCG-3DH, equipped with a hydrogen-flame ionization detector (Yanagimoto Co., Instrument Model GCF-103). The operating condition was as follows:  
- **Column.** 4 mm × 2 m stainless-steel column packed with 80~100 mesh Celite 545 containing 30% dioctyl phthalate.  
- **Column temperature.** 100°C.  
- **Flow rate of helium.** 60 ml/min.  

b) Collection and gas chromatography of volatile carbonyl compounds of cooked rice.  
The apparatus used for the collection of volatile carbonyl compounds of cooked rice is shown in Fig. 1.  

**Fig. 1.** Apparatus Used to Collect Volatile Carbonyl Compounds during Cooking of Rice  

One hundred gram of rice and 800 ml of distilled water were put into a 11 round-bottom flask, to which an adapter with gas inlet and a 30 cm Liebig condenser was fitted. Nitrogen (carbonyl compounds free) was injected into the flask at the flow rate of 100 ml/min, while the flask was kept in boiling water. The vapor evolved during the cooking for two hours was passed through two traps, each of which contained 40 ml of a 2,4-dinitrophenylhydrazine solution (2 g/2N-HCl, 1 l). After two hours of bubbling, the cooked rice was discarded and replaced with a fresh rice and distilled water. At the end of the run, 2,4-dinitrophenylhydrazine in the traps was extracted three times with 50 ml of purified chloroform, then the chloroform was evaporated off. The contaminated 2,4-dinitrophenylhydrazine was eliminated by the method of Schwartz et al.  

The total amount of volatile carbonyl compounds was estimated by measuring the absorbance of the solution against hexane at 340 μm and converting the reading to μmoles, using $E=22,500$.  

The gas chromatography of the 2,4-dinitrophenylhydrazine was carried out as reported previously.  

c) Methods for analysis of lipid. Two hundred grams of rice, powdered to pass through a 50 mesh sieve, was extracted with a chloroform-methanol mixture (2 : 1) for eight hours at room temperature. The method of gas chromatography of fatty acids was reported previously.  

d) Sensory text. The flavors of cooked rice were tested according to Yoshikawa’s methods. The rice stored at 5°C for two months was served as reference sample.  

**RESULTS**  

**Sensory Test**  
The flavor deterioration of the rice stored at 40°C is shown as the mean scores of sensory test in Table I, which revealed the remarkable deterioration of flavor in the rice stored at 40°C for two months.  

**Direct Gas Chromatography of Cooked Rice**  
Fig. 2 shows the gas chromatogram of the head space gas of cooked rice. It indicates that three peaks were greater in the rice stored at 40°C than in the rice stored at 5°C.  

Fig. 3 shows that these three peaks were almost eliminated when rice was cooked with 0.1% acidic hydroxylamine solution, which was prepared by the method of Bassette et al.  

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TABLE I. SENSORY ANALYSIS OF COOKED RICE STORED AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Storage temperature</th>
<th>Appearance</th>
<th>Aroma</th>
<th>Taste</th>
<th>Cohesiveness</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>3°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40°C</td>
<td>-1.125***</td>
<td>-0.667*</td>
<td>-0.625***</td>
<td>-0.917***</td>
<td>-0.792***</td>
</tr>
</tbody>
</table>

*** Significant at 0.1% level
* Significant at 5% level

means they were carbonyl compounds. On the basis of their retention times reported previously, it seems reasonable to assume that they were propionaldehyde (or acetone), n-valeraldehyde and n-caproaldehyde.

These three carbonyl compounds seemed to be responsible for the stale flavor of cooked rice, because the stale flavor of cooked rice was not detected by sensory test when the stored rice was cooked with an acidic hydroxylamine solution.

Difference in the Volatile Carbonyl Compounds According to Storage Temperature of Rice

Table II shows the difference in the content of total volatile carbonyl compounds between the rice stored at 40°C and that stored at 5°C.

TABLE II. COMPOSITION OF VOLATILE CARBONYL COMPOUNDS

<table>
<thead>
<tr>
<th>Storage temperature of rice</th>
<th>% Composition of volatile carb. comp.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>5°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>30.8</td>
</tr>
<tr>
<td>Propionaldehyde or acetone</td>
<td>31.0</td>
</tr>
<tr>
<td>Carbonyl compounds</td>
<td></td>
</tr>
<tr>
<td>Methylethylketone</td>
<td>11.0</td>
</tr>
<tr>
<td>n-Valeraldehyde</td>
<td>trace</td>
</tr>
<tr>
<td>n-Caproaldehyde</td>
<td>7.2</td>
</tr>
<tr>
<td>Total volatile carbonyl comp. (μM)</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>3.7</td>
</tr>
</tbody>
</table>

* Calculated from the peak heights in gas chromatogram.

Total amounts of volatile carbonyl compounds developed from the rice stored at 40°C were larger by about two times than those of the rice stored at 5°C. Table II also shows the composition of volatile carbonyl compounds. They were tentatively represented as μmoles in order to see easily the difference according to storage temperatures. The data in Table II, however, was calculated without considering the rate of regeneration of each carbonyl compound from the exchange reaction of 2,4-dinitrophenylhydrazine and the difference of response of each carbonyl compound to
hydrogen flame ionization detector.

Table II clearly indicates that the contents of propionaldehyde (or acetone), \( n \)-valeraldehyde and \( n \)-caproaldehyde in the volatiles were higher in the rice stored at 40°C than in the rice stored at 5°C.

**Difference of Lipid Composition with Storage Temperatures**

Table III shows that the total amount of lipid in the rice decreased during the storage for two months at 40°C. Moreover, Table III indicates that the decrease in unsaturated fatty acids, especially linoleic and linolenic acids were remarkable.

**Table III. Lipid Composition of Stored Rice**

<table>
<thead>
<tr>
<th>Storage temperatures</th>
<th>% Composition of total lipid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5°C</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>0.6</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>17.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.6</td>
</tr>
<tr>
<td>Fatty acids</td>
<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>30.4</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>47.1</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>4.3</td>
</tr>
<tr>
<td>Total lipid (mg.% of rice)</td>
<td>390</td>
</tr>
</tbody>
</table>

**DISCUSSION**

Table III indicated that the relative amount of linoleic and linolenic acids decreased and that of oleic acid increased during the storage of rice at 40°C for two months. Kawahara et al.\(^{13}\) reported that, the linolenate oxidized 1.5 to 2 times faster than the linoleate, and 16 to 25 times faster than the oleate. Therefore, it is conceivable that the linoleic and linolenic acids in the rice autoxidized more rapidly than the oleic acid and saturated fatty acids; thus the relative amount of linoleic and linolenic acids decreased during storage at 40°C.

As shown in Fig. 2, the rice stored at 40°C had three large peaks. If the rice was cooked with an acidic hydroxylamine solution, these three peaks were eliminated and the stale flavor of cooked rice was also vanished. Moreover, when the rice freshly harvested was cooked with \( n \)-caproaldehyde, most panelists reported that the cooked rice thus prepared has the flavor of stored rice. On the basis of these data, it seems reasonable to assume that the three peaks were those of carbonyl compounds which are mainly responsible for the stale flavor of cooked rice. Moreover, the retention times of carbonyl compounds reported previously also indicate these three peaks are those of propionaldehyde or acetone, \( n \)-valeraldehyde and \( n \)-caproaldehyde.

\( n \)-Caproaldehyde (hexanal) is now generally accepted as the main component of off-flavor of various foods, for example, potato granules, peas, potato chips, and it is supposed to be originated from antioxidative decomposition of linoleic acid. \( n \)-Valeraldehyde and propionaldehyde are also reported to be formed in the oxidation of linoleic and linolenic acids.\(^{14}\)

On the other hand, the contents of linoleic and linolenic acids decreased in the rice stored at 40°C in comparison with the rice stored at 5°C. Thus, it is reasonable to assume that the linoleic and linolenic acids in rice oxidize gradually during storage and give rise to the carbonyl compounds, which contribute to the stale flavor of cooked rice.

In this report, however, we have referred only to the carbonyl compounds in the vapor of cooked rice. Therefore, it is not clear whether the carbonyl compounds exist originally in raw rice or they are developed during cooking. Anyway, the relative quantitative differences in these carbonyl compounds may exert profound effects on the flavor of various cooked rice.

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