Note

Near Infrared Spectra of the Outer Layer of Flour of Stored Milled Rice

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Near infrared (NIR) diffuse reflectance spectrophotometry was applied to measure stored milled rice by focusing on the outer layer flour. Rice grains milled 90% were stored at 37°C and 75% humidity for 0–45 days. NIR and chemical analyses were performed separately on the outer and inner layers and whole flours of the sample. The most sensitive variation during storage of the absorption intensity by NIR is found on the outer layer flour at the near-infrared region of 2300–2310 nm which corresponds to fats; the fat content of the outer layer extracted by ether was about 15 times that of the whole layer flour.

Keywords: outer layer flour, milled rice, near infrared spectroscopy, storage

Near-infrared (NIR) spectroscopic analysis is one of the most sensitive methods that can be applied to characterize various infrared-active food materials. This method is versatile and convenient because it is nondestructive and rapid (Onda *et al.* 1994; Hong *et al.* 1994). It has been employed to evaluate the palatability of rice (Iwamoto, 1992). In this work, we attempt to analyze stored milled rice by NIR. We have focused on the outer layer analysis to develop a sensitive NIR method for monitoring the change in stored rice.

It is well-known that the decrease in the palatability of milled rice during storage is caused by changes in the lipid (Yasumatsu *et al.*, 1964, 1965; Shibuya *et al.*, 1974) and protein compositions (Moritaka *et al.*, 1971) and their combination with starch (Moritaka & Yasumatsu, 1972). The content of free fatty acids increases due to the degradation of neutral fat during storage (Shibuya *et al.*, 1974). Phospholipids decrease rapidly prior to the degradation of non-polar lipids (Takano, 1989). These components other than starch are present more in the outer layer of milled rice than in the interior (Barber, 1972). This is the reason why we pay attention to the outer layer analysis.

Materials and Methods

Sample rice Five samples of “Nipponbare” grown in Shiga Prefecture (1995) were used. Brown rice was stored at 4°C in kraft paper bags. Brown rice was milled 90% in a polishing machine (Toyo Tester, Toyo Seiki Co., Ltd., Tokyo).

Rice storage Milled rice grains of 265 g in a mesh bag made of polyethylene (210×110 mm) were placed in a vessel (250×120×45 mm) having upper and lower sections. Saturated NaCl solution (100 ml) was placed in the lower section to maintain the humidity at 75% relative humidity. The milled rice in the vessel was stored at 37°C for 0–45 days.

Grinding Milled rice grains after storage were ground in a grinder (Cyclone Sample Mill, UDY Corporation, USA)

to a flour form (whole). The outer layer was milled 90–86% by a miller (Satake Grain Testing Mill, Tokyo). The flour was sieved through 355 μ m apertures. The inner layer milled 86–0% was prepared by a grinder.

Measurement of components Moisture contents were measured by drying at 135°C for 3 h. Crude fat contents were measured using ether in a Soxhlet apparatus operated for 24 h. Crude protein contents were determined by the Kjeldahl method. Crude ash contents were obtained by heating the samples at 550°C for 15 h.

Defatting Ether was added to the outer layer flour, and the mixture was kept at 20°C for 24 h with stirring. The ratio of the solvent to the sample was 5 : 1 (v/v). After filtration, the flour was dried at room temperature for several hours to remove the solvent.

NIR analysis NIR analysis was performed using an NIR system Model 6500 (NIRECO Co., Ltd., Tokyo) from 1100 to 2500 nm at intervals of 2 nm. The flour samples of about 6 g were placed in the cell (for powder), and the diffuse reflectance spectra were measured at room temperature and recorded as $\log (1/R)$ (R : reflectance).

Results and Discussion

Comparison of components of outer and inner layers and whole flours First of all, we mechanically separated the outer and inner layer portions to examine how the chemical components differed. As shown by the results of the chemical analysis in Table 1, the crude protein, fat and ash are present more in the outer layer than in the inner layer and the whole. This is true not only for the control rice but also for the stored sample. The ratio of the crude fat extracted by ether in the outer layer to that in the whole amounts to 15 : 1. Although the outer layer flour is composed of only about 4% (w/w) of the whole, almost all the crude fat is localized in the outer layer.

After the 45 day storage, the crude fat showed a significant change only in the outer layer; a *t*-test was done. Although crude protein is distributed more in the outer layer, it was

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Table 1. Comparison of components in the outer, inner layers and whole flours (%).

Sample	Storage days	Moisture	Crude protein	Crude fat	Crude ash
Outer layer	0	12.6±0.2	15.0±0.1	4.6±0.02	2.3±0.04
	45	12.5±0.3	14.9±0.1	4.1±0.02	2.3±0.03
Inner layer	0	13.4±0.2	5.0±0.1	0.2±0.04	0.2±0.01
	45	13.5±0.2	5.0±0.1	0.1±0.05	0.2±0.01
Whole	0	13.2±0.1	5.3±0.1	0.4±0.02	0.3±0.02
	45	13.3±0.2	5.4±0.2	0.3±0.02	0.3±0.01

Samples were stored at 37°C/75% RH.

Fig. 1. Second derivative near-infrared spectra of the outer, inner layers and whole flours of milled rice. R , reflectance; λ , wavelength. The spectra for the 0 and 45 storage days overlap each other in all the layers. The inner layer and the whole show exactly the same spectra.

hardly affected by storage. These results correspond to the previous reports that the taste and flavor of cooked rice are improved by increasing the degree of polishing (Kainuma, 1979), thus defatting the milled rice (Moritaka *et al.*, 1971).

Standing time-dependent NIR spectra of outer layer flour As suggested above, the NIR intensity of the outer layer flour can be useful as a sensitive measure of the storage change in milled rice.

We have obtained the NIR spectra in the region of 1800–2500 nm where the powder samples provide high quality spectra. In Fig. 1, the NIR spectra of the control (not stored) and that of the stored sample for 45 days are compared. It is found that a detectable change in the spectra is observed at 2300–2310 nm only in the outer layer flour and that this band becomes weaker with storage time.

How the intensity of the band at 2300–2310 nm for the

Fig. 2. Storage time dependence of second derivative near-infrared spectra of the outer layer flour of milled rice. R , reflectance; λ , wavelength. The curves are 0, 7, 15, 30 and 45 days.

Fig. 3. Comparison of second derivative near-infrared spectra of defatted and non-defatted outer layer of milled rice. R , reflectance; λ , wavelength.

outer layer flour varies with storage time is illustrated by the expanded spectra in Fig. 2. We can observe the change in the 2300–2310 nm band as a sensitive NIR measure. Analysis of the spectra changes over the whole wavelength region has led us to conclude that the NIR band at 2300–2310 nm provides a potential measure of the freshness of rice and that we need to focus on the outer layer portion of rice.

Although the NIR band at 2300–2310 nm has been variously interpreted (Aramaki *et al.*, 1995; Kamishikiryō *et al.*, 1992), the present study is in favor of the assignment to fats. To confirm this, we have examined the effect of defatting on the NIR band. If the assignment is precise, the defatting is expected to have a remarkable effect on the spectra.

Figure 3 shows the second-derivative spectra of the defatted flour of the outer layer of the control and the 45 day stored

samples together with those of the non-defatted flour of the control. Ether used here for the defatting is unable to extract fats in the starch, the starch-fatty acid complex. Therefore, the disappearance of the absorption at 2300–2310 nm after the defatting cannot be ascribed to bound fats but to extraneous lipids. It is concluded that the spectra change in NIR in the outer layer flour of stored milled rice is associated with the labile lipids.

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