Stale Flavor of Stored Rice

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When rice is stored at room temperature, many palatability factors are gradually deteriorated so that most Japanese are not fond of cooked products of stored rice. The deteriorative changes during storage appear first in the characteristic stale flavor of cooked rice and then in the rheological properties.

Therefore, both the stale flavor and rheological change 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.

For this reason, the investigations on chemical components of stale flavor of stored rice and mechanism of their formation have been carried out in the last few years in Japan.

Major components of flavor in cooked rice

In many cases, the essences of flavor in food are very small in amount and consist of many composite components, and therefore their research has been thought to be comparatively difficult. However, the development of gas chromatograph played an important role in this research.

As to volatiles of cooked rice, Obata and Tanaka[1] first studied chemically, and discovered that the aqueous solutions of L-cysteine and L-cystine in the presence of riboflavin developed the typical flavor of cooked rice when exposed to sunlight, and inferred that the vapor contained hydrogen sulfide, ammonia, carbon dioxide and acetaldehyde.

Furthermore, they also identified hydrogen sulfide, ammonia and carbon dioxide in the vapor of cooked rice. On the other hand, Yasumatsu *et al.*[2] analyzed the volatile carbonyl compounds in cooked rice in detail. They caught volatile carbonyl compounds as 2.4-dinitrophenylhydrazones and employed the flash exchange gas chromatography. Five carbonyl compounds were found as shown in Fig. 1.

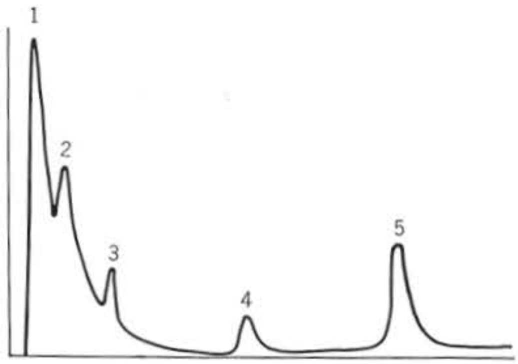

Fig. 1. Gas chromatogram of volatile carbonyl compounds from cooked rice.
30% DOP on Celite at 100°C, 2 m, Flow rate 60 ml/min.

From the retention times of their peaks, these carbonyl compounds were inferred as acetaldehyde, propionaldehyde (or acetone), methylethylketone, n-valeraldehyde (pentanal) and n-caproaldehyde (hexanal).

As it is mentioned above, the major

components of the flavor in cooked rice are thought not to be a single compound but to consist of many compounds such as sulfuric compounds, carbonyl compounds and ammonia.

Stale flavor of stored rice

Moreover, Yasumatsu *et al.*,[3] undertook the direct gas chromatographic analysis of head space vapor after cooking the stored rice, the stale flavor of which was clearly detected by sensory test, and compared with that of fresh rice. The gas chromatograms of the head space vapor of cooked rice are shown in Fig. 2.

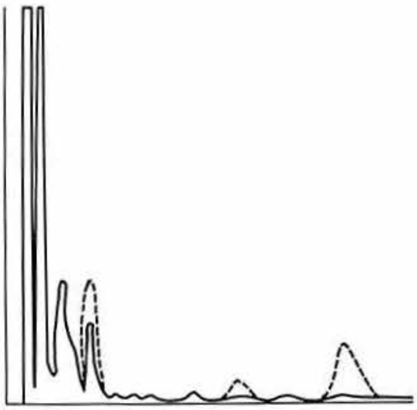

Fig. 2. Gas chromatogram of vapor sample of cooked rice.
DOP on Celite at 100°C, Flow rate 60 ml/min.
———— Vapor from fresh rice.
- - - - - - - Vapor from stored rice.

It indicates that three peaks were greater in stored rice than in fresh rice. These three peaks were almost eliminated when rice was cooked with 0.10% acidic hydroxylamine solution, which means they were carbonyl compounds.

In addition, these three carbonyl compounds seem to be responsible for the stale flavor of stored rice because it was not detected by the sensory test when stored rice was cooked with an acidic hydroxylamine solution. The difference of the content of total volatile carbonyl compounds between stored rice and fresh rice is shown in Table 1.

Total amounts of volatile carbonyl compounds developed from stored rice were two times as large as those of fresh rice. Table 1

Table 1. Composition of volatile carbonyl compounds

Carbonyl compound	% Composition of volatile carb. comp.*	
	Fresh rice	Stored rice
Acetaldehyde	50.8	25.1
Propionaldehyde or acetone	31.0	42.1
Methylethylketone	11.0	8.9
n-Valeraldehyde	trace	4.9
n-Caproaldehyde	7.2	19.0
Total volatile carbonyl comp. (μM)	1.7	3.7

* Calculated from the peak heights in gaschromatogram.

also shows the composition of volatile carbonyl compounds and indicates that the contents of propionaldehyde (or acetone), n-valeraldehyde and n-caproaldehyde in the volatiles were clearly higher in stored rice than in fresh rice, and especially n-valeraldehyde and n-caproaldehyde increased.

When the freshly harvested rice was cooked with these carbonyl compounds, as most panelists reported, the cooked rice had the flavor of stored rice. On the basis of these data, it seems reasonable to assume that carbonyl compounds are mainly responsible for the stale flavor of stored rice.

Endo *et al.*[4] also compared the flavor of stored rice (one or two years in ordinary warehouse) with that of fresh rice. Milled rice was cooked in an automatic electric rice cooker which is practically used by Japanese consumers and the direct gas chromatographic analysis of head space vapor of cooked rice was undertaken.

As the result, except carbonyl compounds which were reported by Yasumatsu *et al.*, isobutylaldehyde, n-butylaldehyde and iso-valeraldehyde were newly inferred in the vapor of cooked rice. Carbonyl compounds were generally higher in stored rice than in fresh rice,

Table 2. Change in lipid compositions of milled rice during storage

Variety	Description of sample	g/100 g of rice*		g/100 g of extraneous lipid			
		Extraneous lipid	Fat-by-hydrolysis	Phospho-lipid	Free fatty acid	Neutral fat	Unsaponifi-able matter
Koshiji-wase (Niigata)	fresh rice	0.35	0.53	1.5	30.6	49.9	5.7
	stored rice	0.34	0.54	0.4	51.9	30.8	6.0
Asahi (Okayama)	fresh rice	0.35	0.55	1.5	32.0	54.9	5.6
	stored rice	0.36	0.54	0.6	51.6	33.0	4.9

* moisture content: 13%

and n-caproaldehyde increased most remarkably and its increment was in proportion to the stored period.

On the other hand, free fatty acids increase clearly during storage of rice. Changes in lipid compositions of rice during storage are shown in Table 2.[5] Tatenuma and Sato[6] reported that free fatty acids existed in distilled solution when imported foreign rice was steamed. Foreign rice is mostly imported to Japan in the form of milled rice and stored for a fairly long time. Therefore, it is supposed to show the similar tendency in case of domestic stored rice.

In case of stored rice, much free fatty acids seem to dissolve into volatiles of cooked rice because contents of free fatty acids are higher in stored rice than in fresh rice as shown in Table 2. These fatty acids as well as carbonyl compounds are supposed to be some components of stale flavor of stored rice.

Mechanism of stale flavor formation

In regard to the formation of carbonyl compounds in cooked rice, two mechanisms are generally supposed as follows: One is the Strecker degradation of amino acids and other is the autoxidation of lipid.

In the Strecker degradation, amino acids change to aldehyde of one less carbon atom by heating with sugar.[7]

$$R-CH(NH_2)-COOH \longrightarrow R\cdot CHO + NH_3 + CO_2$$

And amino acids are thought to be precursor of carbonyl compounds in volatiles of cooked rice as shown in Table 3. However, amino acids proved to exist in rice are only alanine, cysteine and cystine as the precursor of acetaldehyde. Others are peculiar amino acids and

Table 3. Aldehydes produced by the Strecker degradation

Aldehydes in rice	Amino acids as precursor in the Strecker degradation
Acetaldehyde CH_3CHO	Alanine $CH_3\text{-}CH(NH_2)\text{-}COOH$
	Cysteine $HS\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$
	Cystine $S\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$ / $S\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$ (S–S linked)
Propionaldehyde $CH_3\text{-}CH_2\text{-}CHO$	α-Amino butyric acid $CH_3\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$
n-Valeraldehyde $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO$	Norleucine $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$
n-Caproaldehyde $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO$	α-Amino heptylic acid $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$

Table 4. Fatty acid compositions of husked rice and milled rice

Fatty acid component	% Composition of each fraction											
	Koshiji-wase						Asahi					
	Free fatty acid		Neutral fat		Phospholipid		Free fatty acid		Neutral fat		Phospholipid	
	Husked rice	Milled rice	Husked rice	Milled rice	Husked rice	Milled rice	Husked rice	Milled rice	Husked rice	Milled rice	Husked rice	Milled rice
Myristic		1.57		0.90	0.50	0.99	0.81	1.04		1.20	0.67	1.01
Palmitic	15.79	16.59	15.23	15.94	19.78	17.79	15.08	16.31	15.21	16.90	20.74	17.65
Stearic	1.46	0.40	0.77	0.85	0.49	1.09	0.67	0.61	0.48	1.54	0.69	1.07
Oleic	24.77	18.72	37.36	35.93	33.89	31.65	27.53	18.61	35.91	34.65	34.37	31.13
Linoleic	52.77	59.18	48.55	44.16	44.19	46.32	51.20	59.91	46.09	43.13	40.35	46.26
Linolenic	4.98	3.53	3.16	2.32	1.16	2.16	4.24	3.51	2.30	2.51	3.19	2.88

are not reported to exist in rice. Therefore, other carbonyl compounds except acetaldehyde are not thought to be formed through this mechanism.

The other mechanism is the autoxidation of lipid mentioned previously. Fatty acid compositions of the extraneous lipids of rice are shown in Table 4. The major fatty acids of lipid in rice are palmitic, oleic and linoleic acids.

General mechanism of autoxidation of lipid, especially the formation of hydroperoxide is thought as follows:

$$\text{Initiation: } RH \longrightarrow R\cdot + H\cdot$$

$$\text{Propagation}\begin{cases} R\cdot + O_2 \longrightarrow RO_2\cdot \\ RO_2\cdot + RH \longrightarrow ROOH + R\cdot \end{cases}$$

At the initiation stage, hydrogen disconnects easily from an alpha position relative to a double bond and therefore peroxide forms at that position. In case of linoleic acid contained mostly in rice, mechanism of autoxidation is shown in Fig. 3. It is discovered in Fig. 3 that the formation of 11-C-peroxide is extremely remarkable and those of other 8-C, 14-C-peroxides are very few.[8] These formed peroxides are decomposed to aldehydes by heat, light, metal and radiation as follows:

$$R_1-\underset{\displaystyle O+OH}{\underset{|}{CH}}-R_2 \longrightarrow R_1 \overset{(ii)}{+} \underset{\displaystyle O\cdot}{\underset{|}{CH}} \overset{(i)}{+} R_2 \begin{cases} \overset{(i)}{\longrightarrow} R_1-CHO+R_2\cdot \\ \underset{(ii)}{\longrightarrow} R_2-CHO+R_1\cdot \end{cases}$$

Volatile substances isolated and theoretically postulated from autoxidized model C_{18} unsaturated fatty acid are shown in Table 5 by Hoffman.[9] Namely, C_3, C_5, C_6-aldehydes are proved to be decomposition products of oleic and linoleic acids not only theoretically but also experimentally. C_6-aldehyde (hexanal) is reported to be a major product in these aldehydes.

As already mentioned, C_3, C_5 and C_6 aldehydes are much in volatiles when stored rice is cooked. Therefore, it is reasonable to analogize that these aldehydes were formed through autoxidation of lipid in rice.

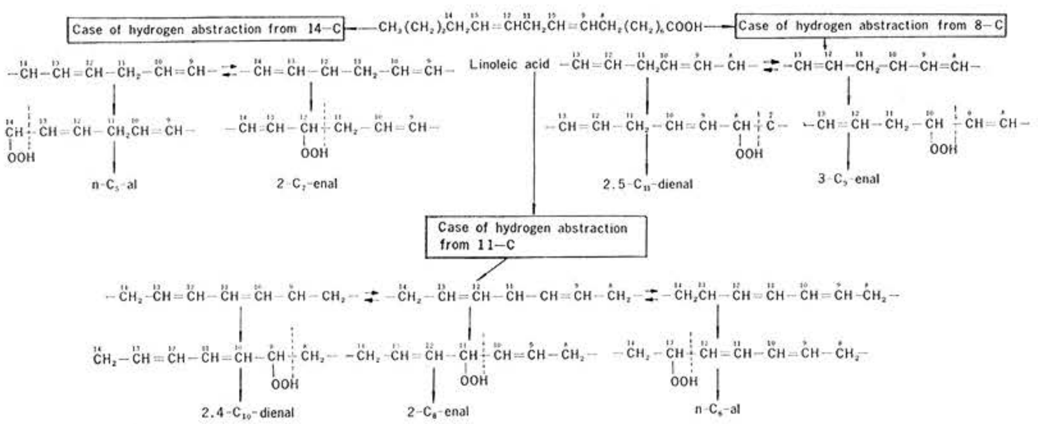

Fig. 3. Autoxidation of linoleic acid.

Table 5. Volatile substances isolated and theoretically postulated from autoxidized model C_{18}-unsaturated fatty acid[1]

Acid	Aldehydes							Other compounds
	Sat. a	Δ2	Δ2, 4	Δ3	Δ2, 5	Δ3, 6	Δ2, 6	
Oleic pract.	$C_5C_6C_7C_3C_9$[2] C_{10}	$C_8C_9C_{10}$[2] C_{11}[2]						
Oleic theor.	C_8C_9	$C_{10}C_{11}$						
Linoleic pract.	C_2C_3 C_5C_6[2]	$C_2C_5C_6$ C_7[2] C_8C_9[2] C_{10}	C_9C_{10}[2] C_{11}					1-Octen-3-ol
Linoleic theor.	C_5C_6	C_7C_8 $\underline{C_9}$	$C_{10}\underline{C_{11}}$	C_9	C_{11}			
Linolenic pract.	C_2C_3[2] C_4	C_4C_5[2] C_6[2] C_7 C_9	C_7[2] C_9[2]					Methyl ethyl keton Hexene-1, 6-dial
Linolenic theor.	C_2C_3	C_4C_5 $\underline{C_6}$	$C_7\underline{C_8}$ Δ2, 4, 7—C_{10}	C_6	C_8 Δ2, 5, 8-C_{11}	C_9	$\underline{C_9}$	

[1] Compiled from literature.
[2] Main product.
Underscoring indicates possible only by shifts of double bonds and/or rearrangement.

References

1) Obata, Y. and Tanaka, H.: Studies on the photolysis of L-cysteine and L-cystine. Formation of the flavor of cooked rice from L-cysteine and L-cystine. *Agr. Biol. Chem.* **29**, 191–195 (1965).
2) Yasumatsu, K., Moritaka, S. and Wada, S.: Studies on cereals. Part IV., Volatile carbonyl compounds of cooked rice. *Agr. Biol. Chem.*, **30**, 478–482 (1966).
3) Yasumatsu, K., Moritaka, S. and Wada, S.: Studies on cereals, Part V., Stale flavor of stored rice. *Agr. Biol. Chem.*, **30**, 483–486 (1966).
4) Endo, I., Chikubu, S. and Tani, T.: Cooking and eating qualities of milled rice, Part. V., Measurement of flavor components in cooked rice. (in preparation).
5) Yasumatsu, K. and Moritaka, S.: Fatty acid compositions of rice lipid and their changes during storage. *Agr. Biol. Chem.* **28**, 257–264 (1964).
6) Tatenuma, M. and Sato, S.: Flavor of imported foreign rice, *J. Soc. Brewing, Japan*, **70**, 818–820 (1965). [In Japanese.]
7) Casey, J. C., Self, R. and Swain, T.: Factors

influencing the production of low-boiling volatiles from foods, *J. Food Sci.* **30**, 33–34 (1965).
8) Sakurai, Y. and Arai, S.: Food Preservations. Asakura Publ. 250 (1966). [In Japanese.]
9) Hoffman, G.: Symposium on foods; Lipids and their oxidation. Avi. Publ., 222 (1962).