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CALORIMETRIC STUDIES ON THE SWELLING OF RICE. II. EFFECT OF STORAGE TIME ON HEAT OF SWELLING

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ABSTRACT

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Differences in heats of swelling of aged rices (stored for 2 to 6 years) were measured at 30°C. Total heats of swelling (about 8 J/g at 30°C) do not change appreciably with the age of rice. The thermograms, however, differ with the different lengths of storage. That is, the heat of swelling of longer-stored rice evolved more slowly than that of fresh rice. Suito plots of $\log\left(\frac{Q}{W}\frac{dx}{dt}\right)$ *vs.* time, t, become two consecutive straight lines with a single break. The time from beginning of the reaction to the break point, t_i, is closely related to the age of rice. Degree of polishing of rice has no effect on t_i values, but the moisture content of rice has a large effect. The t_i values of the rices which have been stored at equal moisture content (14% of its weight) have a linear relationship to the age of rice.

The heat of swelling of rice kernels was measured and discussed in a previous report (1) and it was found that the heat of swelling of rice was about 8 J/g rice at 30°C. Starch molecules in the rice kernels form hydrogen bonds with water molecules when swelling occurs; the heat of swelling is due to the energy of hydrogen bonds. The quality of rice deteriorates when stored for a long time, *e.g.*, 2, 3, or more years. It is possible that the tissue of rice might change on storage and, with it, the amount and rate of absorption of water. Thus, one would expect that the heats of swelling would vary with the differences in absorption of water between fresh and long-stored rice. Change in the quality of rice could then be evaluated by calorimetric measurement. In this study we investigated the correlations between heats of swelling and the age of the rice.

MATERIALS AND METHODS

Samples

The Koshiziwase strain of rice cultivated at Niigata prefecture in 1966, 1967, and 1969, and at Toyama prefecture in 1970, and the Honenwase strain cultivated at Toyama prefecture in 1967 and 1968 were used. Unknown strains cultivated at Niigata prefecture in 1967 and 1968 were also used. These samples were kindly supplied by the Osaka Daiichi Shyokuryo Cooperative Society.

Methods

These rices had been stored as brown rice and were polished by a laboratory polisher (Kett) just before the experiments. The moisture of the polished rices was measured by oven-drying at 105° C. To obtain the rices which have different moisture content, the moisture of the samples was controlled by their equilibration at different humidities determined by the density of different aqueous solutions of sulfuric acid at 30° C. In order to get rices which have as equal a moisture content as possible, moisture of the samples was controlled at 75% humidity at 30° C for 30 days. For calorimetry, a twin conductive calorimeter CM204S1 (LESCA Co., Ltd., Japan) and ampoule-type cells were used in the manner previously reported (1). About 1 g of white rice (about 55 grains) was sealed in a glass ampoule. After reaching the equilibrium temperature at 30° C, the ampoule was broken in the reaction cell, so that the sample was thrown into 30 ml of distilled water. The heat of swelling (Δq in J/g rice) was calculated from the area between the thermogram and the base line compared with the area of a thermogram of a known heat. The present experiments were carried out in January and February, 1973.

Theoretical

If we define $\frac{dT}{dt}$ as change of temperature, T, in the reaction cell with time, t, $-\frac{dT'}{dt}$ as rate of cooling, W as heat capacity of the reaction system, Q as heat of the reaction, $\frac{dx}{dt}$ as rate of the reaction, and x as the amount of substrate which has already reacted, the following equation is valid:

$$\frac{dT}{dt} - \frac{dT'}{dt} = \frac{Q}{W} \cdot \frac{dx}{dt} \qquad (1)$$

If it is supposed that cooling follows Newton's law, the following equation is valid according to Suito (2):

$$-\frac{dT'}{dt} = K \cdot \Delta T = K\,(T - T_o) \qquad (2)$$

where T is the temperature of the reaction cell, T_o is the external temperature, and K is the cooling constant of the reaction system. Substituting equation 2 for equation 1, we get the following equation,

$$\frac{dT}{dt} + K \cdot \Delta T = \frac{Q}{W} \cdot \frac{dx}{dt} \qquad (3)$$

and $\frac{dT}{dt}$ can be obtained from the slope of the tangent line on any point of the reaction curve (ΔT *vs.* t curve). Thus, if the cooling constant, K, is known, $\frac{Q}{W} \cdot \frac{dx}{dt}$ can be easily computed from equation 3. If the plots of $\log\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)$ *vs.* time, t, give a straight line, the reaction is first order. And if k_1 is defined as the reaction constant, the equation of the first-order reaction can be written as follows:

$$\frac{dx}{dt} = k_1\,(a-x) = k_1\, a \times 10^{-k_1 t/2{,}303} \qquad (4)$$

where a is the initial density of the substrate.

Replacing equation 4 for equation 3,

$$\frac{dT}{dt} + K \cdot \Delta T = \frac{Q}{W} \cdot \frac{dx}{dt} = \frac{Q}{W} \cdot k_1 a \times 10^{-k_1 t/2{,}303} \tag{5}$$

Taking logarithms of both sides, we get the following equation:

$$\log\left\{\frac{dT}{dt} + K \cdot \Delta T\right\} = \log\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right) = \log \frac{Qk_1 a}{W} - \frac{k_1 t}{2{,}303} \tag{6}$$

Thus, from the slope of the plots of $\log\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)$ *vs.* time, t, we can compute the first-order reaction constant k_1.

Analysis of the thermogram of the swelling of rice at 30°C using the above equation yields a curve such as the one shown in Fig. 1. The cooling constant of the system, K, is a constant peculiar to the equipment at a given temperature and can be calculated by the Guggenheim method (3). In the case of rice kernels, the plot $\log\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)$ *vs.* t becomes two consecutive straight lines meeting at one point as shown in Fig. 1. Therefore, t_i is taken as the time from the beginning of the reaction to the break point.

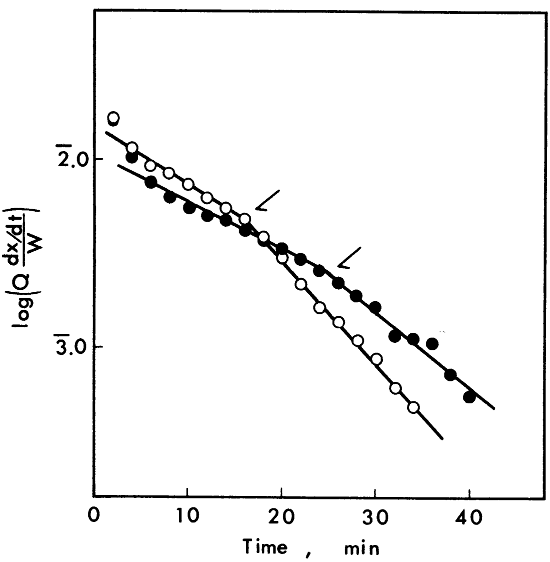

Fig. 1. Suito plots of heat evolution for rice of different storage age. (√ shows the break point.) —O— Koshiziwase strain stored for 2 years, and —●— Koshiziwase strain stored for 6 years.

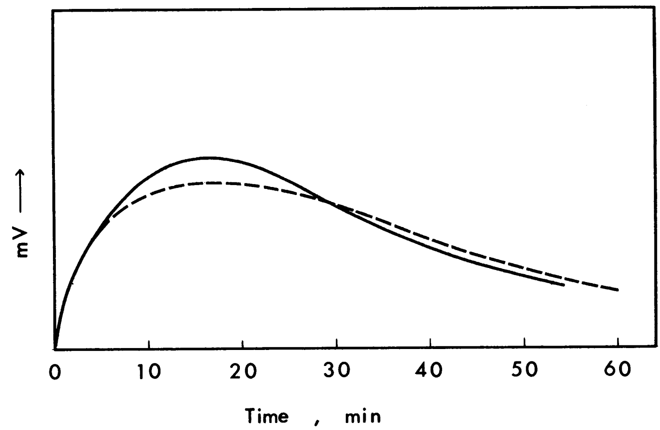

Fig. 2. Thermograms of the swelling of polished rice grains at 30°C. The solid line represents the rice stored for 2 years; the dotted line shows rice stored for 6 years. The thermogram is plotted as change in millivolts (mV), which is proportional to T.

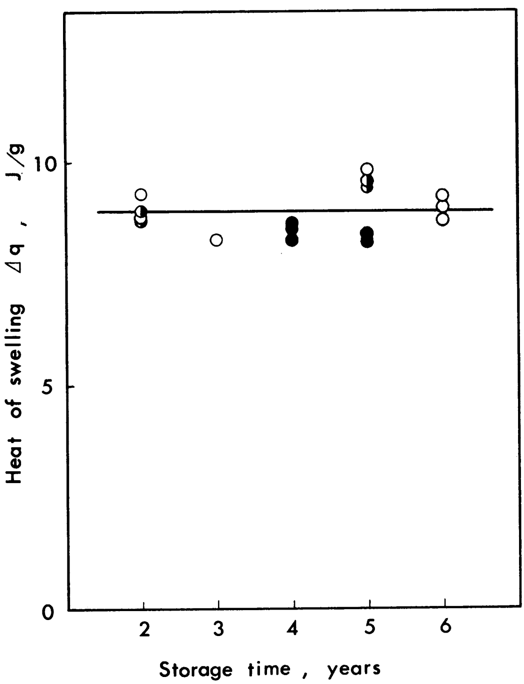

Fig. 3. The effect of storage time on heat of swelling. —O— Koshiziwase strain, —◑— Honenwase strain, and —●— unknown strain.

RESULTS

Heat evolution occurred immediately upon entry of the sample into the water. Figure 2 shows the thermograms of swelling of Koshiziwase rice cultivated in 1966 and 1970 (stored for 6 and 2 years, respectively). Change in mV reveals the change of temperature in the cell. The thermograms differ with the age of rice. In the case of longer-stored rice, the thermogram has a broader peak because the reaction proceeded more slowly. Figure 3 shows the total heats of swelling (Δq in J/g) of all the samples. From these data, no influence of storage time on total heat of swelling is shown. Analysis of the thermograms of Fig. 2 with equation 6 shows that t_i values of the older rice were greater than those of the fresher rice, as shown in Fig. 1.

To see the effect of the degree of polishing and moisture content on t_i values, the following experiments were done. Figure 4 shows the plots of $\log\left(\frac{Q}{W}\cdot\frac{dx}{dt}\right)$ *vs.* t for rice samples which have received different amounts of polishing. When the rice was polished for 1 min, the residual grain was 92.5% by weight of the brown rice. When the rice was polished for 2 min, the residual grain was 90.2%, and for 3 min it was 86.7%. (Rice polished for 2 min is ordinary white rice.) The plot for brown rice is a straight line, but that for white rice polished 1, 2, or 3 min shows a single break, and the t_i values of all samples are almost the same. Figure 5 shows the plots of $\log\left(\frac{Q}{W}\cdot\frac{dx}{dt}\right)$ *vs.* t of some polished samples which have different

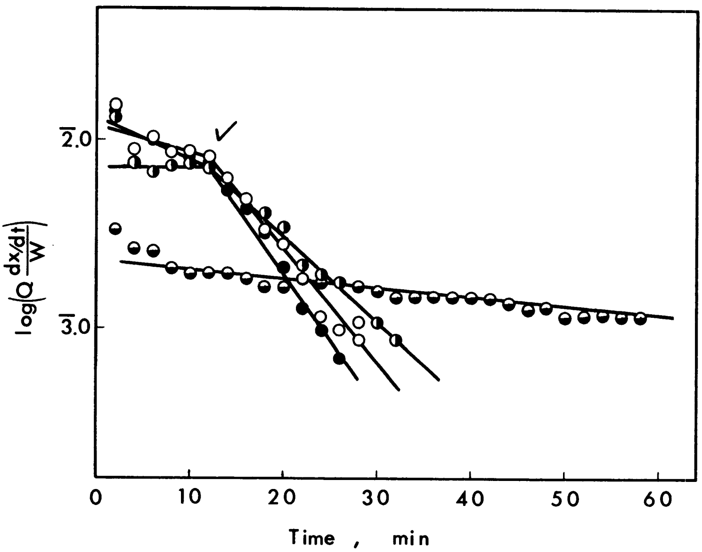

Fig. 4. Suito plots of heat evolution with different conditions of polishing. (√ shows the break point.) —◒— Brown rice, —◑— polished for 1 min, —O— polished for 2 min, and —●— polished for 3 min. Sample: Koshiziwase strain cultivated at Niigata prefecture in 1970.

moisture contents. The equilibrium moisture of untreated rice was 14.04%. As shown in Fig. 5, t_i values increase with the increase in moisture content. Therefore, the relation between t_i and age of the rice is valid only when the moisture contents are kept as equal as possible.

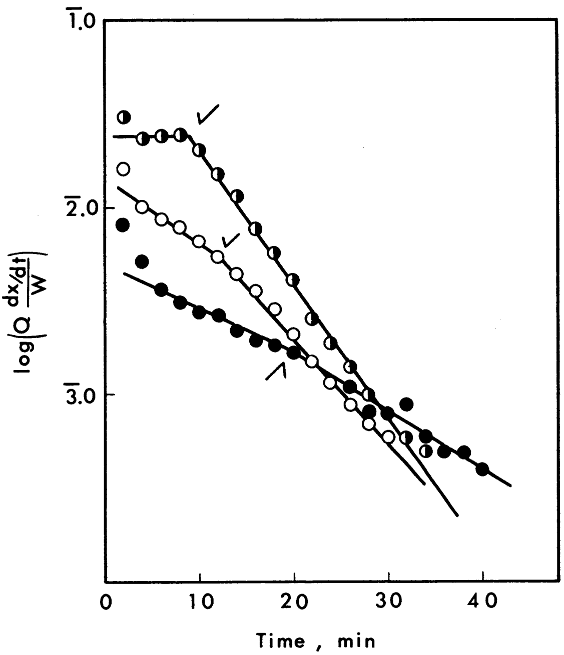

Fig. 5. Suito plots of heat evolution for rice samples with different water contents. The t_i values are defined in the text. (√ shows the break point.) —◐— Moisture = 10.54%, t_i = 10.7 min; —O— moisture = 14.00%, t_i = 14.0 min; and – ● – moisture = 16.23%, t_i = 20.2 min. Sample: Koshiziwase strain cultivated at Niigata prefecture in 1970.

TABLE I
List of the Samples and their Moisture Contents after being Equilibrated against Fixed Aqueous Solutions of Sulfuric Acid at 30°C (75% R.H.)

Rice Strain	Place Cultivated	Year	Equilibrium Moisture % Wet Basis
Koshiziwase	Niigata	1966	14.22
Koshiziwase	Niigata	1967	13.97
Koshiziwase	Niigata	1969	14.38
Koshiziwase	Toyama	1970	14.19
Honenwase	Toyama	1967	13.72
Honenwase	Toyama	1970	14.28
Unknown	Niigata	1967	14.38
Unknown	Niigata	1968	13.84

The moisture contents of samples after equilibration under 75% humidity at 30°C for 30 days are listed in Table I. The contents were not absolutely equal because of variations in the nature of the samples, but rice moisture could be controlled to an average of 14.12 ± 0.4%. From the results of the calorimetric determination of the swelling of these moisture-controlled samples, we get t_i values from equation 6, and the values are plotted in Fig. 6. Age of storage of rice and t_i values have a nearly linear relationship.

DISCUSSION

During long storage, rice tissues and starch granules must change, so that the characteristics of water absorption of the rice differ with different storage times. Therefore, the heat of swelling must be influenced by the time of storage of rice. As shown in Fig. 3, total heat of swelling of long-stored rice apparently did not differ appreciably from that of fresh rice. It is obvious, however, that there were differences in the thermograms as shown in Fig. 2. That is, in the case of fresh rice, evolution of heat is fast and the peak is higher and sharp, but for long-stored rice the heat evolves more slowly and the thermogram shows a broad curve. The results mean that absorption of water in old rice requires a longer time than that

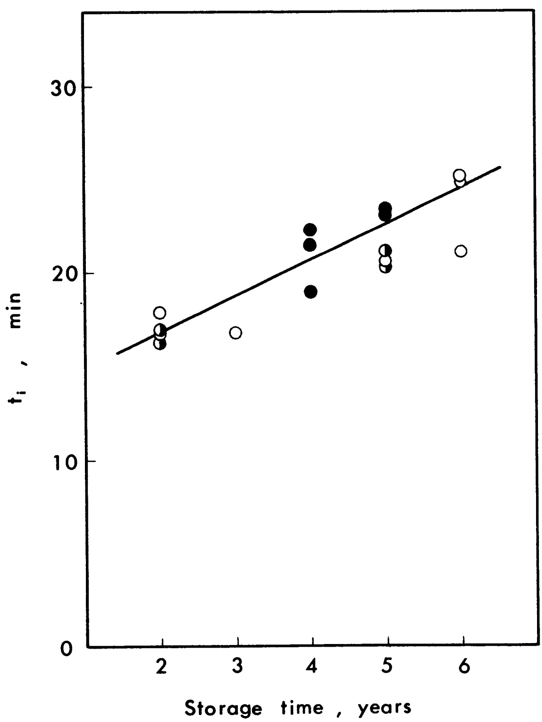

Fig. 6. Relation between storage age of rice and break points in the Suito plots. —O— Koshiziwase strain, —◐— Honenwase strain, and —●— unknown strain.

of fresh rice. In order to obtain quantitative results, the data in the thermogram were analyzed with equation 6.

The t_i values obtained by plotting log $\left(\frac{Q}{W} \cdot \frac{dx}{dt}\right)$ *vs.* t according to equation 6 are little changed by the rice-producing district, species of rice, and degree of polishing, as shown in Fig. 4. However, when the moisture contents of the rices are controlled, it is clear that the age of the rice is closely related to t_i values, as shown in Fig. 6.

The stored age of rice can be determined by several methods: one is to measure its ability to germinate (4), another is to measure its enzymatic activities, such as catalase or peroxidase (5), and still another is to measure the acidity of its free fatty acids (5). From the results shown above, we suggest that the calorimetric method of measuring rice swelling may become a valuable method for determining the age of rice from a single batch. But, as the sample size for calorimetry is about 1 g, this method cannot be applied at present for mixed rices which are of different ages.

Acknowledgments

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