Studies on Cereals

Part IV Volatile Carbonyl Compounds of Cooked Rice*

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Five carbonyl compounds were found in the vapour of cooked rice, of which acetaldehyde, and *n*-caproaldehyde were identified from their retention times in gas chromatography and by their infrared spectra. Propionaldehyde or acetone, methylethylketone, and *n*-valeraldehyde were tentatively identified. The mechanisms of the formation of these carbonyl compounds were discussed from the view-point of Strecker degradation and lipid oxidation.

INTRODUCTION

As rice is an important grain in the world, many works have been carried out on its quality.^{1,2)} But almost all of them have been directed to the chemical components of rice, especially to starch,³⁾ protein,⁴⁾ lipid⁵⁾ and amino acid.^{2,6)} The literature on the volatile flavor of cooked rice, however, is very scanty, though cooked rice has weak but characteristic flavor.

On the other hand, it has been generally accepted that the carbonyl compounds contribute to the flavor of various foods. The mechanism of the formation of the volatile carbonyl compounds has recently been discussed in detail. Casey et al.,⁷⁾ for example, studied the factor influencing the production of low-boiling volatiles in food and regarded

the common metabolites like amino acid and sugar as the precursors of the volatiles. Mookherjee et al.,⁸⁾ have also indicated that many volatile carbonyl compounds were produced as the autoxidation products of the lipid in cooked foods.

As to volatiles of cooked rice, Obata and Tanaka⁹⁾ reported 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 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.

The present work was undertaken to analyze the volatile carbonyl compounds in cooked rice in detail. Relatively new flash exchange gas chromatography was employed and five carbonyl compounds were found in the volatiles of cooked rice.

EXPERIMENTAL

Materials

Rice Senbon-asahi was used. It was polished at

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2) B. O. Juliano et al., *J. Agr. and Food Chem.*, **12**, 131 (1964).

3) H. Fukuba, *J. Agr. Chem. Soc. Japan*, **28**, 38, 41 (1954).

4) B. O. Juliano et al., *Food Tech.*, **19**, 116 (1965).

5) K. Yasumatsu and S. Moritaka, *This Journal*, **28**, 257 (1964).

6) S. Okazaki and Y. Oki, *J. Agr. Chem. Soc. Japan*, **35**, 194 (1961).

7) J. C. Casey, R. Self and T. Swain, *J. Food Sci.*, **30**, 33 (1965).

8) B. D. Mookherjee, R. E. Deckand and S. S. Chang, *J. Agr. Food Chem.*, **13**, 131 (1965).

9) Y. Obata and H. Tanaka, *This Journal*, **29**, 191 (1965).

our laboratories to remove 10% of the weight of the grain. *n*-Hexane for column chromatography was purified by the method of Corbin et al.¹⁰⁾ Methanol and benzene were purified by the method of Schwartz et al.¹¹⁾

Methods

a) Collection of volatile carbonyl compounds in the vapour of cooked rice. The trains of traps are illustrated in Fig. 1.

FIG. 1. Apparatus Used to Collect Volatile Carbonyl Compounds from Cooked Rice.

- A, E. 2,4-Dinitrophenylhydrazine
- B. Distilled water
- C. Cooked rice
- D. Water bath kept at 50°C

Rice (1.4 kg) was cooked and transferred into the sample bottle C., which was bubbled for two hours with purified nitrogen gas at flow rate of 100 ml/min. Then the cooked rice was discarded and replaced with freshly cooked rice. This process was repeated to catch volatile carbonyl compounds as 2,4-dinitrophenylhydrazones in trap E. The content of trap E was filtered and precipitate was dried in vacuo. The 2,4-dinitrophenylhydrazone thus obtained was dissolved in methanol-benzene mixture (1:1) to remove the contaminated 2,4-dinitrophenylhydrazine by the method of Schwartz et al.¹¹⁾

b) Gas chromatography of 2,4-dinitrophenylhydrazones. The method of gas chromatography of 2,4-dinitrophenylhydrazones was virtually identical with the modified flash exchange procedure of Stephens and Teszler.¹²⁾ The chloroform solution of 2,4-dinitrophenylhydrazones was pipetted onto 10 mg of celite (80~100 mesh) in glass vials (2 ml capacity) and dried with a hair-drier.

After the chloroform had been evaporated off, 5 mg of *o*-phthalic acid was weighed into the vials. The contents were mixed thoroughly and transferred into a glass capillary tube. The exchange reaction between *o*-phthalic acid and the hydrazone was carried out at approximately 350°C by heating the capillary in the Pipetter (Yanagimoto Co. Ltd.). A few peaks of heat decomposition products of *o*-phthalic acid appeared when the exchange reaction was carried out at 350°C, but when the exchange reaction was done below 350°C, the resolution of the carbonyl compounds produced from hydrazones was unsatisfactory. Thus, the gas chromatograms and the compositions of carbonyl compounds were given after withdrawing the peaks correspond to the heat decomposition products of *o*-phthalic acid. The retention times of authentic carbonyl compounds were obtained by the same method. 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

c) Column chromatography of 2,4-dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazones of carbonyl compounds were fractionated with the column of Celite and acetonitrile in the manner described by Corbin et al.¹⁰⁾

RESULTS

Gas Chromatogram of Carbonyl Compounds in the Volatiles of Cooked Rice

Fig. 2 shows the existence of five carbonyl compounds.

Both the retention times of peaks shown in Fig. 2 and those of authentic carbonyl compounds which are supposed to have the same retention times as those of the peaks in Fig. 2, are shown in Table I.

On the basis of their retention times in Table I, these carbonyl compounds may be acetaldehyde, propionaldehyde (or acetone), methylethylketone, *n*-valeraldehyde and *n*-caproaldehyde.

Separation of 2,4-Dinitrophenylhydrazones by Column Chromatography

In order to identify the carbonyl compounds by infrared spectroscopy, 2,4-dinitrophenyl-

10) E.A. Corbin, D.P. Schwartz and M. Keeney, *J. Chromatog.*, **3**, 322 (1960).

11) D.P. Schwartz, A.R. Jhonson and O.W. Parks, *Microchem. J.*, **6**, 37 (1962).

12) R.L. Stephens and A.P. Teszler, *Anal. Chem.*, **32**, 1047 (1960).

FIG. 2. Gas Chromatogram of Volatile Carbonyl Compounds from Cooked Rice.

30% DOP on Celite at 100°C, 2 m, Flow rate 60 ml/min.

TABLE I. RETENTION TIMES OF CARBONYL COMPOUNDS

Peak No.	Sample		Authentic carbonyl comp.	
	100°C*	75°C*	Name of comp.	100°C* 75°C*
			Formaldehyde	1.48
1	2.00		Acetaldehyde	1.90
2	2.53	5.08	Propionaldehyde	2.52 5.07
			Acetone	2.67 5.20
			<i>n</i> -Butylaldehyde	4.73 10.20
3	4.85	10.70	Methylethylketone	4.87 10.90
4	9.37	23.20	<i>n</i> -Valeraldehyde	9.40 22.40
			Isovaleraldehyde	9.25 15.70
			Diethylketone	9.53 21.20
			Crotonaldehyde	8.80 19.30
			2-Pentanone	9.00 20.67
			3-Pentanone	9.20 21.00
5	21.20	54.00	<i>n</i> -Caproaldehyde	20.63 53.60
			2-Hexanone	18.40 45.30

* Column temperatures

hydrazones were fractionated by column chromatography.

Two fractions were obtained as shown in Fig. 3a.

Fraction I was rechromatographed in the same method except that the eluate was collected in 5 ml, and was divided into three fractions (Fig. 3b). Fractions IA and II were analyzed by gas chromatograph and result showed that Fraction IA and II correspond to peaks 5 and 1 in gas chromatogram, re-

FIG. 3. Column Chromatogram of 2,4-Dinitrophenylhydrazones.

Column of Celite and Acetonitril; (a) Chromatogram fractionated in 10 ml each. (b) Fraction I was rechromatographed in 5 ml each.

spectively. The yields of Fractions IB and IC were too little to be analyzed by gas chromatography.

Identification of Acetaldehyde and *n*-Caproaldehyde

Fractions IA and II prepared by column chromatography were analyzed by infrared spectroscopy. The results are shown in Figs. 4 and 5, which were completely the same as the infrared spectra of 2,4-dinitrophenylhydrazones of authentic *n*-caproaldehyde and acetaldehyde. This means that, the peaks 1 and 5 in Fig. 1 were acetaldehyde and *n*-caproaldehyde, respectively.

DISCUSSION

Acetaldehyde, propionaldehyde (or acetone), methylethylketone, *n*-valeraldehyde and *n*-caproaldehyde were found as the volatile carbonyl compounds of cooked rice.

Acetaldehyde was identified by infrared spectroscopy. It was also reported by Obata and Tanaka⁹⁾ as one of the components of such decomposition products of cysteine and cystine that gave the typical flavor of cooked rice. Self et al.¹³⁾ studied the volatiles of cooked potato and reported alanine as the precursor of acetaldehyde. They also prepared the model system and reported that alanine, cysteine, cystine, asparagine, glucose and fruc-

13) R. Self, H. L. J. Rolley and A. E. Joyce, *J. Sci. Fd. Agric.*, **14**, 8 (1963).

FIG. 4. Infrared Spectrum of Fraction IA.

— 2,4-Dinitrophenylhydrazone of fraction IA
 --- 2,4-Dinitrophenylhydrazone of authentic *n*-caproaldehyde

FIG. 5. Infrared Spectrum of Fraction II.

— 2,4-Dinitrophenylhydrazone of fraction II
 --- 2,4-Dinitrophenylhydrazone of authentic acetaldehyde

tose produced acetaldehyde during cooking.⁷⁾ As rice contains cystine as well as alanine, they all may be responsible for the production of acetaldehyde.

Peak 2 is supposed to be propionaldehyde or acetone from their retention times. In this experiment, the amount of the compound corresponding to peak 2 was not enough to

confirm the structure by absorption spectroscopy.

Peak 3 is tentatively identified as methyl-ethylketone on the basis of its retention time. Neither Strecker degradation nor autoxidation of fatty acid can explain the formation of this ketone. However, it was reported that methylethylketone was produced on the pyrolysis of starch at 300°C.¹⁴⁾ So, methyl-ethylketone may be formed through a more complicated reaction.

Peak 4 was supposed to be *n*-valeraldehyde from its retention time. If this compound was formed through Strecker degradation, the precursor might be norleucine, but this amino acid has not been found in rice yet. On the other hand, *n*-valeraldehyde is one of the components of autoxidation products of linoleic acid.⁸⁾ Thus *n*-valeraldehyde in the volatiles of cooked rice may arise from linoleic acid.

Peak 5 was identified as *n*-caproaldehyde

(hexanal) by infrared spectroscopy. Many workers have shown that caproaldehyde is a major component of off-flavor of food, for example, peas,¹⁵⁾ potato granules^{16,17)} and potato chips,⁸⁾ and that this compound can easily be formed in reactions following the oxidation of linoleic acid. Therefore *n*-caproaldehyde in the volatile of cooked rice originates from linoleic acid which is the main component of rice lipid.

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17) M. B. Boggs, R. G. Buttery, D. W. Venstrom and M. L. Belote, *J. Food Sci.*, **29**, 487 (1964).

14) D. J. Bryce and C. T. Greenwood, *Die Stärke*, **15**, 285 (1963).