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Analysis of *n*-Hexanal in Headspace Vapor over Cooked Brown Rice by Direct Vapor Injection Gas Chromatography

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현미취반시 생성되는 *n*-hexanal의 가스크로마토그래피에 의한 분리및 정량

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Abstract

n-Hexanal in headspace over the cooked brown rice stored at 5°C and 35°C for 0, 4, 8 and 12 months was determined by a modified direct vapor injection gas chromatographic method. The retention time of *n*-hexanal was 3.5 min and *n*-hexanal could be rapidly separated from other compounds at the operational conditions of gas chromatography. *n*-Hexanal contents of cooked brown rice also showed a standard deviation of less than 10% of the average.

Introduction

It is well known that the volatile flavor of stored rice mainly originates from its lipid deterioration,[1,2] and *n*-hexanal, one of the main volatile components, may arise from oxidative degradation of unsaturated fatty acids, especially linoleic acid.[3]

Analysis of the volatile components in headspace vapor over cooked rice using gas-liquid chromatography has been carried out by several researchers. Yasumatsu *et al.*[4] reported that volatile carbonyl components of cooked rice could be quantitatively analyzed by direct vapor injection method using packed column gas chromatography and hexanal was separated at 23 min retention time. Tsugita *et al.*[5,6] analyzed headspace volatiles over cooked rice using glass capillary gas chromatography after trapping tube to minimize the deterioration of the capillary column. However, all of these methods require a relatively long retention time for *n*- hexanal and most of them involve capillary columns which are not readily accessible for ordinary quality control purposes.

During the course of our recent study on the quality control of the brown rice at various storage conditions, a simple and rapid method of quantitative analysis of *n*-hexanal in the headspace over the cooked brown rice was needed. The objective of this study was to develop a rapid and simple gas chromatograpic method of determining *n*-hexanal in the headspace vapor over cooked brown rice.

Materials and Method

Materials

Indica/Japonica brown rice *(Sam Kang Variety)* was obtained by dehulling with a Satake dehuller. The brown rice was packed in polyethylene bags and stored at 5°C and 35°C until the sample was taken out after 0,4,8 and 12 months of storage period to determine the *n*-Hexanal of analytical standard grade was purchased from Poly Sciences (Warrington, PA).

preparation of brown rice vapors

Eighty grams of brown rice (12% moisture, wet basis) was soaked with 125 *ml*(distilled water maintained at 25°C for 30 min in a 250 *ml*)two-necked round bottom flask fitted with a 50 *ml*

Liebig condenser and rubber septum. The flask was then dipped into a water bath and the rice in the flask cooked at 98°C for 40 min. Two milliliters of headspace vapor were removed with a 5 *ml* gas tight Hamilton syringe inserted through the rubber septum into the headspace vapor over the cooked brown rice and injected immedicately into a gas chromatograph.

Analysis of hexanal in headspace vapors

Vapor sample was analyzed with Hewlett-Packard Model 5840 gas chromatograph equipped with a flame ionization detector and an electronic integrator. The column used was of stainless steel (1/8 inch O.D., 10 ft) packed with 10% Carbowax 20M 100-120 mesh acid washed Chromosorb HP. Temperatures of the column oven, injector and detector were 80°C, 180°C and 250°C, respectively.

GC-MS spectra were recorded with a Hewlett-Packard Model 5985B mass spectrometer equipped with a Hewlett-Packard Model 5840 gas chromatograph using previously described procedure for vapor preparation and analysis. Ionization voltage was 25 eV, and the ion source temperature was kept at 200°C. *n*-Hexanal was identified by comparing GC-MS data and GC retention time of the sample with that of authentic compound.

Amounts of *n*-hexanal were determined by standard curve of peak area vs *n*-hexanal concentration obtained by adding aliquots of standard solution ranging from 0.1μg to 0.7 μg *n*-hexanal.

Results and Disscusion

A chromatogram of headspace vapor over cooked brown rice shows at least 13 compounds (Fig. 1). Peak 10 was identified by retention time

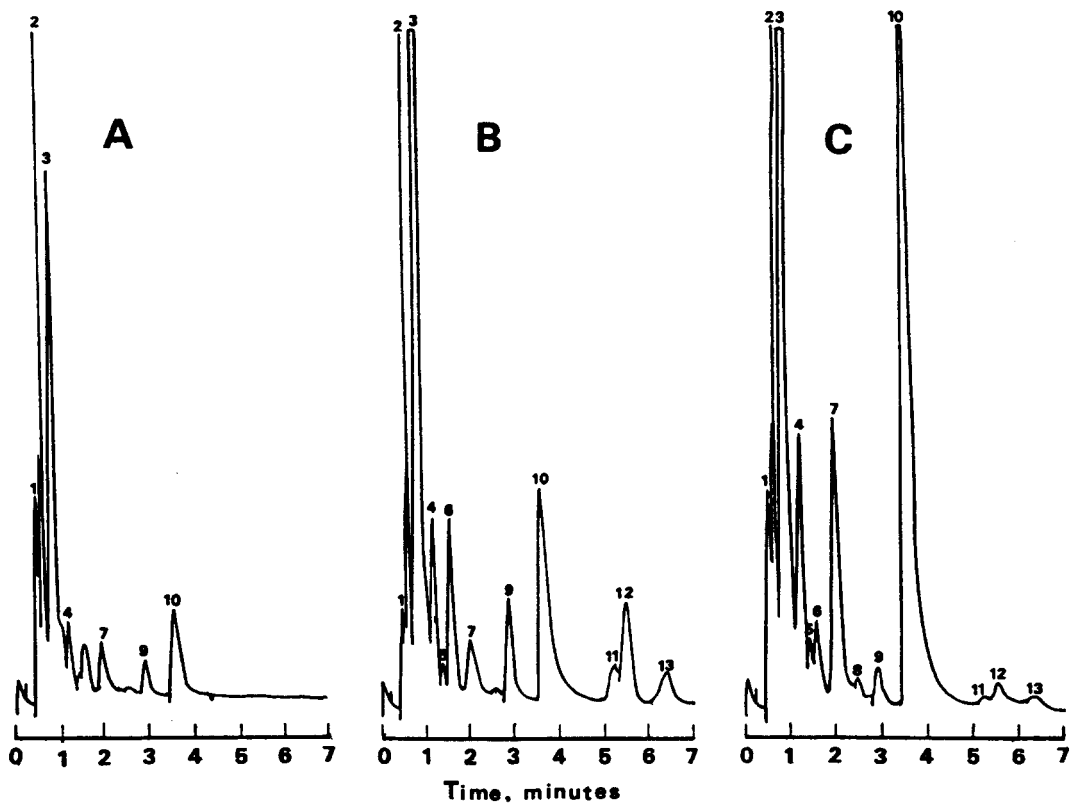

Fig. 1. Gas chromatogram of headspace vapor of cooked fresh brown rice(A), cooked brown rice previously stored at 5°C for 8 months(B), and cooked brown rice previously stored at 35°C for 8 months(C), Peak 10: hexanal peak, peak 1-9 and 11-13: unidentified

and mass spectroscopy as *n*-hexanal. The retention time of hexanal was 3.5 min and *n*-hexanal could be rapidly separated from other compounds at the operational conditions of gas chromatography. Buttery *et al*[7] reported that Carbowax gave relatively high noise levles from "bleeding" when heated above 100°C and, therefore, could not be used for direct vapor injection gas chromatographic analysis of vapor samples. However, the Carbowax 20M used as stationary phase gave good resolution with volatile compounds, especially *n*-hexanal without a high noise level at a column temperature, 80°C.

In order to quantify the amount of *n*-hexanal, aliquots of standard solutions ranging form 0.1 to 0.7 *μg n*-hexanal were chromatographed and the plot of the peak area against *n*-hexanal concentration of the samples was found to be linear. Based on the standard curve, *n*-hexanal in 2 *ml* headspace vapor for cooked brown rice was obtained from direct vapor injection gas chromatography and the results are shown in Table 1.

Table 1 shows that *n*-hexanal in headspace vapor increased significantly depending on the storage temperature (35°C vs 5°C). These results were very close to the data obtained by Tsugita *et al.*[8] Furthermore, the *n*-hexanal in 2 *ml* headspace vapor was found to increase substantially in proportion to the storage periods at each of the storage temperature. In the meantime, the packed column with 10% Carbowax 20M provided reasonably long column life in the direct vapor injection gas chromatography. In fact, over 100 vapor sample injections resulted in no detectable differences in column efficiency.

Based on the above-mentioned results, *n*-hexanal in headspace vapor over cooked brown rice can be determined rapidly by the modified direct vapor injection gas chromatographic method.

Table 1. *n*-Hexanal contents of cooked brown rice determined by direct vapor injection gas chromatography

Storage temperature (℃)	Storage period (month)	Hexanal content (*μg*)[a]
5	0	0.022±0.001[b]
	4	0.045±0.003
	8	0.074±0.004
	12	0.097±0.005
35	0	0.022±0.001
	4	0.113±0.006
	8	0.240±0.018
	12	0.304±0.021

a. Hexanal content in 2 *ml* headspace vapor.
b. Mean±SD based on 5 samples.

요 약

본 연구에서는 현미취반시 생성되는 고휘발성 향기성분중 고미취의 주성분인 *n*-hexanal의 가스크로마토그래피에 의한 분리및 정량방법을 개선하였다. 개발된 가스크로마토그래피의 운전조건하에서 n-hexanal의 분리를 시도한 결과, *n*-hexanal은 다른 고휘발성 향기성분으로부터 완전히 분리가 되었고, 특히 *n*-hexanal의 머무름시간(retention time)은 3.5분으로 아주 빨리 분리가 되었다. 그리고 Direct vapor injection 방법에 따른 *n*-hexanal의 정량시 각 시료의 *n*-hexanal 값은 10%이내의 오차를 보여주어, 고휘발성 향기성분중 *n*-hexanal의 정량분석이 가능하였다.

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