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Effect of Storage Time and Temperature on Volatile Aroma Compounds and Physicochemical Properties of Rice

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ABSTRACT

Storage affected to physicochemical properties of Khao Dawk Mali 105 rice variety. The pasting temperature of the samples stored at 25°C decreased over time while pasting temperature of the samples stored at 37°C increased over the storage time. The colour (b) value increased according to storage temperature and the b value at 37°C was higher than the storage at 25°C. The aroma changes of rice was dued to the decreasing changes volatile compounds, 2-acetyl-1-pyrroline (2-AP) and increasing of hexanal. Storage time had a significant positive correlation with the b-value, pasting properties and a negative correlation with 2-AP content. Lower storage temperature was considered to be used to preserve 2-AP of the aromatic rice during storage**.**

Key words: 2-acetylpyroline, hexanal, rice, storage

INTRODUCTION

Most physicochemical properties of rice change during storage. As rice aged, cooked rice texture became fluffier and harder. Perdon *et al*. (1997) suggested that rice aging is a complex process that is seen in the paddy, brown rice, milled rice, rice starch and cooked rice. One of the most sensitive indices of the aging process in rice was the change in pasting properties which was usually measured by thermoviscometry. The data have been inconsistent but suggested that viscosity of rice paste increases dramatically after short- to intermediate-term storage (months) of milled rice but decreased during longer-term storage (years) (Sowbhagya and Bhattacharyat, 2001). Attempts to explain the changes in functionality associated with aging had focused on the properties of rice components, such as starch, protein, and lipids, and the interactions between them during storage (Chrastil and Zarins, 1992). However, it is now apparent that the minor components at the granule surface (lipids and proteins) have a disproportionate influence on granule properties and that aging-induced changed in these components may account for the changes in physicochemical properties seen after storage. Storage is an integral part of the post-harvest handling of rice. Rice may be stored in the paddy forms for lengthy periods of time prior to consumption. During storage, the flavour of rice can deteriorate due to changes in its volatile components by way of several mechanisms. These include breakdown of desirable volatile constituents, losses via diffusion out of the rice into the environment and generation of undesirable volatile materials by one or more of a number of mechanisms. This is of particular importance for

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fragrant rices in which the unique aroma characteristics rely on the relative proportions of many individual components.

This study investigated changes in pasting properties following rice storage and recognizable aroma description which was obtained for 2-AP of the rice stored at different temperature and time.

MATERIALS AND METHODS

Rice samples

One hundred kilos of the Khao Dawk Mali 105 paddy rice were provided by the Rice Research Center, Phathumthani province. The contaminant free paddy rice was cleaned, then air dried on the floor to 14-15% moisture content and packed into polypropylene bags of 70 micrometer thickness. The bags were placed at 25°C and 37°C in thermostatically controlled incubators. Rice samples were analyzed for physical, and physicochemical properties. Every month the paddy rice was analyzed for moisture content. The rice sample was ground into flour and sieved to 50 mesh powder and analyzed for 2-AP and hexanal contents and its physicochemical properties.

Physical analysis

The color of brown rice was determined by colorimeter Minolta Model DP-301. Color values (L, a and b) were measured. A white standard tile was used to calibrate the colorimeter (L = 100.01, a = -0.01, b = -0.02) before measurements. Therefore L measures lightness (luminosity) and varies from white to black. The chromatically values (a and b value) gives designations of colour as follows; a-value measures redness (positive value), gray (zero value) and greenness (negative value), b-value measures yellowness (positive value), gray (zero value), and blueness (negative value).

Rapid viscoanalysis (RVA)

The pasting properties of the various samples were determined with a Rapid Visco Analyser (Model 4D, Newport Scientific, Australia). Rice flour was slurried with distilled water. The temperature profile involved an initial 10 s high-speed stir that dispersed the sample prior to the beginning of the measuring phase at 160 rotations/min. Temperature was held at 50°C for 1 min and then raised to 95 °C in 3.75 min, held for 2.5 min, cooled to 50°C in 3.75 min, and held for 5 min. Values are reported in min, °C or rapid viscoanalyser units (RVU).

Sample extraction

The extraction vials used were 12 × 32 mm with a TFE septa and crimp top. Extractions were performed using 0.3 g of ground rice in 0.5 ml of stock solution. The stock solution consisted of methylene chloride with 0.459 ng/ml of 2, 4, 6-trimethylpyridine used as an standard.

Gas Chromatography

Method development and sample analysis were performed on a gas chromatograph (GC) using DB-1701 (15 m × 0.32 mm i.d. × 0.15 µm film thickness) column and flame-ionization detection (FID). After optimization, the GC operating parameters were chosen: injector 155°C; detector 300°C; initial temperature 35°C; initial time 1 min, first rate 9°C/min to 120°C, second rate 25°C/min to 275°C: final temperature 275°C; final time 2 min. Helium was the carrier gas and was set at a constant flow rate of 7.2 ml/min. The time required to analyze the peaks of interest and purge and cool the system was 25 min. The 2-AP peak was originally identified by chromatography coupled aroma perception with simultaneous FID similar to the procedure described by Tanchotikul and Hsieh (1989), analytical reagent-grade hexanal was used for its verification.

RESULTS

The b values represented yellow color of the paddy, brown and milled rice during storage time and temperature at 25°C and 37°C is shown in Table 1. The results shows b value increased according storage and the b value at 37°C was higher than the storage at 25°C. As shown in Table 1, there was increased in b value after storage at 25°C and 37°C for 4 months and 3 months, respectively.

All pasting properties, peak viscosity, setback, and pasting temperature, showed significant differences among the stored rice as shown in Table 2. Pasting temperature of different rice storage flours ranged from 71.35 - 78.42°C, for storage at 25°C, and 72.26 - 79.51°C for storage at 37°C. The physicochemical properties of the rice starch stored at 25°C and 37°C changed during the 7 months. The setback values of that stored at 37°C increased more than that at 25°C. The setback values might depend on temperature and storage duration and these values might also indicate the quality of cooked starch. The final viscosity and peak viscosity values increased during 7 months of storage and these values of the storage at 37°C were more than those at 25°C. However the pasting temperature of the storage at 25°C and 37°C

Table 1 Effects of storage temperature and time on b value of brown rice. (Error bar denotes ± 1 S.D. from the mean).

Rice storage (month)	Rice form	b value 25°C	b value 37°C
0	Paddy	25.21 ± 0.24a	25.21 ± 0.24a
0	Brown	22.14 ± 0.65b	22.14 ± 0.65b
0	Milled	9.12 ± 0.84c	9.12 ± 0.84c
1	Paddy	25.14 ± 0.64a	25.59 ± 0.19a
1	Brown	22.29 ± 1.14b	22.87 ± 0.69b
1	Milled	9.25 ± 0.57c	9.37 ± 0.29c
2	Paddy	25.67 ± 0.49a	26.47 ± 0.67d
2	Brown	22.54 ± 0.64b	22.98 ± 0.60b
2	Milled	9.57 ± 0.94c	10.58 ± 0.72h
3	Paddy	25.74 ± 0.29a	26.89 ± 0.61d
3	Brown	23.21 ± 0.67b	23.58 ± 0.35bf
3	Milled	10.14 ± 0.27c	10.94 ± 0.39h
4	Paddy	25.98 ± 0.54a	27.24 ± 0.57d
4	Brown	23.28 ± 0.47b	23.94 ± 0.76bf
4	Milled	10.68 ± 0.58cd	11.27 ± 0.74hi
5	Paddy	25.84 ± 0.46a	27.65 ± 0.27d
5	Brown	23.75 ± 0.34b	24.17 ± 0.45f
5	Milled	11.21 ± 0.24de	11.84 ± 0.51i
6	Paddy	26.39 ± 0.48a	28.82 ± 0.29e
6	Brown	24.15 ± 0.67b	24.68 ± 0.39fg
6	Milled	11.74 ± 0.51de	12.25 ± 0.36i
7	Paddy	26.84 ± 0.52f	28.86 ± 0.72e
7	Brown	24.37 ± 0.67b	25.39 ± 0.65g
7	Milled	12.26 ± 0.74e	12.87 ± 0.84j

Results with different letters in the same column are statistically significant ($P \leq 0.05$).

decreased during the 7 months of storage. Temperature and storage duration affected to the paddy rice flour viscosity (Table 2).

Peak viscosity of rice stored at 25°C increased throughout storage but the rice stored at 37°C caused the value to increase in the first month but later the value decreased. The pasting temperature, set back and final viscosity values increased according to the duration of storage and the storage at 37°C showed higher values than that at 25°C (Table 2). The gas chromatography method is shown by the results found from aromatic rice samples obtained from Rice Research Center. Those samples stored at 25°C had 2-AP levels of 274.25-562.35 and 229.36-417.24 ng/g in brown rice and milled rice, respectively, and the samples stored at 37°C had 2-AP levels of 112.45-562.35 and 87.43-417.24 ng/g in brown rice and milled rice, respectively (Table 3).

The gas chromatography method is shown by the results found from aromatic rice samples stored at 25°C had hexanal levels of 204.71-512.35 and 115.28-406.37 ng/g in brown rice and milled rice, respectively, and the samples stored at 37°C had hexanal levels of 204.71-805.73 and 115.2-427.26 ng/g in brown rice and milled rice, respectively (Table 4).

DISCUSSION

The storage of rice caused increasing in b value that came from brown pigments increased during storage. Brown pigments increasing provides an index for evaluating the intensity of browning reactions that was caused by Maillard reaction.

The viscosity of rice paste increased after storage of paddy rice. These changes depended on storage temperature and duration. Peak viscosity of flour pastes generally increased with both temperature and time of storage. Fresh flour paste exhibited lower peak viscosity. The peak

Table 2 The changes of pasting temperature, peak viscosity, setback and final viscosity of milled rice flour during storage.

Temperature (°C)	Storage (month)	Pasting Temperature (°C)	Peak viscosity (RVU)	Setback (RVU)	Final viscosity (RVU)
25°C	0	75.34 ± 1.04a	207.42 ± 9.51a	69.21 ± 2.14a	144.24 ± 7.54a
	1	78.42 ± 1.23b	264.42 ± 11.27b	75.42 ± 4.67a	195.46 ± 2.73b
	2	75.28 ± 1.35a	282.23 ± 7.46bc	88.53 ± 2.84b	204.27 ± 8.65bc
	3	74.59 ± 2.24a	297.21 ± 6.57cd	92.58 ± 7.52bc	212.37 ± 9.28c
	4	74.24 ± 1.34a	302.84 ± 14.86cd	95.64 ± 9.69bcd	221.35 ± 8.42cd
	5	73.21 ± 0.73c	307.21 ± 9.84d	98.23 ± 7.58bcd	234.72 ± 9.62df
	6	71.96 ± 1.41cd	312.57 ± 14.25d	101.28 ± 6.37cd	242.61 ± 9.54f
	7	71.35 ± 0.42d	324.25 ± 8.41d	104.51 ± 5.47cde	247.26 ± 7.42f
37°C	0	75.34 ± 1.04a	207.42 ± 9.51a	69.21 ± 2.14a	144.24 ± 7.54a
	1	76.42 ± 0.24a	242.57 ± 8.45e	78.24 ± 5.82a	197.54 ± 8.65b
	2	79.51 ± 1.26b	274.94 ± 10.24b	114.52 ± 8.47de	235.84 ± 9.42d
	3	74.21 ± 2.41a	287.15 ± 9.64cd	127.34 ± 7.43ef	248.51 ± 7.75dg
	4	73.14 ± 0.85a	312.35 ± 7.62d	132.51 ± 4.28ef	254.39 ± 8.54g
	5	72.26 ± 0.57a	327.35 ± 6.74df	136.34 ± 2.42fg	274.92 ±10.75h
	6	72.63 ± 1.24a	341.68 ± 9.36fg	145.65 ± 7.58gh	276.94 ± 8.49h
	7	73.52 ± 0.32a	347.21 ± 9.37g	148.72 ± 8.24h	284.52 ± 9.27h

Results with different letters in the same column are statistically significant ($P \leq 0.05$).

viscosity, set back and final viscosity values of the rice stored at 37°C were higher than that at 25°C. It was shown that the starch of the milled rice stored at 37°C was more viscous than at 25°C and longer storage duration resulted in higher viscosity, final viscosity and set back values. It might also be shown that the storage rice at 37°C retrodegrades better than the rice stored at 25°C.

Table 3 The changes of 2-AP of brown and milled rice starch during storage.

Storage (month)	Rice Form	2-AP (ng/g) at 25°C	2-AP (ng/g) at 37°C
0	Brown	562.35 ± 18.42a	562.35 ± 18.42a
0	Milled	417.24 ± 23.52j	417.24 ± 23.52h
1	Brown	485.32 ± 12.24b	374.21 ± 15.35b
1	Milled	395.75 ± 16.43d	328.54 ± 14.72c
2	Brown	427.32 ± 21.75c	324.73 ± 11.64c
2	Milled	351.49 ± 11.51e	271.45 ± 12.82e
3	Brown	384.22 ± 9.62d	284.32 ± 17.53d
3	Milled	339.47 ± 12.57f	237.28 ± 21.41e
4	Brown	357.25 ± 7.85e	253.45 ± 9.72e
4	Milled	307.43 ± 12.53h	201.53 ± 15.17f
5	Brown	329.72 ± 14.22f	197.32 ± 14.23f
5	Milled	251.45 ± 8.51j	182.78 ± 16.45f
6	Brown	306.23 ± 14.47h	124.16 ± 12.64g
6	Milled	237.51 ± 11.72jk	107.63 ± 14.27gh
7	Brown	274.25 ± 9.81i	112.42 ± 6.82g
7	Milled	229.36 ± 12.48k	87.43 ± 11.78h

Results with different letters in the same column are statistically significant ($P \leq 0.05$).

Table 4 The changes of hexanal of brown and milled rice flour during storage.

Storage (month)	Rice Form	Hexanal (ng/g) at 25°C	Hexanal (ng/g) at 37°C
0	Brown	204.71 ± 14.64a	204.71 ± 14.64a
0	Milled	115.28 ± 9.15h	115.28 ± 9.15i
1	Brown	254.73 ± 15.26b	224.87 ± 24.76a
1	Milled	112.54 ± 21.47h	142.51 ± 14.23j
2	Brown	294.27 ± 18.26c	267.52 ± 16.75c
2	Milled	142.34 ± 15.73h	158.49 ± 11.43j
3	Brown	354.19 ± 14.24d	341.35 ± 15.27dh
3	Milled	159.85 ± 11.72h	247.25 ± 24.16ac
4	Brown	395.17 ± 14.65e	472.71 ± 15.84e
4	Milled	247.32 ± 9.53b	268.35 ± 9.56c
5	Brown	472.44 ± 17.28f	549.24 ± 22.61f
5	Milled	258.62 ± 24.19b	341.36 ± 12.79d
6	Brown	494.71 ± 14.84g	647.27 ± 17.15g
6	Milled	357.62 ± 15.35d	364.35 ± 8.46h
7	Brown	512.35 ± 17.28g	805.74 ± 12.62i
7	Milled	406.37 ± 11.45e	427.26 ± 17.44j

Results with different letters in the same column are statistically significant ($P \leq 0.05$).

This might be due to the changing of the solubility and the gelatinization of the starch and protein in the grain after storage to produce more stable substances and less solubility resulted in a harder rice grain (Asaoka *et al.*, 1985). The increase in peak viscosity showed that the starch granules of stored rice were more resistant to swelling than those of fresh rice and indicated that the capacity of the starch granules to rupture after cooking was reduced significantly by ageing of the granules (Juliano and Perze, 1984). The pasting temperature of the rice stored at 37°C was higher than that at 25°C, which might be due to higher the number of the intermolecular interaction as well as the complex molecule formation of the macromolecules more within rice at 37°C than at 25°C.

Buttery *et al.* (1983) reported being able to detect 2-AP (<0.008 ppm) in nonaromatic rice samples. The 2-AP content of three commercial basmati-type rice samples examined by Sarreal *et al.* (1997) was less than 208 ng/g. The experiments showed the decrease in 2-AP during storage. The decrease of 2-AP during storage rice at 37°C was higher than that of storage rice at 25°C.

The results demonstrate the instability of 2-AP in stored brown and milled rice. Browning volatiles detected, such as 2-AP, have been reported in cooked rice (Buttery *et al.*, 1983). 2-AP was first reported as an important aroma component of aromatic rice (Buttery *et al.*, 1988) and its occurrence in wheat bread crust, popcorn and rice cake has also been reported. Proline, a precursor of 2-AP, is also abundant in acha (Haq and Ogbe, 1995) and its Strecker degradation product, l-pyrroline (Yoshikawa *et al.*, 1965), has been shown to react readily with sugar degradation products to form 2-AP.

Hexanal was increased in the brown rice than white rice. This increasing pattern suggested that the rate of oxidation on storage is increased due to the protective bran and hull. The chemical nature of the compound that increased (n-hexanal in particular, which was by far the major component of the rice volatiles) strongly suggests that lipid oxidation, probably accelerated by lipase and lipoxygenase activity in the rice (Frankel, 1991).

CONCLUSION

In this study, the colour of stored rice was measured, to investigate the effect of storage on the colour parameters of paddy rice, brown rice and milled rice. The analyses of the colour indicated that the level of pigments of rice increased during storage. The increase in yellow pigments of brown rice indicated the bran and outer endosperm contained yellow pigment higher than endosperm and the levels of yellow pigment of stored rice at 37°C increased more than the stored rice at 25°C. To gain more insight into the different rice pigments, identification of the rice pigments present in the different storage time is needed. The study of the effect of storage time on the pasting properties confirmed that the level of peak viscosity, setback and final viscosity of stored rice were higher than that of the non-stored rice, while the pasting temperature of the milled rice flour decreased during storage. From the experiments, we determined 2-AP which is an important contributor to the character of fragrant rice flavour. The increase of this compound contributes to enhanced fragrance, as the flavour impact of this compound is critically related to its concentration. At relatively high level it contributes favourably, but at lower level it imparts an unpleasant note to rice. As the rice stored had a distinct aroma, it is probable that the level of 2-AP was rather low and that of other carbonyl compounds of off-flavours, such as hexanal, had exceeded their desirable limit. In a complex flavour system as complex as that found for rice volatiles, it is not to be expected that the origins of all components could be explained by a single mechanism, and there were operating in parallel, the magnitude of the decreases of these decreases may not involve oxidation or enzymatic activity.

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