Ageing of Stored Rice: Changes in Chemical and Physical Attributes

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ABSTRACT

Rice ageing is a complicated process, which involves changes in physical and chemical properties of the rice grain. Starch, protein and lipids are the main rice grain components which affect cooking and eating quality. While the overall starch, protein and lipid contents in the rice grain remain essentially unchanged during storage, structural changes do occur. These changes affect the pasting and gel properties, flavour and texture of cooked rice. This paper reviews research on the physical and chemical properties of the rice grain and how these change during storage. The effects of these changes on rice functionality are discussed.

INTRODUCTION

Cultivated rice (Oryza sativa L.) at present sustains two-thirds of the world’s population. Production is expected to keep pace with demand until about 2005, but forecasts give cause for concern over the longer term1. Many Asian countries are expected to move away from self-sufficiency and become net importers of rice over the next 10 to 20 years. There are a number of different markets for rice which has traditionally been thinly traded with a market of less than 5% of the c. 350 million tons of milled rice worldwide. A small amount of the rice crop is used as ingredients in processed foods and as feed but the bulk is consumed as cooked rice. This pattern of usage results in the need to store rice over varying periods. Moreover, some markets (e.g. India) have a preference for stored rice whilst others (e.g. Japan, China) favour fresh rice. Freshness is considered so highly in the Japanese market that tests are devised for its measurement2.

During storage, a number of physicochemical and physiological changes occur, this is usually termed ageing. These changes which include pasting properties, colour, flavour, and composition affect rice quality3–13. As rice ages cooked rice texture becomes fluffier and harder4,5,7,8. Pushpamma and Reddy14 reported that the optimum cooking time for milled rice was 4–6 min longer after 6 months of storage than it was at harvest. Sensory evaluation techniques have been used by several researchers to evaluate the effects of storage on end-use quality of rice15–17.

The ageing process in rice is reviewed in this paper.

RICE AGEING

Ageing commences before harvest and continues as a time, temperature and moisture dependent index10,16. Interactions amongst the variables are also important. The resulting polynomial models10 suggest that rice ageing is a complex process that is seen in the native rice grain, brown rice, milled rice, rice starch and cooked rice3,5,10,12,17,18,26. Al-
though the mechanism of rice ageing is not fully understood, appreciation of the changes during storage is important in the evaluation of milling, cooking and eating quality.

Storage conditions are important in the ageing process. Nitrogen was superior to air in preserving palatability of cooked rice during brown rice storage at 10 °C for 2 years. No great difference in quality was found between the brown rice stored in nitrogen or carbon dioxide. Storage in nitrogen had little effect on the texture changes of rice on cooking relative to storage in air. Hermetic storage of milled rice at 30 °C for 3 months under vacuum or in nitrogen, carbon dioxide, and air atmospheres had little effect on reducing sugars, fat acidity, texturometer hardness and adhesiveness of cooked rice at 14-7% storage moisture. At 15-7% moisture storage, vacuum package showed the least changes in reducing sugars, acidity hardness and adhesiveness, followed by gas package and then air package. Perez and Juliano showed that at 15 °C ageing was most significant during the first 3 to 4 months of storage.

A number of changes that impact on sensory quality have been observed in rice physical properties during storage. For example, one study identified eight textural properties that were important to sensory characteristics of cooked Cypress rice as adhesion to lips, hardness, cohesiveness of mass, roughness of mass, toothpull, particle size, toothpack, and loose particles. Postharvest storage conditions had significant effects on these properties. Tensile strength, crushing and breaking hardness and resistance to grinding increased after ageing. During ageing of freshly harvested rice, regardless of storage form – rough (i.e. unprocessed rice), brown, or milled, increase in volume expansion and water absorption was generally observed. Indudhara Swamy et al. reported an increase in water uptake for up to 1 year on storage, after which water uptake decreased, and these results have been substantiated.

**PASTING PROPERTIES**

One of the most sensitive indices of the ageing process in rice is the change in pasting properties, as measured by thermoviscometry and particularly amylography. Rice exhibits very wide ranges of cooking quality and rheological properties that are largely determined by the swelling, gelatinization and retrogradation characteristics of its starch.

The viscosity of rice paste increased dramatically after storage of milled rice. These changes depended on storage temperature and duration. For instance, starch isolated from freshly harvested rice for both waxy and non-waxy samples and stored at 29 °C for 6 months gave harder gels and higher viscosity than those of starches stored at 2 °C. However, the amylograph viscosity of pastes prepared from starch stored at both temperatures was higher than that of the corresponding fresh starch. In other studies, viscosity increased at higher storage temperature during the first three months of storage and then plateaued.

Contradictory data have been reported on the effect of ageing on amylograph peak viscosity. Amylograph peak viscosity of slurries prepared from aged rice was lower than that from fresh rice, although the opposite effect was reported by Villareal et al. (Table I). After an initial increase in amylograph peak viscosity and setback during the first 6 months of storage, a steady decrease was noted during the subsequent 3 years of storage of rough and milled rice. The peak viscosity of slurries made from medium grain rice showed a 30-50% increase during the first 3 months of storage. A similar trend was observed in the final viscosity. There was no difference in surface structure as seen by scanning electron microscopy (SEM) or in gelatinization characteristics measured by photopastegrams for starch prepared from Japanese rices stored at 23 °C and at 4 °C.

A distinction has been made between the ageing of rice flour and rice starch. Thus, Shibuyu et al. showed that the pasting properties of fresh and aged rice flours were different but that the properties of the corresponding starches did not differ. They also reported that the cell wall structure was decomposed by endo-xylanase during storage which led to the changes in amylograms of rice flours. More recently, Rapid Viscoanalysis has been adopted as the AACC approved method for rice quality assay. Figure 1 compares RVA curves for fresh milled rice and the same rice after storage for 7 and 12 months. During short term storage (<4 months) there was no change in peak viscosity (PV) but there was an increase in final viscosity (FV). After storage for 7 months, PV decreased and FV had reduced to the same value as for fresh rice. There was a significant change in breakdown at all storage times.

These changes can be attributed to the char-
Table I  Changes in amylograph peak viscosity, extractable solids and water uptake ratio of rice and rice starch gels following storage for 6 months at 2 °C and at 29 °C.

<table>
<thead>
<tr>
<th>Type of rice and form stored</th>
<th>Crop season</th>
<th>Amylograph peak viscosity of milled rice and starch (B.U.)</th>
<th>Cooking properties of milled rice</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water uptake ratio</td>
<td>Extractable solids (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 month 6 months 0 month 6 months</td>
<td>0 month 6 months</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 °C 29 °C 2 °C 29 °C</td>
<td>2 °C 29 °C</td>
</tr>
<tr>
<td>Non-waxy milled rice dry</td>
<td>772</td>
<td>778 880 2·90 2·92</td>
<td>3·06 10·1 10·7 8·1</td>
</tr>
<tr>
<td>Milled rice wet</td>
<td>718</td>
<td>773 900 2·82 2·88</td>
<td>3·03 9·1 9·5 6·5</td>
</tr>
<tr>
<td>Rough rice wet</td>
<td>718</td>
<td>720 878 2·82 2·79</td>
<td>3·03 9·1 8·4 5·0</td>
</tr>
<tr>
<td>Defatted milled rice wet</td>
<td>800</td>
<td>795 1035 2·98 3·01</td>
<td>3·20 9·4 8·2 6·1</td>
</tr>
<tr>
<td>Starch dry</td>
<td>820</td>
<td>825 1015 — — —</td>
<td>— — — — — —</td>
</tr>
<tr>
<td>Starch wet</td>
<td>720</td>
<td>970 1035 — —</td>
<td>— — — — — —</td>
</tr>
<tr>
<td>Waxy milled rice dry</td>
<td>480</td>
<td>— 550 2·47 2·35</td>
<td>2·56 17·8 17·6 15·4</td>
</tr>
<tr>
<td>Rough rice wet</td>
<td>480</td>
<td>490 635 2·47 2·48</td>
<td>2·79 20·8 18·7 16·2</td>
</tr>
</tbody>
</table>

Figure 1 RVA curves for fresh milled rice (cv. Doongara) and following storage for 7 and 12 months at 37 °C.

Figure 1 RVA curves for fresh milled rice (cv. Doongara) and following storage for 7 and 12 months at 37 °C.

characteristics of the starch granules. The increase in peak viscosity shows that the starch granules of stored rice are more resistant to swelling than those of fresh rice. The decrease in breakdown value indicates that the capacity of the starch granules to rupture after cooking is reduced significantly by ageing of the granules.

Differential scanning calorimetry (DSC) has provided valuable insights into the order-disorder phenomena of granular starches. The gelatinization of rice flour occurred at temperatures from 73 to 86 °C, with an enthalpy of 8·3 to 9·7 J g⁻¹, but was significantly affected by storage. Thus, both enthalpies and temperatures of gelatinization and retrogradation of rice flour were affected (P<0·05) by rough rice cultivar, storage temperature, moisture content, and storage duration. Rice stored at 38 °C exhibited higher gelatinization enthalpies and temperatures than those stored at 4 °C or 21 °C. Retrogradation enthalpy was increased significantly (P<0·0001) by storage of rough rice, but the peak temperature of the retrogradation endotherm was unaffected.

Recrystallization during ageing for 0–15 days was significantly suppressed by cross-linking in non-waxy rice starch. The restricted swelling and reduced hydration in starch granules resulting from the cross-linking delayed gelatinization and retrogradation. Rice amylopectin systems generally showed two stages of retrogradation behavior during short (less than or equal to 7 days) and long (greater than or equal to 7 days) storage. The enthalpy values for late and infinite retrogradation stages showed significantly positive correlations with the proportions of short chain [chain length (CL) less than or equal to 15 glucose units] and long chain (CL = 16–100 glucose units) fractions, respectively.

A weak endotherm at 47 °C to 66 °C in the DSC thermograms was attributed to the denaturation of oryzenin (rice storage protein – glutelin). Addition of the latter to isolated starch provided valuable insights into the order-disorder phenomena of granular starches. The gelatinization of rice flour occurred at temperatures from 73 to 86 °C, with an enthalpy of 8·3 to 9·7 J g⁻¹, but was significantly affected by storage. Thus, both enthalpies and temperatures of gelatinization and retrogradation of rice flour were affected (P<0·05) by rough rice cultivar, storage temperature, moisture content, and storage duration. Rice stored at 38 °C exhibited higher gelatinization enthalpies and temperatures than those stored at 4 °C or 21 °C. Retrogradation enthalpy was increased significantly (P<0·0001) by storage of rough rice, but the peak temperature of the retrogradation endotherm was unaffected.
rogradation behaviour (as measured by pulsed nuclear magnetic resonance spectrometry, NMR) of either the flour or isolated starch. It was concluded that modification of the protein component rather than starch was primarily responsible for rheological changes associated with ageing of rice flour. Cell wall affects are also involved (see below).

CHEMICAL COMPOSITION

Attempts to explain the changes in functionality associated with ageing have focused on the properties of rice components, such as starch, protein, and lipids, and the interactions between them during storage. As with functionality, changes in starch, lipid and protein components were most apparent at an elevated storage temperature although gross changes in starch, amylose, and protein contents of the rice grain were minimal. However, the alkali lability number (alkali soluble components) of both waxy and non-waxy rices increased during storage up to 7 years, indicative of some degree of de-polymerisation of the starch.

Starch and amylose

Amylose content is considered the single most important characteristic for predicting rice cooking and processing behaviour. Amylose content is directly related to water absorption, volume expansion, fluffiness, and separability of cooked grains. It is inversely related to cohesiveness, tenderness, and glossiness. The amylose acts as both a diluent and an inhibitor of swelling, especially in the presence of lipid. Bhattacharya et al. reported the importance of percentage insoluble amylose, calculated from total amylose and soluble amylose at 100°C, as a determination of rice quality.

Cooking loss and soluble amylose content in the cooking water of rice samples have been used to assess quality. The soluble amylose method was statistically more precise and efficient in indicating differences in the cooking quality of rice. The amount of leached amylose, which depended on the total amylose content of the rice, correlated positively with the texture of cooked rices, which possessed total amylose contents in the range 18.4–29.5%. It was suggested that the leached starch content resulted in a similar correlation between the setback value (as measured by amylography) and the texture of the cooked rice. However, gelatinization temperatures from DSC were not correlated with the texture of the cooked rice. Based on the results it was hypothesised that the longest amylopectin chains interacted with other rice components, and that the resultant complexes were retained in the cooked grain where they inhibited softening.

A reduction in the amount of extractable solid for aged rice was reported by Villareal et al. (Table I), although Shibuya et al. found an opposite effect. The amount of amylose from 45-mesh flour that was soluble in boiling-water decreased during rice storage. These results probably reflect the increase in water-insolubility of rice starch and protein during ageing, resulting in a slower rate of cooking.

Although there is minimal change in gross chemical composition of the rice grain during storage, some hydrolysis or degradation probably occurs, leading to a significant proportional increase in reducing sugars and a decrease in non-reducing sugars and starch. There are few, if any, reports on the ageing-induced structural changes in the starch molecule (amylose and amylopectin). This may be due to low sensitivity of analytical methods and the high concentration of starch in rice grains plus the large size of the starch molecules.

Protein

The characteristics of rice with lower protein content have been reported and it was subsequently demonstrated that protein content was inversely related to adhesiveness. The content of free amino acids increased during storage of milled rice. However, the protein content did not change during storage, although its general solubility was reduced, with the decrease in albumin (water soluble protein) solubility being greater. Bolling et al. also found a decrease in acetic acid-soluble proteins of milled rice during storage for up to 7 years. More significantly, Chrastil and Zarins reported that in both medium and long rice grains the number of disulphide bridges increased during storage. Oryzenin from the medium-grain rice contained 0.2% S (as -SH) before storage and 0.14% S (as -SH) after storage. A similar trend was found in oryzenin from long-grain rice. During storage the lower molecular weight peptides decreased and the higher molecular weight peptides
increased in both varieties. These relative changes in the distribution of peptide subunits in the oryzenin fraction caused by storage were smaller than the changes of the average molecular weight of the whole oryzenin molecule, which almost doubled during storage. These changes in peptide subunit composition could influence the association forces and thus play an important part in the increase of the apparent molecular weight of the whole (undissociated) oryzenin fraction during storage. The loss in free amino nitrogen (FAN) content of the outer layers of the rice grain during storage was also noted and related to Maillard-type non-enzymatic browning as suggested by the parallel losses in FAN and whiteness of the rice.

**Enzyme activity**

The alpha-amylase and beta-amylase activities of rough rice samples decreased significantly during storage. These changes paralleled the decrease in soluble protein in the grain. Alpha-amylase is concentrated in the bran fraction. Hence, the alpha-amylase content of milled rice is low and has a negligible effect on the amylogram, except in the case of waxy milled rice, which contains appreciable amounts of alpha-amylase in the endosperm and exhibits a lower amylograph viscosity. Peroxidase and catalase activities were lost rapidly during storage of rice. As these are easily measured, they are used as good indices of quality deterioration of rice grains during storage in Japan. Dhaliwal et al. reported that stored samples had increased activities of proteases, lipases and lipoxygenase.

**Lipid**

Rice lipids are usually stable in the intact spherosomes in the cell. However, when the lipid membrane is destroyed by phospholipase, physical injury or high temperature, lipid hydrolysis is initiated by the action of lipases. For example, the lipid content of brown rice was stable during storage for 12 months at 5°C but decreased significantly during storage at 35°C (Table II). Of the various lipid fractions, the greatest proportional change was observed in free fatty acids. Oleic and linoleic acids were quantitatively the most important fatty acids in the various lipid fractions. The proportion of oleic acid in each lipid fraction increased slightly at the expense of

Z. Zhou et al.
Table II Changes in lipid content of brown rice during storage<sup>45</sup>

<table>
<thead>
<tr>
<th>Storage temp. (°C)</th>
<th>Storage period (months)</th>
<th>Lipid content (%)</th>
<th>Lipid fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Neutral lipid</td>
<td>Glycolipid</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1.75</td>
<td>89.2</td>
</tr>
<tr>
<td>4</td>
<td>1.74</td>
<td>88.4</td>
<td>6.3</td>
</tr>
<tr>
<td>8</td>
<td>1.73</td>
<td>87.5</td>
<td>6.2</td>
</tr>
<tr>
<td>12</td>
<td>1.73</td>
<td>86.7</td>
<td>6.1</td>
</tr>
<tr>
<td>35</td>
<td>0</td>
<td>1.75</td>
<td>89.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.70</td>
<td>84.5</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.68</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.65</td>
<td>81.7</td>
</tr>
</tbody>
</table>

Mapes<sup>75</sup> suggested the complexation of free fatty acids with amylose probably occurred after starch gelatinization which explained the influence of storage on the amylograph.

Phenolic acids

Of the minor components, the phenolic acids are of particular interest because of their involvement in plant cell walls. Of course, intense interest in these compounds is also related to their physiological activity and potential dietary uses. It is this role that is currently driving research in this area<sup>76</sup>.

Grains are characterised by various phenolic acids<sup>77</sup> and particularly hydroxycinnamic acids. Among them, ferulic acid (FA) and p-coumaric acid (PCA) are the main phenolic acids present in the cell walls of monocots and especially of Gramineae<sup>78–81</sup>. Sosulski <sup>82</sup> reported that FA constituted more than 90% of the total phenolic acids in wheat flour. Data are also available on the concentration of ferulic acid in rice<sup>83</sup>. Data<sup>84</sup> reported for rice endosperm cell walls are 12 g kg<sup>−1</sup> esterified cinnamic acids comprising 9 g kg<sup>−1</sup> FA, 2.5 g kg<sup>−1</sup> PCA and 0.5 g kg<sup>−1</sup> diferulic esters. However, ferulates and diferulates are never fully released by any solvolytic method and are always underestimated<sup>85</sup>. The phenolic acids are usually concentrated in the outer aleurone layer of the seed, which is rich in arabinoxylans<sup>86</sup>. A portion of the total cinnamate exists as ferulate dimers<sup>87</sup> linked in various ways including the historically quantified O-[5-O-(trans-feruloyl)-α-L-arabinofuranosyl)-(1 →3)]-O-β-D-xylopyranosyl-(1 →4)-D-xylopyranose<sup>88</sup>. Cinnamates, and particularly FA, are introduced into cell wall matrices attached to waxy rice was lower in gel consistency and higher in amylograph viscosity after storage at 29 °C<sup>17,33</sup>. Defatting of milled rice flours increased the amylograph viscosity of waxy rice flours more than that of non-waxy rice flours<sup>74</sup>. This is probably due to higher non-starch lipid content in waxy rice than in non-waxy rice. Thus, the defatting of non-starch lipids is more effective on waxy rice than on non-waxy rice. Ageing at 25–45 °C had no apparent effect on the pasting behaviour of isolated non-waxy rice starch, but markedly affected that of the corresponding flour<sup>47</sup>.

Removal of starch lipids by more polar solvents, such as 85% methanol under reflux affected the amylogram<sup>57</sup>. Yasumatsu <sup>et al.</sup><sup>36</sup> concluded that the increase in amylograph viscosity during storage is due mainly to an increase in free fatty acids complexed with amylose. However, Donovan and

**Figure 2** Changes in carbonyl (broken lines) and free fatty acid (dotted lines) contents in raw (R) and parboiled (P) rice on semi-open storage at 60 °C in the dark<sup>66</sup>.
polysaccharides. Thus, FA becomes esterified to arabinose residues in primary cell wall arabinoxylan matrices. The attachment involves a covalent ester linkage between the carboxylate group of FA and the primary alcohol on the C-5 carbon of arabinosyl side chains attached to a xylan backbone. The formation of ferulate dimers facilitates covalent coupling of the polysaccharides by radical mediated dimerisation. As the wall lignifies, ferulates and diferulates become involved in radical cross-linking reactions with lignin monomers to intimately incorporate the ferulates into lignin.

The phenolic compounds exert a significant effect on the properties of the cell wall which is mechanically strengthened by the cross-linking (Fig. 3). The content of free phenolic acids increased during storage of milled rice. Tsugita et al. suggested the bound phenolic acids were released by enzymatic and non-enzymatic reaction and there were large increases in the concentration of p-hydroxybenzoic acid, vanillic acid, syringic acid, caffeic acid, PCA and FA when rice was stored at 40 °C (80% RH) for 60 days compared with storage at 4 °C. They considered that the change in the concentration of phenolic acids contributed partly to the change of cooking properties of aged rice. The change in the ferulic acid concentration was useful in predicting the end-use quality of grains.

**FLAVOUR**

Instrumental and sensory analyses of four popular rice varieties in Taiwan, using trained and naïve sensory panels, indicated that the composition of the volatile components of rice was complicated and no single volatile compound contributed to the characteristics of rice aroma. However, the compound, 2-acetyl-1-pyrroline has usually been identified as the most important volatile constituent contributing to the aroma in several aromatic rice varieties.

The components of cooked rice flavour change rapidly during ageing. In some cultures, rice is consumed within a month of milling, since off-flavours are noted by 2 to 4 weeks of storage. Carbonyl compounds, particularly hexanal, are suggested to be the major contributors to the off-flavour since they increase during storage. Milled and unmilled commercial rice and breeders’ aromatic rice samples contained from 10 to 110 ng g⁻¹ of 2-acetyl-1-pyrroline and from 148 to 2541 ng g⁻¹ of hexanal. During storage at 40 °C, the appearance of stale flavour corresponded to higher levels of propanal, pentanal, and hexanal with accompanying decrease in the content of linoleic and linolenic acids. Lipids were hydrolysed and oxidised to free fatty acids or peroxides, causing acidity to increase and significantly deteriorating the taste and flavour. The amount of hexanal (Fig. 4) was linearly proportional to that of oxidized linoleic acid. Propanal, pentanal, and hexanal were reported to be the major carbonyl compounds that increase the
most during storage.\textsuperscript{63,99} Formation of carbonyl compounds is attributed to oxidation of unsaturated fatty acids. Other compounds that increased during storage were butan-1-ol\textsuperscript{80}, 2-methylpropanal (isobutyraldehyde)\textsuperscript{80}, and 3-methylbutanal (isovaleraldehyde)\textsuperscript{55,100}. Nevertheless, hexanal is considered the major stale flavour constituent of cooked rice, as it more than doubled during storage of 60–75 days\textsuperscript{43,92}. Waxy rice tends to have higher carbonyl content than non-waxy rice\textsuperscript{133,88}, due to its higher content of non-starch lipids in the endosperm\textsuperscript{59}.

Lipoxygenase-3 (LOX-3) is thought to play an important role in the formation of desirable or undesirable flavour and aroma in many plant products\textsuperscript{13,67}. The LOX activity is localized in the bran fraction in rice seeds where unsaturated fatty acids represent the normal substrates that are oxidised to hydroperoxides. Total free fatty acids and linoleic acid (Table III) in four rice varieties increased\textsuperscript{13} with increasing storage at 4°C and 35°C. The amounts in glutinous varieties were also higher than those in non-glutinous varieties. However, the amounts in LOX-3-less varieties were almost the same as in normal LOX-3 varieties. The amounts of hexanal, pentanal, and pentanol in normal raw rice markedly increased during storage at 35°C (Fig. 5) whereas in rice that did not contain LOX-3 the levels did not increase to the same extent\textsuperscript{13}. These results suggest that LOX-3 is involved in the production of volatile constituents in stored rice and that the development of stale flavour is delayed in LOX-3-less rice. Moreover, the degradation mechanisms of lipid hydroperoxides in rice evidently differ from those in other plants. Hexanal is produced in rice either non-enzymatically or by an unknown pathway from linoleic acid.

The carbonyl compounds formed from the oxidation of unsaturated fatty acids can further react with sulphhydryl groups in protein molecules and reduce the content of volatile sulphur com-

### Table III

<table>
<thead>
<tr>
<th>Storage period (weeks)\textsuperscript{b}</th>
<th>Variety</th>
<th>Glutinous No LOX-3</th>
<th>Normal LOX-3</th>
<th>Non-glutinous No LOX-3</th>
<th>Normal LOX-3</th>
<th>Linoleate</th>
<th>Total FFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>246</td>
<td>228</td>
<td>99</td>
<td>111</td>
<td>170</td>
<td>334</td>
<td>253</td>
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<tr>
<td>2</td>
<td>262</td>
<td>237</td>
<td>114</td>
<td>106</td>
<td>180</td>
<td>389</td>
<td>275</td>
</tr>
<tr>
<td>4</td>
<td>264</td>
<td>244</td>
<td>125</td>
<td>157</td>
<td>235</td>
<td>454</td>
<td>306</td>
</tr>
<tr>
<td>8</td>
<td>285</td>
<td>222</td>
<td>165</td>
<td>170</td>
<td>300</td>
<td>502</td>
<td>384</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Quoted in micrograms per gram of brown rice.

\textsuperscript{b} At 35°C. Similar trends were observed at 4°C.

### Table IV

<table>
<thead>
<tr>
<th>Type of rice and form stored</th>
<th>Crop season</th>
<th>Hardness index</th>
<th>Stickiness (g/10 grains)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 month</td>
<td>6 months</td>
</tr>
<tr>
<td>Non-waxy milled rice</td>
<td>dry</td>
<td>36·6</td>
<td>41·7</td>
</tr>
<tr>
<td>Milled rice</td>
<td>wet</td>
<td>26·5</td>
<td>31·9</td>
</tr>
<tr>
<td>Rough rice</td>
<td>wet</td>
<td>26·5</td>
<td>40·6</td>
</tr>
<tr>
<td>Defatted milled rice</td>
<td>wet</td>
<td>20·6</td>
<td>20·3</td>
</tr>
</tbody>
</table>
drogen sulfide; the content of hydrogen sulfide and dimethyl sulfide (plus sulphur dioxide) was lower in stored rice, whereas that of methyl mercaptan remained high. Dimethyl sulfide was the off-flavour compound in Sake prepared from rice stored above 15 °C.

Figure 5 Typical gas chromatographic profiles of headspace volatiles in raw brown rice seeds with and without LOX-3 during 8 weeks of storage. Profiles are shown for fresh brown rice (variety lacking LOX-3) before (a) and after storage at 35 °C (c); normal brown rice before (b) and after storage at 35 °C (d). Peaks are identified as (1) acetaldehyde; (2) acetone; (3) methanol; (4) ethanol; (5) pentanal; (6) chloroform; (7) hexanal; (8–11) unknown; (12) pentanol.

TEXTURE OF COOKED RICE

Cooked rice texture has been shown to govern the acceptance of rice by consumers when consumed as the whole grain. Texture has been defined as a multidimensional characteristic that only humans can perceive, define, and measure. Thus, sensory evaluation is critical although instrumental measurement of textural properties is also common practice. For instance, the Ottawa extrusion cell has been used for predicting cooked rice texture in conjunction with a miniature extrusion cell and a novel data analysis method called Spectral Stress Analysis (SSA). Although texture is multidimensional, hardness and stickiness are critical and these textural characteristics govern palatability of cooked rice in Asian markets, with hardness being the most important and most commonly measured parameter.

Rice texture is affected by factors such as variety, amylose content, gelatinization temperature, processing factors and cooking method. For instance, cooked rice with low amylose is soft and sticky, while rice with high amylose is firm and fluffy. Lyon et al. reported that sensory properties relating to stickiness had statistically significant correlation coefficients with amylose content (+0·31) and protein content (−0·67). Most hardness indices were positively correlated with amylose content, whereas indices of stickiness were negatively correlated with amylose content. Other important sensory textural characteristics were the mouthfeel properties of residual loose particles, toothpack and starchy mouthcoating, which showed significant correlation coefficients with protein content (+0·31). However, attempts to predict textural properties of cooked rice from compositional characteristics are still inadequate.

Storage time, temperature and duration influenced the texture of cooked milled rice. The texture of cooked aged rice was harder and less sticky than cooked freshly harvested rice, as measured by both sensory methods and textural evaluation methods.
The Instron cooked rice hardness value of seven milled rices stored at 28–30°C increased from 5·8 to 6·9 kg during 3 months of storage and then levelled off. Meullenet et al. investigated the effect of storage conditions on long grain rough rice on sensory profiles of cooked rice using sensory descriptive methods. They evaluated 10 sensory attributes and storage temperature influenced only textural characteristics. Perceived intensities from clumpiness, hardness, glueiness, cohesiveness of mass, and geometry of slurry were significantly different for samples stored at various temperatures (4, 21 and 38°C). Clumpiness and glueiness significantly decreased as storage temperature increased from 4°C to 38°C. Cooked kernel hardness was significantly greater in rice stored at 38°C whereas cohesiveness of mass significantly decreased with increasing storage temperature. Finally, the geometry of the slurry was grittier for samples stored at 38°C as compared to those stored at 4°C. Similarly, rice stored at 40°C showed a harder and less sticky texture when cooked than that stored at 4°C. During storage, retrogradation of the starch led to an increase in hardness as well as a decrease in the adhesion of cooked rice. In general, as the degree of starch retrogradation increased during storage, rice firmness increased and stickiness decreased.

In summary, hardness increases during storage, although some work suggests that hardness reaches a maximum and then declines. Most indices of hardness showed significant negative correlation with stickiness indices. Hardness was also affected by storage moisture content (R² = 0·38). Tamaki et al. reported that rice stored at 12% moisture content was initially found to be harder than rice stored at 15 or 18% moisture content. Meullenet et al. also found similar results in that cooked kernel hardness decreased with increasing storage moisture content and reached a maximum between 15 weeks and 22 weeks of storage depending on the rough rice storage moisture content. A significant interaction was found between rough rice moisture content and storage duration. Increasing rough rice moisture contents delayed the perception of maximum hardness, although Champagne et al. reported no difference in hardness as rough rice moisture content increased.

Stickiness was greatest when a rice was freshly harvested and decreased with ageing or when treated to accelerate ageing. Tamaki et al. reported that rice stickiness measured by instrumental methods decreased consistently during the first 90 days of storage regardless of storage moisture content or storage temperature. Meullenet et al. also reported that storage temperature and duration significantly affected adhesives to lips, an indicator of rice stickiness (R² = 0·58). Increasing storage temperature decreased rice stickiness. On the other hand, Tamaki et al. reported that rice stickups reached a maximum after 20 weeks of storage and decreased significantly after 36 weeks of storage.

**Figure 6** Schematic model of the aging process in rice. Modified from.

### MECHANISM OF AGEING

Moritaka and Yasumatsu proposed a mechanism of ageing involving lipids and proteins. Lipids form free fatty acids, which can complex with amylase and carbonyl compounds and hydroperoxides, which can accelerate protein oxidation and condensation plus accumulation of volatile carbonyl compounds. Protein oxidation (formation of disulfide linkages from sulphhydryl groups), together with an increase in the strength of micelle binding of starch, inhibits swelling of starch granules and affects cooked rice texture. Mod et al. proposed that oxidation of ferulate esters of hemicellulose would contribute to cross-linking and increased strength of cell walls during storage.

It is apparent that ageing is a complicated process involving physical, chemical, and biological change. We propose that release of free phenolic acids alters integrity of the cell wall and at the same time the phenolic acids exert an effect via their antioxidant activity on the formation of FFA that can further complex with amylase during storage. A model for the ageing process is presented in Figure 6.
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REFERENCES

1. International Rice Commission, FAO.


AUTHOR QUERIES

Folio 2 - ? Keywords after Abstract.
Folio 3 - Please check sense of sentence - There are a number of different markets... - and change if necessary.
Folio 14 - Please check sense of sentence - Data reported for rice endosperm cell walls... - and change if necessary.
Table IV - Not cited in text.
References - All journals should be spelt out in full.
Reference 1 - Please supply more info.
Reference 58 - ? initials for Oñate.