Calorimetric Studies on Swelling of Rice. I. Swelling of Rice Grain and Rice Powder

T. KANEMITSU and K. MIYAGAWA, Osaka Joshigakuen College, Tennoji, Osaka, Japan

ABSTRACT

Heats of swelling of rice kernel (white rice) and rice powder were measured at 30°C. Rice kernel with about 14% moisture content evolves heat of 1.6 to 2.1 cal. per g. rice with swelling. Degree of polishing of rice has no effect on water absorption and heat of swelling. Heat of swelling of rice powder is a little larger than that of rice kernel and the finer the powder, the greater the heat of swelling. Calorimetrically, swelling of rice powder follows the first-order reaction, but swelling of rice kernel does not. That is, the plotting of first-order reaction of swelling of rice kernel is not straight-line but twofold. The reaction velocity constant, *k*, of the first-order reaction, increases with the diameter of the powder particle and *k* also is proportional to the total surface area of the powdered grain.

Physicochemical studies are important to the fundamental knowledge of rice. Some of the properties that have been commonly studied include granule density, granule diameter, alkali lability of rice starch, rate of swelling, and rheological changes that occur when starch or rice is cooked. Since the initial step in all such work involves the addition of water to rice, it appeared desirable to investigate the energy released under these conditions.

The literature revealed only a few references to heat of hydration of starch (1,2); no measurement at all has been made on the heat of swelling of rice kernels. A rice kernel is not a pure substance but a complex, multicomponent system, and its swelling involves adsorption, absorption, permeation, diffusion, etc. Therefore, it is difficult to analyze the thermal data. Even though thermal measurement on swelling has such defects, thermal behavior might reflect chemical and physical changes on swelling.

In the present studies, heats of swelling of rice kernels and rice powder were measured by twin-type calorimeter, and swelling of rice is also discussed.

MATERIALS AND METHODS

Calorimeter

A twin conductive calorimeter CM204 S1 (Applied Electric Lab., Ltd.) was used. The symmetrical twin cells are in an aluminium block that has a large thermal capacity. One of the cells is for the reference material and the other is for the reaction. About 1 g. of sample was enclosed in the glass ampoule. After the system had reached thermo-equilibrium, the sample was thrown into 30 ml. of distilled water (30°C.) by breaking the ampoule.

Calibration of the calorimeter system was made by sending known amounts of electric current to the heater mounted in the calorimeter and measuring the temperature change in the reaction cell. From the integral of this thermogram we can obtain the area of thermogram per calorie.

Because the calorimeter is a conductive type rather than an adiabatic, an exotherm coincides with cooling. If we define $g(t)$ as the observed temperature change, at time t in a calorimeter and $f(t)$ as the true temperature change of a thermal process, we get the following equation:

$$\frac{dg(t)}{dt} = \frac{df(t)}{dt} - Kg(t) \tag{1}$$

where K is the cooling constant of the system. Integral of equation 1 is:

$$f(t) = g(t) + K\int g(t)dt + g_0 \tag{2}$$

where g_0 is an integral constant which is reduced to zero by the nature of the problem. If the cooling constant, K, can be calculated from the Guggenheim method (3) and $\int g(t)dt$ can be measured by weighing, equation 2 can be applied to a kinetic study of the thermal process. Plotting $f(t)$ versus t, a curve is obtainable which shows the thermal process (4).

Sample and Material

Manryo strain cultivated at Shiga Prefecture in 1968, and Koshiziwase strain cultivated at Niigata Prefecture in 1970, were secured from Daiichi Shyokuryo

Co-operative Society. Moisture of the former was 14.3% and the latter was 13.9%. A laboratory polisher (Kett TP-2) was used to polish the samples. Figure 1 shows the relation between the polishing time and residual grain for Manryo. Nearly the same results were obtained with Koshiziwase. The rice polished for 2 min. retains 90% of its original weight which is ordinary cleaned rice (polished rice). With longer polishing times, the rice was not only cracked on the surface but broken as well. For milled rice (rice powder), the rice was milled with the laboratory mill and separated with sieves as listed in Table I.

RESULTS

Figure 2 shows the relation between the residual portion of the polished rice and water absorption. Water absorption was calculated from weights of rice before and after swelling. It was impossible to avoid some errors in weighing the rice after swelling because of excess water which was adsorbed on the surface of the rice; the rice was weighed after removing the excess water on the surface with filter paper. In the range of residual grain from 80 to 100%, amounts of water absorption of Manryo were 0.24 to 0.25 g. H_2O per g. rice. The size of the residual grain showed no effect on water absorption.

Figure 3A shows the thermogram of swelling of the rice grain. When the rice was thrown into distilled water, immediate evolution of heat occurred. The change of temperature in the reaction cell reached maximum after 20 to 30 min. and returned to the base line within 2 to 3 hr. From the integral of this thermogram, the total calories of the swelling were obtained.

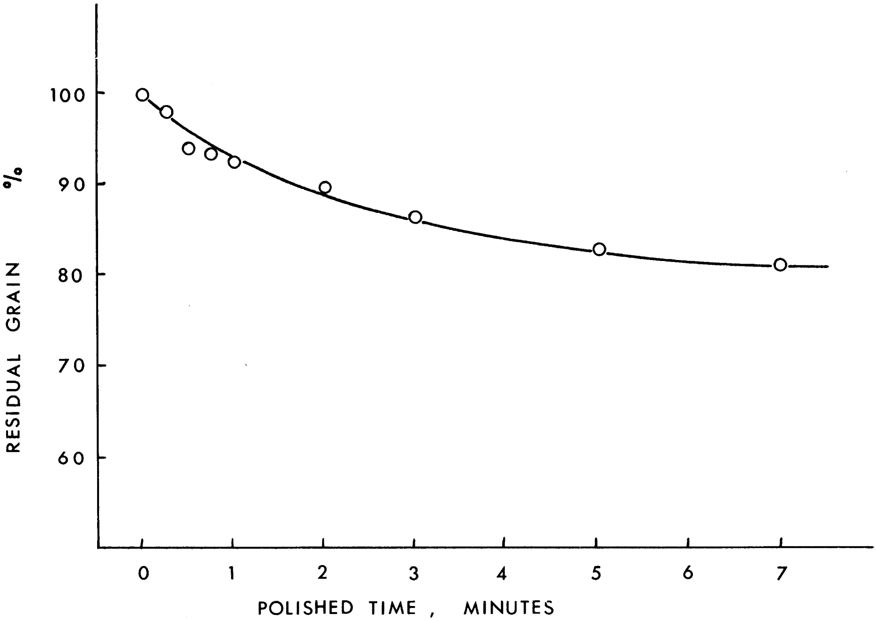

Fig. 1. The relation between polishing time and size of residual grain. Laboratory polisher was used with 1,250 r.p.m. Residual is shown as weight percent. Sample: Manryo.

TABLE I

	Sample	Mesh	Mean Diameter of Particle
Rice grain	1		Long axis 4.0 mm., short axis 2.5 mm.
Rice powder	2	on 9	2.5 mm.
Rice powder	3	9 to 16	1.5 mm.
Rice powder	4	16 to 32	0.75 mm.
Rice powder	5	through 32	0.4 mm.

Figure 4 shows the relation between the total calories of the swelling and the residual grain. In the range of residual grain from 80 to 100%, the total calories of swelling were 1.8 to 2.0 cal. per g. rice, and no change was found in calorie of the swelling with the size of the residual grain.

Figure 3B,C shows the thermogram for the swelling of some of the rice powders. If we convert the thermograms to curves in a manner which is shown in equation 2, it is found that the time from beginning to end of heat evolution was shorter than that of the rice grain. The rice grain needed 30 to 40 min. from the beginning to the end, while the finest powder (through 32-mesh) was ended within 4 or 5 min. after beginning of the reaction. Figure 5 shows the relation between diameter of the milled rice and the total heat which was obtained from thermograms such as Fig. 3. In case of rice powder of mesh 9 to 16, for example,

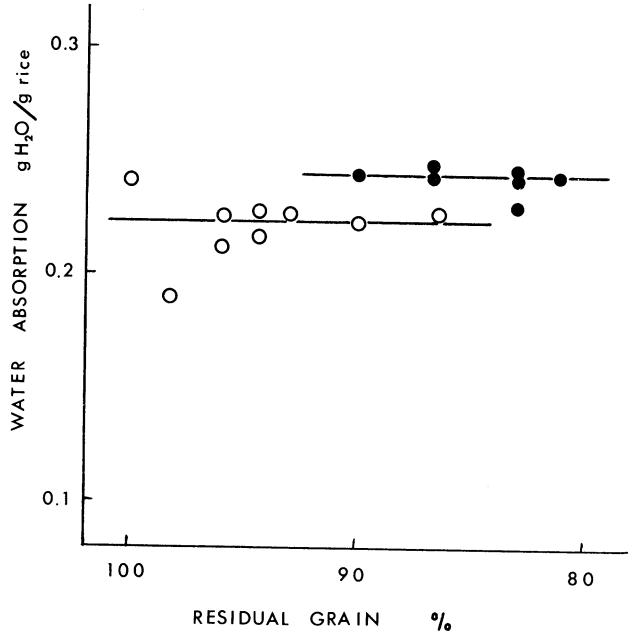

Fig. 2. The effect of size of residual grain on water absorption. —○—, Manryo strain cultivated in 1968; —●—, Koshiziwase strain cultivated in 1970.

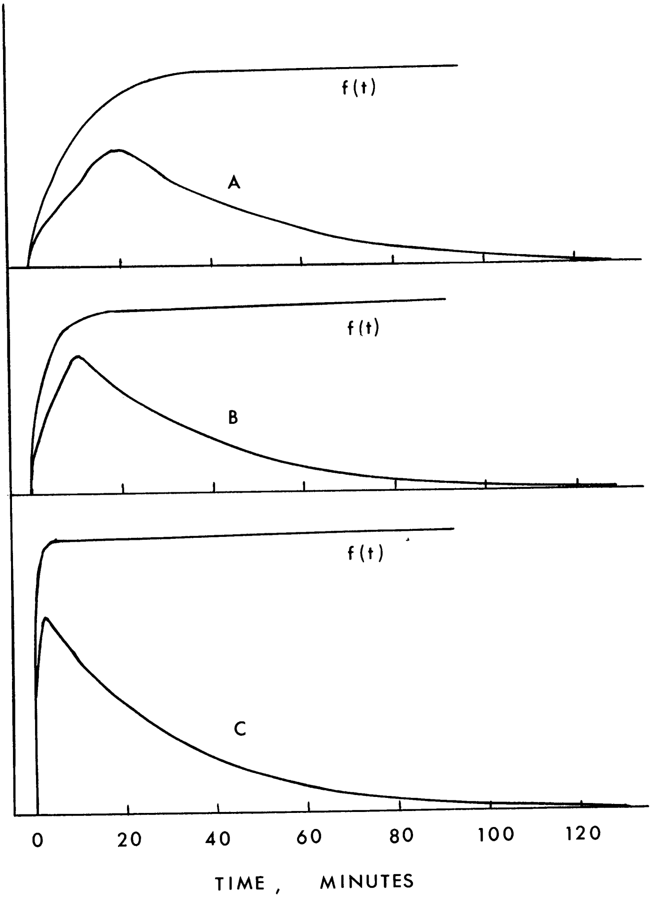

Fig. 3. Thermograms of swelling of rice grain and rice powder. About 1 g. sample was thrown into 30 ml. distilled water at 30.0°C., and temperature rise was detected. *f(t)* was calculated following equation 2. A = rice grain; B = rice powder on 9-mesh; C = rice powder through 32-mesh (finest powder). Sample: Koshiziwase strain cultivated in 1970; temperature, 30.0°C.

diameter of the particle has a range of 1.0 to 2.0 mm. In Fig. 5, average diameters are shown. The horizontal line shows the heat of swelling of the rice grain (1.75 cal. per g. rice). Heat of swelling becomes greater with decreasing diameter; that is, heat of swelling of the rice grain was less than the milled rice. If it is assumed that the change of temperature in the cell [f(t)] is directly proportional to swelling of the rice, it is possible to plot the percentage of the swelling against time. When data are calculated in this way and plotted logarithmically, we obtain the results as shown in Fig. 6. All the rice powder shows a linear relationship but not the rice grain. Therefore, swelling of the rice powder apparently follows a first-order reaction as measured calorimetrically.

The reaction velocity constant, *k*, is given from the slope of the linear line of Fig. 6. Rice grains can be simply thought of as oval and powdered grain is regarded to be

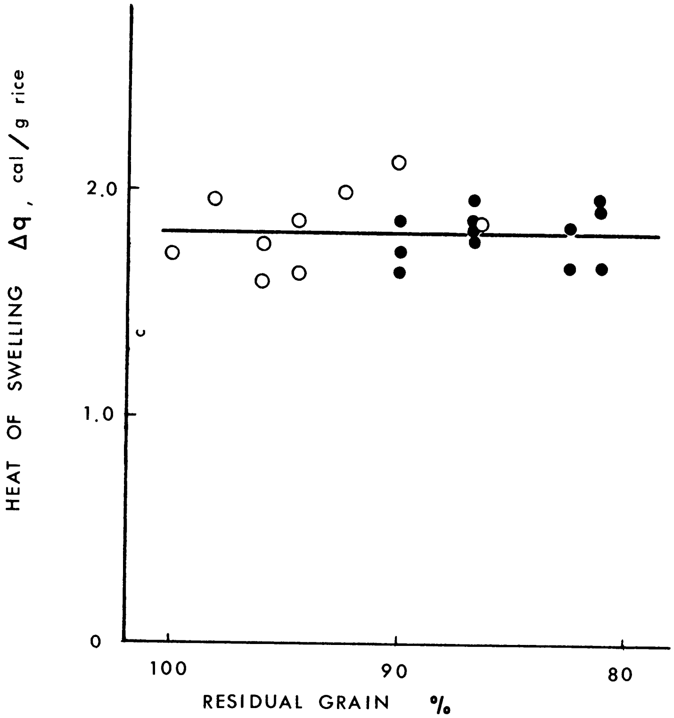

Fig. 4. The effect of size of residual grain on heat of swelling of rice grain. —o—, Manryo; —•—, Koshiziwase; temperature, 30.0°C.

a ball. From mean diameters in Table I, total surface areas were of rice kernel and rice powder were calculated and the relation between total surface area and the reaction velocity constant, *k*, is shown in Fig. 7. Reaction velocity constant of the second step of swelling of rice kernel (Fig. 6) was used.

DISCUSSION

When the rice grain is thrown into water at 30°C., it absorbs 0.20 to 0.25 g. of water per g. of rice with swelling within 20 or 30 min., and it is accompanied with release of heat of about 2 cal. per g. rice. The degree of polishing of the rice has no effect on water absorption nor on the heat of swelling, as shown in Figs. 2 and 4. The polished rice of 80% residual is unusually high. However, no changes in water absorption and heat of swelling were found. Elution of water-soluble components of the rice grain and rice powder was measured only for reduced sugar (Somogyi-Nelson method, 5) in our laboratory. Amount of reduced sugar as glucose which is eluted from rice grain was 4×10^{-6} mole per g. rice and rice powder (sample 4) was 5.5×10^{-6} mole per g. rice. If we convert from the heat of dissolution of glycogen (-4.67 kcal. per mole) (6), the heat of elution of water-soluble components of rice grain is 0.019 cal. per g. rice and that of the rice

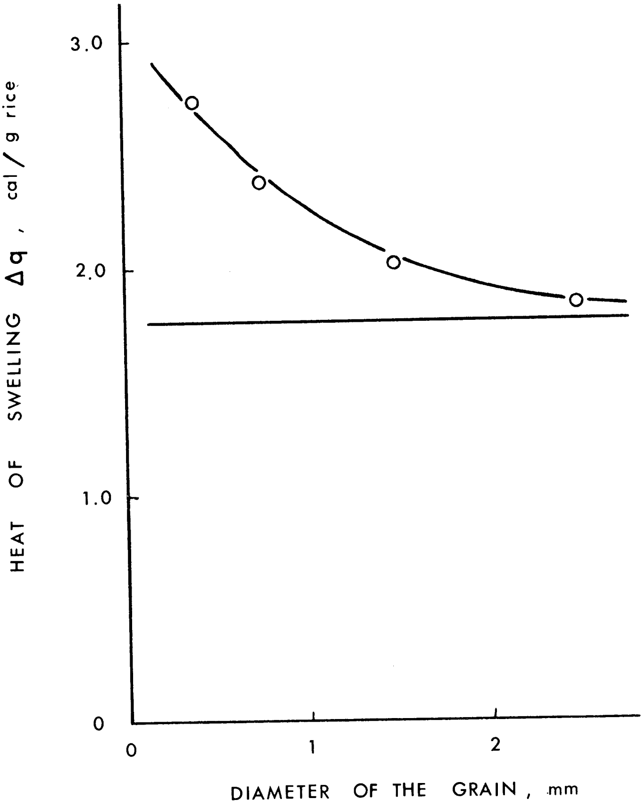

Fig. 5. The effect of diameter of particle of the milled rice on heat of swelling. Average diameters of the particle are shown. The heat of swelling of rice grain is shown as 1.75 cal. per/g. rice. Sample: Koshiziwase; temperature, 30.0°C.

powder (sample 4) is 0.026 cal. per g. rice. Accordingly, the heats of elution are negligible.

Moreover, it is necessary to consider the heat of wetting, which is included in the heat of swelling of rice. It is considered that heat of wetting is proportional to surface area. Surface area of the finest powder (sample 5) is about 7.5 times as much as that of rice grain from Fig. 7. But the heat of swelling of rice powder (sample 5) is only 1.6 times that of rice grain. Therefore the heat of wetting has not much contribution to the heat of swelling.

It is reasonable to assume that almost all the heat of swelling of rice must be considered to be due to hydrogen bonds between water and starch molecules in the rice. However, hydrogen bonds should be increased by milling. Accordingly a total heat for swelling should be slightly increased by milling.

As shown in Fig. 6, swelling velocity seems to calorimetrically follow the law of a first-order reaction. As described before, swelling is accompanied by water absorption, permeation, diffusion, etc., and it is difficult to consider it simply as a first-order reaction. On a molecular-unit basis, however, swelling can be based upon

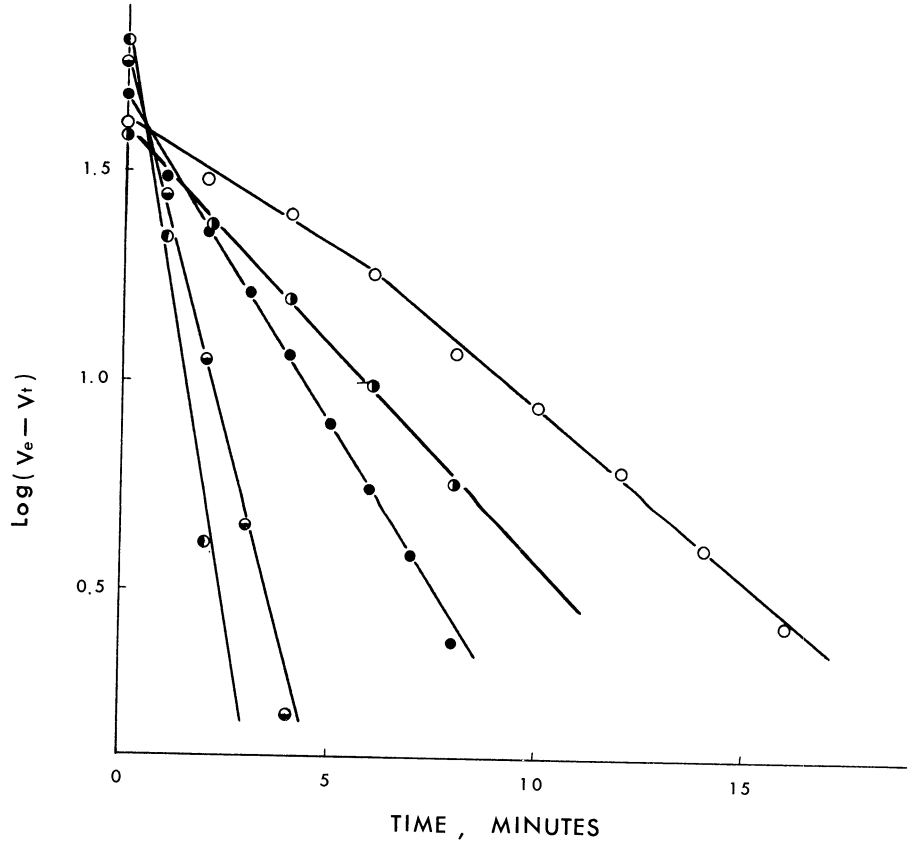

Fig. 6. Plotting of log (*a-x*) vs. time *t*, where *a* is *f(t)* at infinite time and *x* is *f(t)* at time *t*. —●—, rice grain; —◑—, rice powder on 9-mesh; —●—, rice powder on 9 to 16-mesh; —◒—, rice powder on 16 to 32-mesh; —◐—, rice powder through 32-mesh.

the reaction of starch and water molecules: in case of powder, especially, the factors of permeation and diffusion are small. Therefore, we can consider it as a reaction mainly between starch and water and it is reasonable that swelling follows first-order kinetics.

In case of the rice grain, swelling does not follow a first-order reaction. The reaction shows two steps and reaction velocity changing at 5 or 10 min. after the beginning of the reaction. The thermogram of swelling of the rice grain has a shoulder at 5 or 10 min. after beginning of the reaction, but this shoulder is not found on the swelling of the powder as shown in Fig. 3. It is supposed that, if there is a layer near the surface, which has a different density, the reaction velocity should be changed.

Reaction velocity constant, *k*, and total surface area have a linear relationship (Fig. 7). These total surface areas are mean values and, though not absolutely accurate, they will serve as a rough standard. The reaction velocity constant, *k*, of

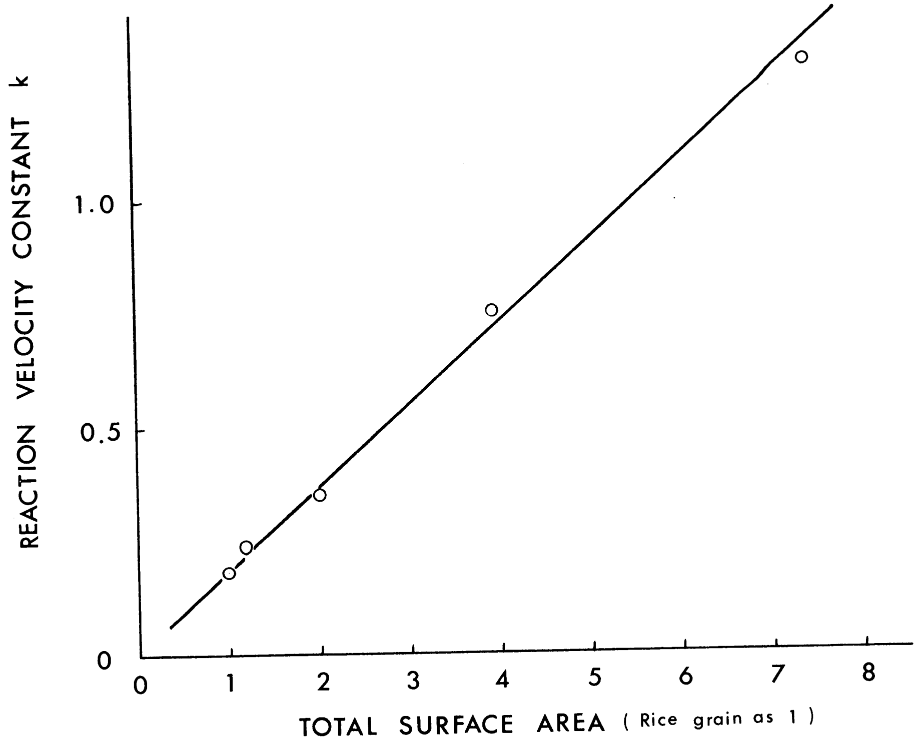

Fig. 7. Relation between total surface area and the reaction velocity constant, *k*. Total surface area shown is based on the rice kernel having a value of 1.

swelling of rice powder seems to be determined by the total surface area of the powder particle.

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Literature Cited

1. SCHRENK, W. G., ANDREWS, A. C., and KING, H. H. Calorimetric measurements of heats of hydration of starches. Ind. Eng. Chem. 39: 113 (1947).
2. COLLISON, R., and DICKSON, A. Heats of starch dehydration by differential thermal analysis. Staerke 23: 45 (1971).
3. GUGGENHEIM, E. A. On the determination of the velocity constant of a unimolecular reaction. Phil. Mag. 2: 538 (1926).
4. ONO, S., HIROMI, K., and TAKAHASHI, K. Calorimetric studies on hydrolysis of glucosides. J. Biochem. 57: 799 (1965).
5. AKABORI, S. Quantitative analysis of reduced sugar. Zikkenkagakukoza 23: 417 (1957).
6. NIHON KAGAKUKAI (Chemical Society of Japan). Chemical kinetics and equilibrium. In: Kagaku Binran (Chemical index in Japanese), p. 716. Maruzen Co. (1958).

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