Volatile Flavor Components of Cooked Rice

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Volatile flavor components of cooked rice were studied. Steam distillate of cooked rice was extracted with methylene chloride and the extract was separated into four fractions: acidic, weak acidic, basic and neutral fractions. The neutral fraction was further separated into hydrocarbons and oxygenated compounds by column chromatography. All fractions were analyzed by a combination of glass capillary gas chromatography and mass spectrometry.

One hundred constituents, including 13 hydrocarbons, 13 alcohols, 16 aldehydes, 14 ketones, 14 acids, eight esters, five phenols, three pyridines, six pyrazines, and eight other compounds, were identified. Of these, 92 were newly identified volatile flavor components of cooked rice.

Many studies have been carried out on rice, especially on its nutritional and chemical compositions, but few have focused on the volatile flavor components of cooked rice. Obata and Tanaka¹⁾ identified hydrogen sulfide, ammonia and carbon dioxide in the vapors of cooked rice, and Yasumatsu *et al.*²⁾ found volatile carbonyl compounds such as acetaldehyde, propanal (or acetone), 2-butanone, pentanal and hexanal and discussed the mechanism of their formation. Ayano and Furuhashi³⁾ also investigated the carbonyl compounds from cooked rice and reported them to be mainly acetaldehyde, pentanal and hexanal. Only a few volatile compounds have thus been reported for cooked rice. This investigation was undertaken to identify additional volatile flavor components in cooked rice.

MATERIALS AND METHODS

Materials.

The rice used was Koshihikari harvested in Niigata Prefecture. It was newly hulled and 80% polished.

Methods

a) *Steam distillation of cooked rice.* A mixture of 6 kg of rice, washed with water, and 6.5 kg of water was placed in a 50-liter closed stainless steel vessel illustrated in Fig. 1. The mixture was heated to and maintained at 120°C for 40 min to cook the rice. This cooked rice was immediately steam distilled by intro-

ducing steam into the same vessel, resulting in 3 kg of distillate containing volatile flavor components.

This process was repeated eight times, giving 23.5 kg of distillate from 48 kg of rice.

b) *Extraction of flavor components.* The distillate was extracted three times with 2.5 liters of methylene chloride and the extract was concentrated to a volume of 600 ml. Of this 600 ml of aroma concentrate, 100 ml was further concentrated to approximately 0.1 ml for analysis by gas chromatography (GC) and the remaining 500 ml was fractionated by the following method.

c) *Fractionation of aroma concentrate.* As shown in Fig. 2, aroma concentrate was separated into four fractions: acidic, weak acidic, basic and neutral. Each fraction was concentrated to approximately 0.1 ml.

The neutral fraction was further subjected to column chromatography in order to separate hydrocarbons from oxygenated compounds. It was placed at the top of a 10 mm × 50 mm column packed with silica gel and eluted with 50 ml of *n*-pentane, followed by 50 ml of ethyl ether and finally 50 ml of methanol. Each fraction was concentrated to approximately 0.1 ml.

All these fractions were analyzed by GC and gas chromatography-mass spectrometry (GC-MS), with the exception of the acidic fraction which was analyzed after methylation.

d) *GC conditions.* A Hitachi Model 163 gas chromatograph with a flame ionization detector and a 0.28 mm i.d. × 50 m glass capillary column coated with PEG 20M was used. The column temperature was programmed from 60°C to 190°C at a rate of 2°C/min and the flow rate of helium carrier gas was 1 ml/min.

FIG. 1. Apparatus for Steam Distillation of Cooked Rice.

FIG. 2. Fractionation of Aroma Concentrate of Cooked Rice.

c) *GC-MS conditions.* A Hitachi Model RMU-6MG mass spectrometer was used. GC column conditions were as described above for GC. Other operating parameters were as follows: column oven temperature and programmed rate of gas chromatograph, 50°C to 170°C at a rate of 2°C/min; ionizing voltage, 70 eV; accelerating voltage, 3200 v; ion source temperature, 200°C.

RESULTS AND DISCUSSION

Yields of flavor compounds obtained from each fraction are listed in Table I. The total flavor compound yield is 230 mg, which is equivalent to only 4.8 ppm of the weight of the rice used. It was found from this that the cooked rice contained only small amounts of flavor compounds.

Also, as can be seen from Table I, weakly acidic and neutral oxygenated compounds

TABLE I. YIELDS OF FLAVOR COMPOUNDS OF COOKED RICE

Fractions	Yields
Total amounts of flavor compounds	230 mg (4.8 ppm)
Acidic fraction	145 mg
Weak acidic Fr.	141 mg
Acidic Fr.	4 mg
Basic fraction	2 mg
Neutral fraction	73 mg
Hydrocarbon Fr.	7 mg
Oxygenated compounds Fr.	61 mg

comprise approximately 90% of the total flavor compounds, and therefore it can be assumed that the volatile flavor components of cooked rice are mainly phenols, higher acids and neutral oxygenated compounds such as alcohols, aldehydes, ketones and esters.

A gas chromatogram of aroma concentrate

FIG. 3. Gas Chromatogram of Aroma Concentrate of Cooked Rice.

of cooked rice is shown in Fig. 3. The chromatogram indicates the presence of over 210 compounds, of which 100 were identified. Identifications were made by comparing and matching the mass spectra and GC retention times of the unknown compounds with those of authentic compounds.

The 100 compounds thus identified from cooked rice are shown in Table II. Of these, 92 were identified in cooked rice for the first time, though some are known to be volatiles of unprocessed rice⁴⁾ and rice bran.⁵⁾

Of the acidic compounds other than higher fatty acids, 4-vinylphenol and 4-vinylguaiacol were the major components. These phenols are considered to be formed by thermal decomposition of the *p*-coumaric and ferulic acid existing in rice during cooking and/or steam distillation.⁶⁾

Most of the basic compounds identified, though present in small quantities, were pyridines and pyrazines which are thought to have been developed by Maillard reaction.

The major neutral oxygenated compounds were alcohols and aldehydes such as *n*-butanol, *n*-pentanol, 2-ethylhexanol, *n*-hexanal, *n*-non-

TABLE II. VOLATILE FLAVOR COMPOUNDS IDENTIFIED FROM COOKED RICE

Peak No.	Compounds
<u>Hydrocarbons</u>	
13	Xylene
21	Limonene
29	<i>p</i> -Cymene
31	Cumene
67	Pentadecane
81	Hexadecane
96	Naphthalene
104	Heptadecane
119	Methylnaphthalene
121	Octadecane
138	Nonadecane
149	Eicosane
163	Heneicosane
<u>Alcohols</u>	
12	Butanol-1
20	3-Methyl-1-butanol
24	Pentanol-1
42	Hexanol-1
55 ^a	2-Ethyl-4-methylpentan-1-ol
60	1-Octen-3-ol
61	2-Ethylhexanol
70	Linalool
71	Octanol-1
123	Benzyl alcohol
130	2-Phenylethyl alcohol
152	Nerolidol

Peak No.	Compounds	Peak No.	Compounds
188	Pentadecanol-1	133	Phenol
	<u>Aldehydes</u>	154	<i>p</i> -Cresol
5 ^b	Pentanal	172	4-Vinylguaiacol
8 ^b	Hexanal	200	4-Vinylphenol
17	Heptanal		<u>Acids</u>
22	<i>trans</i> -2-Hexenal	107	Caproic acid
32	Octanal	147	Caprylic acid
39	<i>trans</i> -2-Heptenal	166	Nonanoic acid
50	Nonanal	185	Capric acid
54	<i>trans</i> -2-Octenal	213	Lauric acid
59	Furfural		Tridecanoic acid
62	Decanal	^b	Myristic acid
66	Benzaldehyde		Pentadecanoic acid
69	<i>trans</i> -2-Nonenal	^b	Palmitic acid
86	Phenylacetaldehyde	^a	Hexadecenoic acid
89	<i>trans</i> -2-Decenal	^b	Stearic acid
107 ^a	<i>trans</i> -2- <i>cis</i> -4-Decadienal	^b	Oleic acid
113	<i>trans</i> -2- <i>trans</i> -4-Decadienal	^b	Linoleic acid
	<u>Ketones</u>	^b	Linolenic acid
9	<i>trans</i> -3-Penten-2-one		<u>Miscellaneous</u>
19	2-Heptanone	103	Aniline
27	3-Octanone	133	B.H.T.
31	2-Octanone	134	Quinoline
40	6-Methylhept-5-en-2-one	135	Benzothiazol
46	2-Nonanone	163	2,3-Dimethyl-2-nonen-4-olide
74	Isophorone	207	Indole
78	6-Methylhepta-3,5-dien-2-one		Diethyl phthalate
81	2-Undecanone		Dibutyl phthalate
88	Acetophenone		
146	2-Pentadecanone		
162	6,10,14-Trimethyl pentadecan-2-one		
179	2-Heptadecanone		
212	2-Nonadecanone		
	<u>Esters</u>		
100	Ethyl benzoate		
122	Geranyl acetate		
153	Ethyl myristate		
178	Methyl palmitate		
182	Ethyl palmitate		
	Ethyl stearate		
	Ethyl oleate		
	Ethyl linoleate		
	<u>Pyridines</u>		
18	Pyridine		
26	2-Methylpyridine		
33	3-Methylpyridine		
	<u>Pyrazines</u>		
25	Pyrazine		
28	2-Methylpyrazine		
34	2,5-Dimethylpyrazine		
37	2,6-Dimethylpyrazine		
43	2,3-Dimethylpyrazine		
48	2,3,5-Trimethylpyrazine		
	<u>Phenols</u>		
114	Guaiacol		

^a Tentatively identified.^b Previously reported.

anal and *trans*-2-octenal. Most of ketones, though minor constituents, were identified as methyl ketones.

It is generally recognized that alcohols are formed by oxidation of lipids, aldehydes by oxidation of certain amino acids and fatty acids, and methyl ketones by beta-oxidation of fatty acids during heating.

These oxygenated compounds seem to be the major contributors to the flavor of cooked rice, but none of the individual compounds were found to have the characteristic odor of cooked rice.

Further detailed experiments are necessary.

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